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Article · December 2021

DOI: 10.48422/IMIST.PRSM/ajees-v7i4.25797

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THE THEORETICAL DESCRIPTION FOR 4-NITROQUINOLINE-N-OXIDE ELECTROCHEMICAL DETERMINATION ON V(OH)₂-MODIFIED ELECTRODE

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Received 12 Apr 2021, Revised 12 Oct 2021, Accepted 16 Oct 2021

Abstract

In this work, the possibility of use of vanadium (II) dioxide as an electrode modifier for the cancer marker 4-nitroquinoline-N-oxide has been made. Two parallel mechanisms of assisted electroanalytical determination are possible, due to the presence of peroxide group and nitric group. Both of them provide the electrode reversibility, due to the formation of V(IV) and V(III) compounds. In both of the cases, the electroanalytical process is efficient. On the other hand, the oscillatory behavior probability in this system is correspondent to the electroanalytical process with sequent or parallel electrochemical stages.

Keywords: electrochemical sensors, 4-nitroquinoline-N-oxide, vanadium dioxide, chemically modified electrodes, stable steady-state.

Introduction

4-Nitroquinoline 1-oxide (Fig. 1) is a quinoline derivative and a tumorigenic compound used in the assessment of the efficacy of diets, drugs, and procedures in the prevention and treatment of cancer in animal models. It induces DNA lesions usually corrected by nucleotide excision repair[1 - 6].

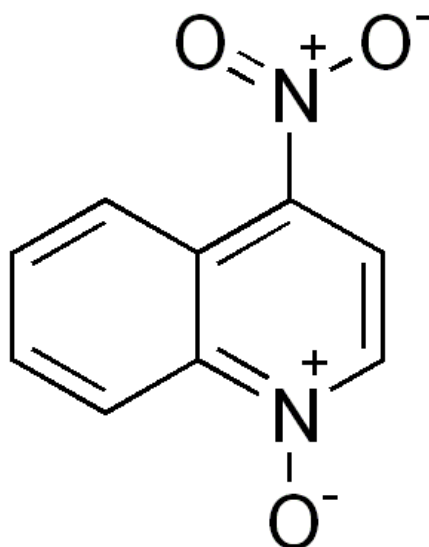


Fig. 1. 4-Nitroquinoline 1-oxide

It may be produced in nature, but is usually synthesized in laboratories[2] being known to reproduce the biological effects of ultraviolet light on various organisms.[3] Both 4-nitroquinoline-N-oxide and its reduced hydroxilaminic derivative bind covalently to cellular macromolecules such as nucleic acids and proteins.[4]

It also induces DNA damage through the production of reactive oxygen species, arising from enzymatic reduction of its nitro group and N-oxide group, although its exact mechanism is unknown[5] These fragments may serve as a byproduct of DNA damage or signaling molecule from damage.[6] In response to damage from 4NQO, cells attempt to repair and initiate a transcriptional response to detoxify the cell from 4NQO and its metabolites.[7] Thus, the development of an efficient method for its determination and quantification is really actual [8 – 12], and the use of electroanalytical methods would be an interesting method for its realization.

Containing the high electrone accepting groups 4-nitroquinoline-1-oxide is more suitable to be determined by cathodic process using the chemically modified electrodes. As metal oxides and oxyhydroxides may be used as efficient electrode modifiers in electroanalysis [13 – 16], vanadium (II) hydroxide may be used for this purpose, as strong reductant.

For now, no works concerning the use of $V(OH)_2$ as electrode modifier have been published. Nonetheless its strong reducing properties would be useful to determinate N-oxides and peroxide compounds.

On the other hand, , the development of a principally new electrode modifier may confront some problems, like:

- the indecision about the mechanism of electrochemical action of the electrode modifier with the analyte;

- the possibility of the appearance of electrochemical instabilities, characteristic for the electrosynthesis and action of $\text{CoO}(\text{OH})$, a similar compound [17 – 18].

These problems may be solved, if the experimental essays are preceded by an *a priori* theoretical investigation of the electroanalytical system. So, in this work, the theoretical mechanistic investigation of $\text{V}(\text{OH})_2$ -assisted 4-nitroquinoline-N-oxide electrochemical determination is given. Also, the behavior of this system is compared with that of the similar electroanalytical processes [19 – 21].

System And Its Modeling

The electroanalytical process of $\text{V}(\text{OH})_2$ -assisted 4-nitroquinoline-N-oxide electrochemical determination may be realized by hybridic mechanism, involving N-oxide group (Fig. 2):

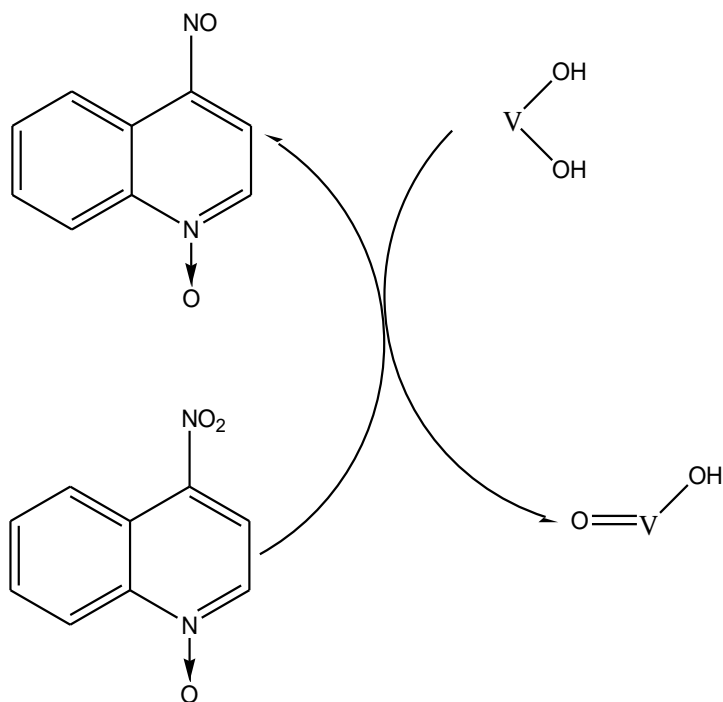


Fig. 2. N-Oxide group reduction

or nitric group (Fig. 3)

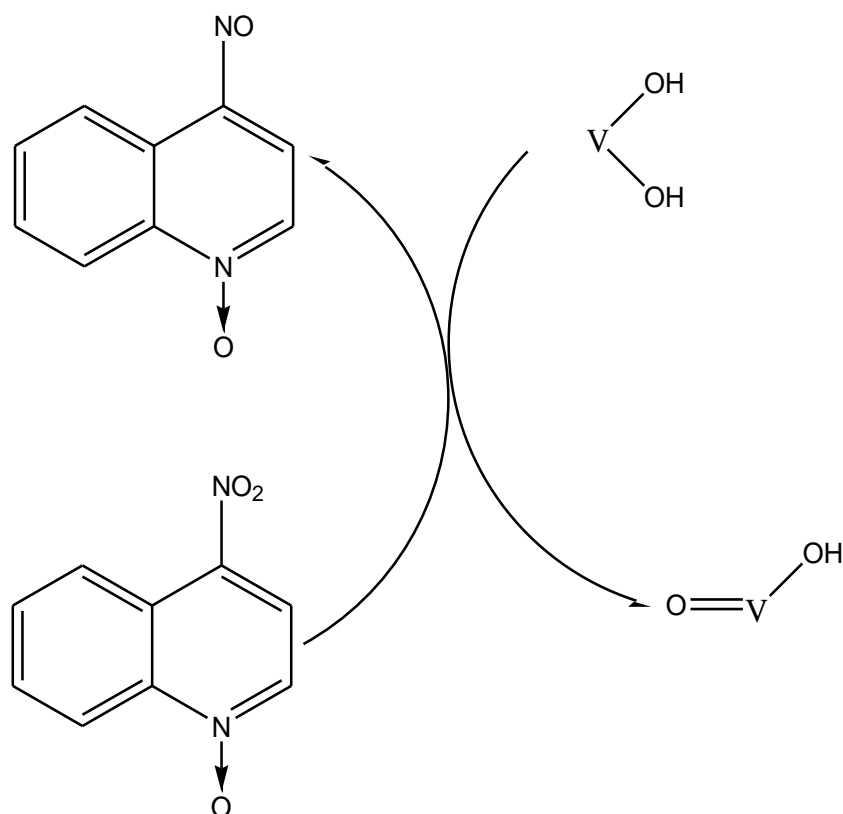


Fig. 3. Nitrogroup reduction

Therefore, in order to describe the behavior of this electroanalytical system, we introduce three variables:

q – 4-nitroquinoline-N-oxide concentration in the pre-surface layer;

v – tetravalent vanadium surface coverage degree;

ω – trivalent vanadium surface coverage degree.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we assume that the background electrolyte is in excess, so we can neglect the migration flow. The diffusion layer is supposed to be of a constant thickness, equal to δ , and the concentration profile in it is supposed to be linear.

4-nitroquinoline-N-oxide enters the pre-surface layer by diffusion and is chemically reduced by vanadium (II) hydroxide, yielding tri- and tetravalent vanadium compounds. Thus, its balance equation will be rewritten as:

$$\frac{dq}{dt} = \frac{2}{\delta} \left(\frac{\Delta}{\delta} (q_0 - q) - r_{1v} - r_{1\omega} \right) \quad (1)$$

In which Δ is the diffusion coefficient, q_0 the 4-nitroquinoline-N-oxide concentration in the pre-surface layer, r_{1v} and $r_{1\omega}$ are chemical reactions yielding tetravalent and trivalent vanadium forms correspondently.

The tetravalent vanadium as vanadyl hydroxide arises while N-oxide group is reduced. In the electrochemical stage, the vanadium recovers the bivalent form. Thus, its balance equation will be described as:

$$\frac{dv}{dt} = \frac{1}{V}(r_{1v} - r_{2v}) \quad (2)$$

In which V is vanadyl hydroxide maximal surface concentration and r_{2v} is vanadyl electrochemical reduction rate.

Analogously, the trivalent vanadium as vanadium oxyhydroxide arises during the nitrogroup reduction to nitroso-fragment. As in the case of tetravalent vanadium, the trivalent vanadium compound is electrochemically reduced, yielding the bivalent form. So, its balance equation will be described as:

$$\frac{d\omega}{dt} = \frac{1}{\Omega}(r_{1\omega} - r_{2\omega}) \quad (3)$$

Here Ω is vanadium oxyhydroxide maximal surface concentration and $r_{2\omega}$ is its reduction rate.

The correspondent reaction rates may be described as:

$$r_{1v} = k_{1v}q(1 - v - \omega) \quad (4)$$

$$r_{1\omega} = k_{1v}q(1 - v - \omega)^2 \quad (5)$$

$$r_{2v} = k_{2v}v \exp\left(-\frac{2F\phi_0}{RT}\right) \quad (6)$$

$$r_{2\omega} = k_{2\omega}\omega \exp\left(-\frac{F\phi_0}{RT}\right) \quad (7)$$

in which the parameters k are correspondent reaction rate constants, F is the Faraday number, ϕ_0 is the DEL potential slope, related to the zero-charge potential, R is the universal gas constant and T is the absolute temperature.

This case represents a typical case of an electroanalytical system with hybridic reduction mechanism. Two electrochemical stages are present and both of them may provoke the electrochemical instabilities. Nonetheless, the electroanalytical system is stable and efficient as shown below.

Results And Discussion

In order to investigate the behavior of the system with 4-nitroquinoline-N-oxide $V(OH)_2$ -assisted electrochemical determination, we analyze the equation set (1 - 3) by means of linear stability theory. The Jacobi functional matrix steady-state elements may be described as:

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

in which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{A}{\delta} - k_{1v}(1-v-\omega) - k_{1v}(1-v-\omega)^2 \right) \quad (9)$$

$$a_{12} = \frac{2}{\delta} (k_{1v}q + 2k_{1v}q(1-v-\omega)) \quad (10)$$

$$a_{13} = \frac{2}{\delta} (k_{1v}q + 2k_{1v}q(1-v-\omega)) \quad (11)$$

$$a_{21} = \frac{1}{v} (k_{1v}(1-v-\omega)) \quad (12)$$

$$a_{22} = \frac{1}{v} \left(-k_{1v}q - k_{2v} \exp\left(-\frac{2F\phi_0}{RT}\right) + \xi v \exp\left(-\frac{2F\phi_0}{RT}\right) \right) \quad (13)$$

$$a_{23} = \frac{1}{v} \left(\lambda k_{2v} v \exp\left(-\frac{2F\phi_0}{RT}\right) \right) \quad (14)$$

$$a_{31} = \frac{1}{\Omega} (k_{1v}(1-v-\omega)^2) \quad (14)$$

$$a_{32} = \frac{1}{\Omega} \left(\xi k_{2\omega} \omega \exp\left(-\frac{F\phi_0}{RT}\right) \right) \quad (15)$$

$$a_{33} = \frac{1}{\Omega} \left(-2k_{1v}q(1-v-\omega) - k_{2\omega} \exp\left(-\frac{F\phi_0}{RT}\right) + \lambda k_{2\omega} \omega \exp\left(-\frac{F\phi_0}{RT}\right) \right) \quad (16)$$

It is possible to show that the *oscillatory behavior* for this system is possible and it will be caused by influences of two electrochemical stages on the double electric layer, described by the positivity of main-diagonal elements $\lambda k_{2\omega} \omega \exp\left(-\frac{F\phi_0}{RT}\right)$ and $\xi v \exp\left(-\frac{2F\phi_0}{RT}\right)$ (positive main-diagonal elements describe the positive callback). The oscillations are expected to be frequent and of small amplitude, being similar to the oscillations, observed in the case of sequent and parallel electrooxidation(reduction) mechanism [19 – 21].

In order to analyze the *steady-state stability*, we apply the Routh-Hurwitz criterion to the equation set (1 – 3). In order to simplify the analysis, avoiding cumbersome expressions, we introduce new variables, so the matrix determinant will be described as:

$$\frac{2}{\delta GM} \begin{vmatrix} -\kappa - \mathcal{E} - X & U + Y & U + Y \\ \mathcal{E} & -U - L & N \\ X & M & -Y - P \end{vmatrix} \quad (17)$$

Opening the brackets, we obtain the steady-state stability condition, expressed as:

$$-\kappa(UY + LY + UP + LP - MN) - \mathcal{E}(LY + LP - MN - MU - MY - YP - Y^2) - X(UP + LP - MN - NU - NY - U^2 - LU) < 0 \quad (18)$$

Describing a reaction-controlled electroanalytical system much more strait than for the analogous systems [19 – 21]. Nevertheless, if the DEL influences of the electrochemical reactions are non-intense with the negativity of the correspondent parameters M, N, L and P, which occurs within the detection

limit, the steady-state is warranted to be stable. In this case, the linearity between the electrochemical parameter and concentration is realized, defining the electroanalytical efficiency of this system.

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 its condition may be described as:

$$-\kappa(UY + LY + UP + LP - MN) - \varepsilon(LY + LP - MN - MU - MY - YP - Y^2) - X(UP + LP - MN - NU - NY - U^2 - LU) = 0 \quad (19)$$

This process may be applied to the electrochemical determination of N-oxide in neutral media. Low pH values will be more favorable for N-oxide reduction, but in this case will be assisted by the redox pairs V^{2+}/VO^{2+} and V^{2+}/V^{3+} . This case will be described in our next works.

Conclusions

From the system with $V(OH)_2$ -assisted 4-nitroquinoline-N-oxide it is possible to conclude that:

- In this case, despite of the major number of destabilizing factors, the electroanalytical system is efficient.
- The electroanalytical process is reaction-controlled;
- The destabilizing factors are realized beyond the detection limit;
- The oscillatory behavior in this system is more probable than for analogous ones, due to the presence of two parallel electroanalytical scenarios.

Conflict of interest

The authors declare that there is no conflict of interests regarding this publication

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