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The Theoretical Description of Sudan Dyes Electrochemical Determination on A Triazolic Derivative

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Abstract

The theoretical description of the electrochemical determination of sudan dyes, assisted by novel triazolic derivatives, using a disulfonic organic acid as a binder, has been made. The correspondent mathematical model was analyzed by means of linear stability theory and bifurcation analysis. It was shown that the electroanalytical process is realized more efficiently than in the case of the direct electrochemical reduction in acid media. The oscillatory behavior for this case is possible, but less probable than for direct dye electrochemical reduction.

Keywords: chemically modified electrodes, sudan dyes, triazole, electrochemical sensors, stable steady-state

Introduction

Sudan dye group traditionally includes six azo- and diazodyes (Fig. 1), widely used in industry [1 - 6]. Being fat-soluble, they are used to color vaxes, oils and solvents into the bright colors – red, orange, yellow:
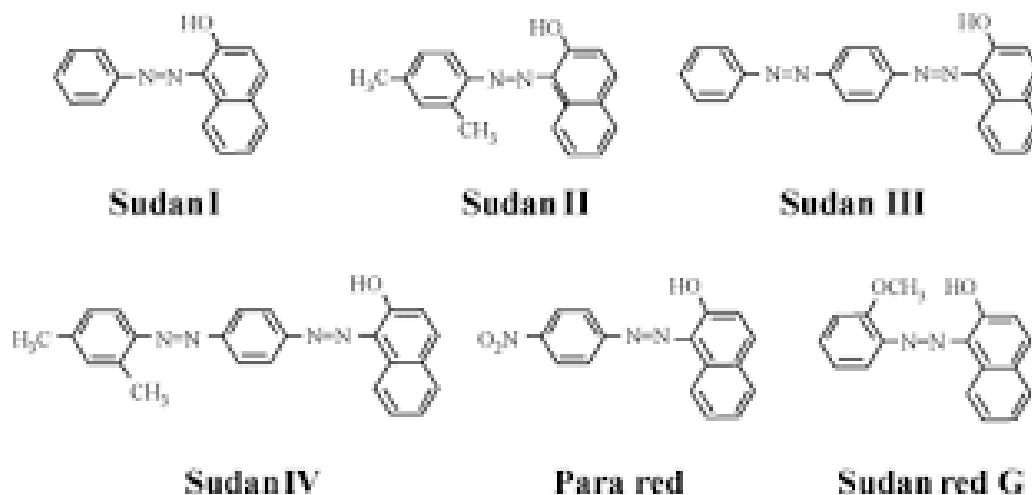
Fig. 1. Some representants of sudan dye group

In some countries like India it has been used as a food dye, in order to give the intensive color to the chilly pepper and curry powder [7 – 9]. Nevertheless, the recent investigations have unveiled the acute toxic effects of these dyes, including carcinogenesis and mutagenesis [10 - 12]. Moreover, these dyes have been extensively used for food falsification. Thus, the development of efficient methodologies for Sudan dyes determination is really actual, and the electroanalytical methods could give them a good service [13 – 18].

Many different electrode modifiers have been used for detect Sudan dyes electrochemically – either anodically, or cathodically [19 – 25]. For the cathodic reaction, a system, capable to transmit efficiently electrons from the cathode and protons from the media, has to be chosen, and the triazolic derivatives (Fig. 2), analogous to yet used in electroanalytical processes [26 – 28] could be interesting candidates for this role.
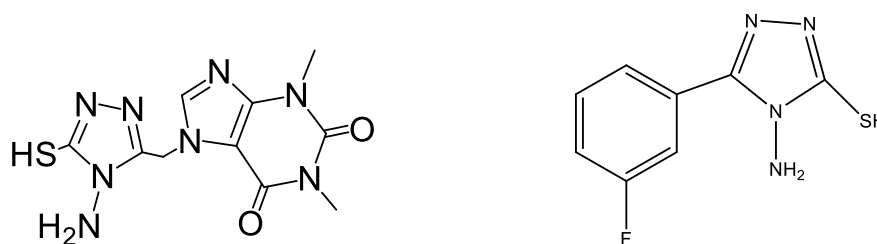

Fig. 2. Triazolic derivatives

Nevertheless, the practical use of the electrode modifier requires the *a priori* theoretical investigation of the electroanalytical use of the triazolic compound with sudan dyes. This investigation helps us to resolve indecisions, surging during the evaluation of the possibility of the realization of electroanalytical process, like:
-      the indecision in the modifier mechanism of action;
-      the compatibility of the modifier with the pharmaceutical tissue or biological object (some modifiers, used *in vitro* may be non-compatible with *in vivo* sensing);

- the presence of electrochemical instabilities, the electrochemical oxidation and electrooxidative polymerization of organic molecules, including conducting polymer electroanalytical function [29 - 32].

The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the electroanalytical system. By modeling it is also capable compare the behavior of this system with that for the similar ones without any experimental essay.

So, the goal of this work is the mechanistic theoretic analysis of the possibility of sartan group electrochemical quantification, assisted by the triazolic derivative monosalt with organic disulfoacid. In order to achieve it, we realize the specific goals:

- suggestion of the mechanism of the electroanalytical reaction consequence, leading to the appearance of analytical signal;
- development of the balance equation mathematical model, correspondent to the electroanalytical system;
- analysis and interpretation of the model in terms of the electroanalytical use of the system;
- the seek for the possibility of electrochemical instabilities and for the factor, causing them;
- the comparison of the mentioned system´s behavior with the similar ones [33 – 35].

System And Its Modeling

The electrochemical determination of sudan dyes on triazolic derivatives includes their electrochemical reduction as the first pass. The reduction may be realized either by triazolic moiety, or by the lateral group (Fig. 3)
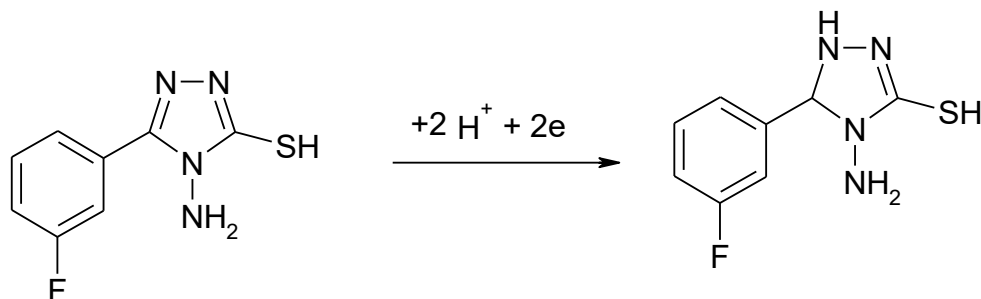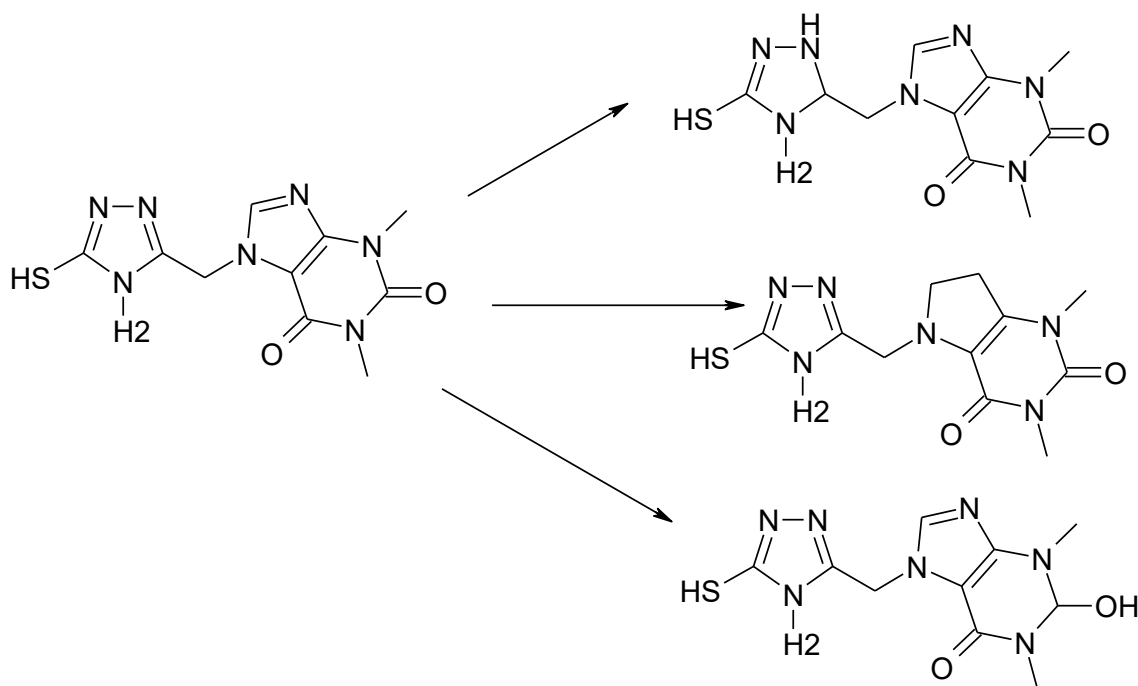
Fig. 3. The triazolic derivatives reduction scheme

Yet the Sudan dye electrochemical reduction will be realized by the scenario of (Fig. 4, for the Sudan I dye):
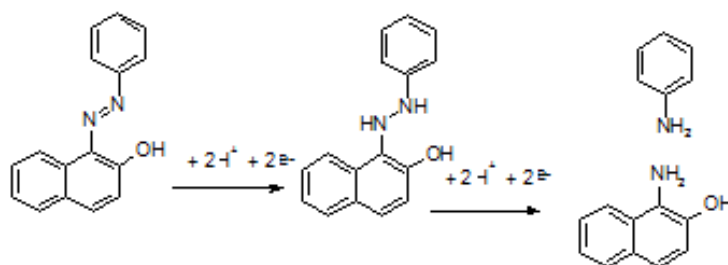

Fig.4. Sudan dyes electrochemical reduction

In this work, in order to simplify the behavior description, we consider both of the triazolic derivatives as a part of a unique compound – a conducting polymer, containing both of them. That polymer may be capable to react with Sudan dyes independently of the presence of triazoles. So, taking into account the above mentioned statements, like also the excess of the background electrolyte, also mentioned below, we introduce two variables:

s – sudan dye concentration in the pre-surface layer;

θ – the coverage degree of the conducting polymer with the oxidized triazolic fragments.

In order to simplify the modeing, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we suppose that the background electrolyte is in excess, so we can neglect the

convection flow. Also we assume that the pre-surface layer concentration profile is linear and that its thickness is constant, equal to δ.

It is possible to show that the behavior of the system will be described by the equation set, represented as:

$$\begin{cases} \frac{ds}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(s_0 - s) - r_{11} - r_{12} - r_{13}\right) \\ \frac{d\theta}{dt} = \frac{1}{G}(r_{11} + r_{12} + r_{13} - r_2) \end{cases} \tag{1}$$

In which Δ is the diffusion coefficient, s_0 is the sudan dye bulk concentration, G is the maximal surface concentration of the polymer and the parameters r are correspondent reaction rates, which may be calculated as:

$$r_{11} = k_{11}s(1 - \theta) \tag{2}$$
$$r_{12} = k_{12}s(1 - \theta) \tag{3}$$
$$r_{13} = k_{13}s(1 - \theta) \tag{4}$$
$$r_2 = k_2\theta \exp\left(-\frac{nF\varphi_0}{RT}\right) \tag{5}$$

In which the parameters k are respective rate constants, n is the number of the electrons transferred, F is the Faraday number, φ_0 is the zero-charge degree related potential slope, R is the universal gas constant, and T is the absolute temperature.

Although the mechanism of the chemical stage is hybrid and includes various reactions, it won´t influence greatly the steady-state stability, which will be discussed below.

Results And Discussion

In order to investigate the behavior of the electroanalytical system with sudan dyes electrochemical determination, assisted by triazolic derivatives, we analyze the equation-set (1) by means of linear stability theory. The Jacobian functional matrix steady-state members may be described as:

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \tag{6}$$

In which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - (k_{11} + k_{12} + k_{13})(1 - \theta)\right) \tag{7}$$
$$a_{12} = \frac{2}{\delta}((k_{11} + k_{12} + k_{13})s) \tag{8}$$
$$a_{21} = \frac{1}{G}((k_{11} + k_{12} + k_{13})(1 - \theta)) \tag{9}$$
$$a_{22} = \frac{1}{G}\left(-(k_{11} + k_{12} + k_{13})s - k_2\exp\left(\frac{nF\varphi_0}{RT}\right) - jk_2\theta\exp\left(-\frac{nF\varphi_0}{RT}\right)\right) \tag{10}$$

The main conditions for bivariant systems are described in the Table 1:

Steady-state stability	Tr J<0, Det J>0
Oscillatory instability	Tr J=0, Det J>0
Monotonic instability	Tr J<0, Det J=0

Table 1. The main conditions for bivariant systems.

In order to avoid the cumbersome expressions, we introduce new variables, so the Jacobian determinant will be rewritten as:

$$\frac{2}{\delta G}\begin{vmatrix} -\kappa - \varXi & \varOmega \\ \varXi & -\varOmega - \varPhi \end{vmatrix} \tag{11}$$

It is possible to show that, *the oscillatory behavior* in this system is possible, as in the similar ones [33 – 35]. It may be only caused by the DEL influences of the polymer redution, described by the positivity of the main diagonal element $-\varPhi = -k_2 \exp\left(\frac{F\varphi_0}{RT}\right) - jk_2\theta \exp\left(\frac{F\varphi_0}{RT}\right)$. The general condition for the oscillatory instability for this system is:

$$\begin{cases} \frac{2}{\delta}(-\kappa - \varXi) = \frac{1}{G}(\varOmega + \varPhi) \\ \kappa\varOmega + \varPhi + \varXi\varPhi > 0 \end{cases} \tag{18}$$

And it may only be realized in the case of the negativity of $\varPhi$ (as the rest of the parameters may only be positive). The oscillations are expected to be frequent and of small amplitude.

The *steady-state stability* for this system may be described as:

$$\begin{cases} \frac{2}{\delta}(-\kappa - \varXi) - \frac{1}{G}(\varOmega + \varPhi) < 0 \\ \kappa\varOmega + \varPhi + \varXi\varPhi > 0 \end{cases} \tag{19}$$

and it is warranted to be satisfied, as the only element, capable to be negative is $\varPhi$, and its negativity, as it was described above, is linked to the strong influences of the electrochemical stage in DEL. So, if these influences are not so strong, $\varPhi$ is positive, so the upper inequation left side tends to possess more negative values, and the lower inequation left side tends to possess more positive values, which is correspondent to the steady-state stability.

As there is no side reactions involving the medium, the electroanalytical efficiency of the stable steady-state isn't compromised, so the steady-state stability is correspondent to the linear dependence between the electrochemical parameter and concentration. The electroanalytical process tends to be diffusion-controlled.

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:

$$\begin{cases} \frac{2}{\delta}(-\kappa - \varXi) - \frac{1}{G}(\varOmega + \varPhi) < 0 \\ \kappa\varOmega + \varPhi + \varXi\varPhi = 0 \end{cases} \tag{20}$$

In the case of the presence of two sudan dyes in the system, the peak separation is achieved, due to the difference in the kinetic of the polymer-assisted reduction. This case will be described in our next works.

Conclusions

From the theoretical investigation of the possibility of the sudan dyes electrochemical detection, assisted by triazole-modified polymer, it is possible to conclude that:

- Triazole-modified polymer may serve as an excellent modifier for sudan dyes electrochemical determination. The system is electroanalytically efficient, although Triazole-modified polymer is used as a reducent;
- The electroanalytical process tends to be diffusion-controlled;

- The oscillatory behavior in this system is possible, being caused only by DEL influences of the electrochemical process. The amplitude is expected to be small and dependent on the solution composition.

Conflict of interest

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

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