# The Theoretical Aspects of The Electrosynthesis and Electropolymerization of Some Naphthoquinonic Derivatives In Neutral And Acidic Media

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## Abstract

For the first time, the possibility of the electrochemical synthesis and polymerization of some novel modified naphthoquinonic compounds has been described. The correspondent mathematical model has been analyzed by means of linear stability theory and bifurcation analysis. It has been shown that the electroorganic synthesis may serve as an interesting substitution for Suzuki reaction for the synthesis of ferrocenyl naphthoquinone and its polymer. The oscillatory and monotonic instability in this case will be more probable than in the general electropolymerization case.

***Keywords****: naphthoquinones, Suzuki reaction, electroorganic synthesis, electropolymerization, stable steady-state*

## Introduction

Electrochemical polymerization is one of the most used conducting polymer synthesis technique [1 – 10]. The electrosynthetized polymers have certain advantages, while compared to the chemically obtained macromolecules. These advantages include:

- Enhanced conductivity;
- Corrosion resistance;

- Facility in modification;
- Tunability.

The most known conjugated conducting polymers contain alkine chains, carbo- and heterocyclic fragments in their moiety. While electrochemically synthetized, they are doped by a background electrolyte counter-ion or another counter-ion present in the solution. The monomer and electropolymerization technique may be chosen according to the further use of the resulting polymer.

Recently, the Organic Chemistry group of Yüzüncü Yil University of Van has obtained a novel ferrocenyl-substituted naphthoquinone derivative [11 – 12] (Fig. 1). The novel derivative has shown sensitivity to the concentration of hydrogen peroxide and may readily be used as a sensor. Nevertheless, the novel derivative has been obtained by a Suzuki-Miyaura reaction, requiring expensive catalysts and reagents. An electroorganic synthesis, used to yield not only polymers, but also their monomers [13 – 17]. From 1970th on, the monomer electrosynthesis techniques are developed to yield monomers and their polymers.
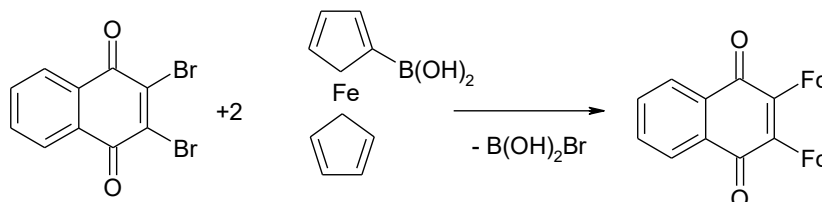


**Fig. 1**. Chemical synthesis of the compound

Nevertheless, the organic electrooxidation processes (including the electropolymerization) tend to be accompanied by electrochemical instabilities. These instabilities include the oscillatory changes in electrochemical potential and monotonic instabilities [18 – 25] and influence the polymer morphology and conductivity.

Thus, in order to investigate the parameter values, correspondent to the most efficient monomer and polymer formation, like also verify the possibility and probability of the electrochemical instabilities in this system, an *a priori* theoretical observation of the electrochemical system is necessary.

So, taking into account the above mentioned statements, the goal of our work will be the theoretical description of the novel ferrocenic naphthoquinones electrochemical synthesis as substitute of the Suzuki reaction, with the further product polymerization.

In order to realize it, we achieve the specific objectives as:
- to suggest the most probable mechanism for the sequence of chemical and electrochemical processes in the system;
- to develop the mathematical model, correspondent to the mechanism,

- by analysis of the model, to derive the steady-state stability conditions and oscillatory and monotonic instability requirements;
- to compare the behavior of this system with that of the similar ones [25 – 28].

## System And Its Modeling

In this case, the naphthoquinone is electrochemically oxidized by a classical Diaz mechanism, yielding a radical-cation and expelling the protons from the conjugated molecule. The chain propagation, at its turn, diminishes the pH value, yielding the protons.

$$M – e- \rightarrow M*+ \qquad (1)$$
$$2M*+ \rightarrow M – M + 2H+ \qquad (2)$$
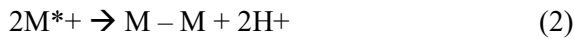
Yet the protons are capable to destroy the ferrocene ring according to the reaction:

$$Fe(C5H5)2 + 2H+ \rightarrow Fe2+ + 2\ C5H6 \qquad (3)$$

This reaction may be realized in monomer molecules, reducing the polymer conductivity by a significant manner.

Also, the electrochemical oxidation of the monomer may also be intramolecular, provoking the electrocyclization, which also yields protons, reducing the pH.

Therefore, the system behavior won't be described by classical models. Thus, in order to describe the behavior of the electropolymerization of ferrocene-substituted naphthoquinones in neutral or acidic media, we introduce three variables:

$c$ – the ferrocene derivative concentration in the pre-surface layer;

$m$ – monomer electrode coverage degree;

$h$ - proton concentration in the pre-surface layer.

Herein, in order to simplify the modeling, we assume that:

- the background electrolyte is taken in excess, so we can neglect the migration flow and the oxidizing dopant oxidation change;

- the reactor is intensively stirred, so we may neglect the convection flow;

- the pre-surface layer concentration profile is linear, and its thickness is constant, equal to $\delta$.

It is possible to show that the behavior of this system will be described by the model below (4):

$$\begin{cases} \dfrac{dc}{dt} = \dfrac{2}{\delta}\left(\dfrac{\Delta}{\delta}(c_0 - c) + r_{-1} - r_1 - r_H\right) \\ \qquad \dfrac{dm}{dt} = \dfrac{1}{M}(r_1 - r_{-1} - r_2) \\ \qquad \dfrac{dh}{dt} = \dfrac{2}{\delta}(r_2 - r_H) \end{cases} \qquad (4)$$

Where $\Delta$ is the diffusion coefficient, $c_0$ is the bulk concentration of the monomer, M is the monomer maximal surface concentration, and the parameters r are correspondent adsorption, desorption and reaction rates, which may be calculated as:

$$r_1 = k_1 c (1 - m) \exp(am) \tag{5}$$
$$r_{-1} = k_{-1} m \exp(-am) \tag{6}$$
$$r_2 = k_2 h m^x \exp\left(\frac{F\varphi_0}{RT}\right) \tag{7}$$
$$r_H = k_H c h^2 \exp(-bch) \tag{8}$$

Herein, the parameters k stand for the correspondent reaction constants, the parameter a describes the interaction of the adsorbed particles, and the parameter b, the DEL ionic force influence of the ferrocene ring destruction, x is the monomer polymerization reaction order, F is the Faraday number, $\varphi_0$ is the potential slope, related to the zero-charge potential, R is the universal gas constant and T is the absolute temperature of the solution.

As yet mentioned and observed, this system will be far more complicated than the classical electropolymerization, as there is a self-depromoting factor in electropolymerization, provided by proton formation. Its influence will be described below.

**Results and discussion**

In order to investigate the electropolymerization of the novel ferrocenyl-substituted naphthoquinones in acidic media, we analyze the equation-set (4) by means of the linear stability theory. The steady-state Jacobian matrix may be exposed like (9):

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \tag{9}$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_1(1 - m)\exp(am) - k_H h^2 \exp(-bch) + bk_H c h^2 \exp(-bch)\right) \tag{10}$$

$$a_{12} = \frac{2}{\delta}\left(k_{-1}\exp(-am) - ak_{-1}m\exp(-am) + k_1 c \exp(am) - ak_1 c(1 - m)\exp(am)\right) \tag{11}$$

$$a_{13} = \frac{2}{\delta}\left(-2k_H c h \exp(-bch) + bk_H c h^2 \exp(-bch)\right) \tag{12}$$

$$a_{21} = \frac{1}{M}\left(k_1(1 - m)\exp(am) + k_H h^2 \exp(-bch) - bk_H c h^2 \exp(-bch)\right) \tag{13}$$

$$a_{22} = \frac{1}{M}\left(-k_{-1}\exp(-am) + ak_{-1}m\exp(-am) - k_1 c \exp(am) + ak_1 c(1 - m)\exp(am) - xk_2 h m^{x-1}\exp\left(\frac{F\varphi_0}{RT}\right) + jk_2 h m^x \exp\left(\frac{F\varphi_0}{RT}\right)\right) \tag{14}$$

$$a_{23} = \frac{1}{M}\left(-k_2 m^x \exp\left(\frac{F\varphi_0}{RT}\right)\right) \tag{15}$$

$$a_{31} = \frac{2}{\delta}\left(-k_H h^2 \exp(-bch) + bk_H c h^2 \exp(-bch)\right) \tag{16}$$

$$a_{32} = \frac{2}{\delta}\left(xk_2 h m^{x-1}\exp\left(\frac{F\varphi_0}{RT}\right) - jk_2 h m^x \exp\left(\frac{F\varphi_0}{RT}\right)\right) \tag{17}$$

$$a_{33} = \frac{2}{\delta}\left(k_2 m^x \exp\left(\frac{F\varphi_0}{RT}\right) - 2k_H c h \exp(-bch) + bk_H c h^2 \exp(-bch)\right) \tag{18}$$

Analyzing the matrix main diagonal members (10), (14) and (18), it is possible to observe that they contain positive addendums. They are responsible for the positive callback, which is, at its turn, responsible for the *oscillatory behavior*.

In system the oscillatory behavior will be far more probable, than in the simplest electropolymerization cases [25 – 28], due to the presence of four factors, causing the positive callback, instead of three or two in analogous systems.

The oscillatory behavior, described by the positivity of $ak_{-1}m\exp(-am) > 0$ and $ak_1 c(1-m)\exp(am) > 0$, deals with the the attraction between the adsorbed monomer particles, followed by their repulsion. It forces the cyclical changes in the surface resistance and conductivity, leading to the oscillatory dynamics in the electrochemical parameter.

Yet the positivity of the addendums $bk_H ch^2 \exp(-bch)$ and $bk_H ch^2 \exp(-bch)$, describe the destruction of the monomer by the protons, leading to the decrease of the monomer concentration and activity. On the other hand, the ferrocenic moiety destruction leads to the appearance and disappearance of the ionic forms (protons disappear, $Fe^{2+}$ appear), leading to the cyclic changes in DEL ionic force, resulting in cyclic changes in DEL conductivity. Thus, the oscillations in the electrochemical parameter may appear.

The positivity of the addendum $jk_2 hm^x \exp\left(\frac{F\varphi_0}{RT}\right) > 0$ describing the positive callback, observed during the monomer synthesis describes the change of the surface compound with the decay, followed by the enhancement of its conductivity, leading to the favorable effect in double electric layer.

The positivity of the element $k_2 m^x \exp\left(\frac{F\varphi_0}{RT}\right) > 0$ describes the self-promotive proton formation during the electropolymerization. The protons attack the polymer backbone, leading to the polymer morphology destruction. It causes the cyclical changes in monomer and polymer conductivity, which firstly augments and then diminishes. Thus, the oscillatory behavior in this system may be caused by four factors. The oscillation amplitude will grow with the pH decrease. It have already been observed in [22 – 25] for both pyrrole and thiophene. In the case of the ferrocenic moiety, which is highly unstable in strongly acidic media, this factor becomes more decisive for the polymer morphology and conductivity.

In order to derive the *steady-state stability* requirement, we apply the Routh-Hurwitz criterion to the equation-set (4). Avoiding the cumbersome equations, we introduce new variables, and the Jacobian determinant will be described as:

$$\frac{4}{\delta^2 M} \begin{vmatrix} -\kappa - \Xi & \Omega & -\Lambda \\ \Xi & -\Omega - \Sigma & -P \\ -\Xi & \Sigma & \Lambda - P \end{vmatrix} \qquad (19)$$

Opening the brackets and applying the Det J<0 condition, salient from the criterion, we obtain the steady-state stability condition, exposed as (20):

$$-\kappa(\Omega P + 2\Sigma P - \Omega\Lambda - \Sigma\Lambda) - \Xi(\Omega P + 2\Sigma P - \Omega\Lambda - \Sigma\Lambda) < 0 \quad (20)$$

The proton-driven autocatalysis diminishes strongly the steady-state stability topological region. The resulting polymer morphology and conductivity will be damaged, due to the proton formation, followed by the proton attacks on both monomer and polymer. Also, the steady-state

stability efficiency will be reduced, due to the proton attacks, reducing the polymer backbone length and conductivity. The process is mostly kinetically controlled.

The *monotonic instability* for this system is possible. It is defining the margin between stable steady-states and unstable states, and its conditions of appearance will be depicted as (21):

$$-\kappa(\Omega P + 2\Sigma P - \Omega \Lambda - \Sigma \Lambda) - \Xi(\Omega P + 2\Sigma P - \Omega \Lambda - \Sigma \Lambda) < 0 \quad (21)$$

Analysis of the model shows that the neutral and acidic media isn't favorable for the efficient ferrocenic polymer formation. Therefore, the alkaline media, provided by the carbonate buffer, has to be used. In this case, the hydroxyl groups capture the leaving proton, yielding the water molecule and protecting the monomer and the polymer from the attacks.

## Conclusions

From the system with the new ferrocenic naphthoquinonic derivative electrochemical polymerization in acidic media it is possible to conclude that:

- The polymerization is highly influenced by the proton attacks, leading to the ferrocene moiety destruction and polymer backbone degradation.;
- The electropolymerization is kinetically controlled. The proton autocatalysis diminishes strongly the steady-state stability topological region;
- The oscillatory instability will be more probable than in other electropolymerization systems, as there are four factors, responsible for its appearance. The proton autocatalysis is decisive for the electropolymerization kinetics and the resulting polymer backbone.

## Conflict of interest

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

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