Electrochimica Acta 132 (2014) 423–433

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Reductive dimerization mechanisms of some streptocyanine dyes

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ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form 1 April 2014
Accepted 6 April 2014
Available online 15 April 2014

Keywords:
Streptocyanine
dye
dimerization
electron transfer
convoluted current
cyclic voltammetry

ABSTRACT

Cyclic voltammetric studies of streptocyanine dyes were carried out on a glassy carbon electrode. For dye electroreduction, logarithmic analysis of the convoluted current indicates an EC2 mechanism with dimerization following electron transfer. Relevant kinetic and thermodynamic values are reported.

1. Introduction

Cyanine dyes are cationic conjugated organic compounds containing a polymethine chain with an odd number of carbon atoms between two nitrogen atoms. [1,2] Due to their photophysical properties they are used in numerous applications, such as photographic sensitizers, [3,4] infrared-dye-sensitized solar cells, [5] optical recording, [6] nonlinear frequency doublers, [7,8] or biological probes. [9–12] Cyanines are also known to possess interesting biological properties. [13] We previously described the synthesis and antimalarial properties of various polymethine chain lengths (5C, 7C and 9C) streptocyanine dyes (SD). [14] Electrochemical study of the redox behavior of three families of streptocyanines was considered here, using cyclic voltammetry to provide mechanistic information as well as physicochemical data on the compounds. Amatore and co-workers [15] uses electrochemical techniques to approach the biochemical mechanism of action of potential drug molecules on the redox machinery of the cells (NADPH-cytochrome P450 reductase). The authors state that the redox ability of these 'bio-reductive' drugs, expressed in terms of the redox potential, has to be in the range: $E_{\text{activation by flavoproteines}} < E_{\text{'bio-reductive' drugs}} < E_{\text{protection against O2}}$. The reduction potentials thus obtained must be in the range of -0.50 to -0.10 V vs. SHE in buffered aqueous media and more negative in non-aqueous media; the values calculated in [15] are: -1.10 to -0.70 V vs. SCE.

Note that the anti-cancer activity of both cyanine and merocyanine dyes has been correlated (patent [16]) with their redox potentials, particularly in the cathodic range from -1.10 to -0.80 V vs. SCE.

The present study, carried out using voltammetry techniques, focuses on both the anodic and cathodic electrochemical behaviors of various streptocyanine dyes. Resulting voltammograms were analyzed using deconvolution techniques, expecting to get a better understanding of their reductive reaction mechanism, especially regarding the evolution of the radicals produced by the cathodic reaction. Coupling of the data obtained here with the biological properties of streptocyanines should help to examine the

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http://dx.doi.org/10.1016/j.electacta.2014.04.023
0013-4686/

Nomenclature

5 C, 7 C, 9C	streptocyanines dyes with 5, 7 and 9 carbon atoms linear chain
c°	concentration of the streptocyanine (mol.m^{-3}).
D	diffusion coefficient (m^2.s^{-1})
E°, E_{pa}, E_{pc}, $E_{p/2}$	various potentials (standard, anodic peak, cathodic peak and at the half of the peak current) used in this study (V)
F	Faraday constant (96500 C.mol^{-1})
I or $I(t)$	convoluted current
I_{lim}	convoluted limiting current
i_p	actual current (A)
k_χ	rate constant of a first or second order chemical reaction (2)
k_{ET}	electron transfer constant (cm.s^{-1})
n	number of electrons exchanged
p	stoichiometric factor
r	potential scan rate (V.s^{-1})
R	gas law constant (J.mol^{-1}.K^{-1})
S	electrode area (m^2)
SCE	saturated calomel electrode
SD	streptocyanine dyes
SHE	standard hydrogen electrode
t	time (s)
T	temperature (K)
TBAP	tetrabutylammonium perchlorate
u	variable dimensioned as a time
α	cathodic transfer coefficient
$\Delta G^{\#}$	Gibbs activation energy (J. mol^{-1})
$\Delta G^{\#}_{\circ}$	intrinsic Gibbs activation energy(J. mol^{-1})
ΔG°	standard Gibbs energy (J. mol^{-1})
$\lambda=(RT/F)(k_\chi c^\circ/r)$	dimensionless parameter allowing characterization the system kinetic answer

possibility to establish possible correlations between the electrochemical behavior of cyanines as well as their redox potential with their biological activity.

2. Experimental

Electrochemical experiments were performed using a previously described [17] three-electrode set-up with an Autolab PGSTAT 30. The medium was deaerated (Ar, 1 bar), acetonitrile containing 0.10 M tetrabutylammonium perchlorate (TBAP) and thermoregulated at 25 °C. The working electrode (3 mm diameter glassy carbon disk) was carefully polished, sonicated in 2-propanol for 10 min and finally dried in a stream of cool air. Before plotting the voltammograms, the electrode was activated by cycling several times from 2 to -2.5 V at 0.2 V.s^{-1}. The counter electrode was a 1 cm^2 platinum plate. A silver wire was used as pseudo-reference electrode; it was calibrated after each experiment against the ferrocene/ferricenium couple (0.475 V vs. SCE). A known concentration of ferrocene was added to the mixture studied and current potentials were plotted in the same conditions as for SD, in order to determine the potential of the position of the ferrocene oxidation peak. This potential is stable whatever the scan rate used, the uncertainty is + - 2 mV. Localization of the position of the ferrocene oxidation peak allowed the potentials of other signals to be determined versus the SCE. Impendence measurements allowed the determination of the ionic resistance of the mixture, and the value obtained was applied (feedback correction) to compensate for the ohmic drop between the working and reference electrodes.

The syntheses of 5C-, 7C-, 9C- streptocyanine dyes and of 5C-hemicarboxonium studied in the present work (Fig. 1), have been reported previously. [18–21]

3. Theoretical part

Cathodic reduction of streptocyanine dyes leads to a radical (shown a one electron cathodic peak, reaction 1), which can be involved in followed chemical reaction (2). This voltammetric study, expects to get a better understanding of their overall process of SD reduction, especially regarding the evolution of the radicals produced by the cathodic reaction. Especially, this section focuses on the kinetics of the process and especially on chemical reaction (2) which is linked to electron transfer (1).

$$SD^{+} + e^{-} \xrightarrow{k_{ET}} SD^{\circ} \tag{1}$$

$$pSD^{\circ} \xrightarrow{k_\chi} products \tag{2}$$

Limitation of the kinetics of the overall process could be due to: -the electron transfer (1), -the chemical reaction (2), -the diffusion process; mixed character limitation could also be observed.

To achieve this goal, the influence of the potential scan rate, r, on both the peak potential (E_p) and the difference $|E_{pc}$-$E_{pc/2}|$ was examined: these parameters can provide information on the limiting step of the overall process. Formal kinetics have been largely described by Savéant and co-workers [22,23] and the values of the two most significant parameters ($|E_{pc}$-$E_{pc/2}|$ and $\frac{\partial E_p}{\partial \log r}$) are indicated in the two extreme cases in Table 1.

3.1. Convolution potential sweep voltammetry assignments

Experimentally obtained voltammograms (see section 4) were analyzed using the convolution potential sweep voltammetry method [24]. The convoluted current $I(t)$ is related to the actual current $i(t)$ through the convolution integral:

$$I(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \tag{3}$$

The convoluted limiting value of $I(t)$, solely controlled by the diffusion flux at the electrode, is expressed by:

$$I_{\text{lim}} = n \times F \times S \times c^\circ \times D^{1/2} \tag{4}$$

where n is the electron exchanged, S is the electrode area, D is the diffusion coefficient, c° is the concentration of the streptocyanine.

The potential of the cathode can be expressed as a function of both the convoluted and the actual current, as well as the chemical rate constant k_χ according to the limitation (chemical or electrochemical.

-low rate constant k_χ for the chemical reaction (2):

The overall system is in pure diffusion control (the influence of the chemical reaction is negligible with charge transfer remaining Nernstian). The following equations allow the potential of the cathode to be determined:

$$E = E^\circ + \frac{RT}{F} \ln \frac{[I_{\text{lim}} - I]}{I} \tag{5}$$

$$\left|E_p - E_{p/2}\right| = 2.20\frac{RT}{F} = 57.5mV \tag{6}$$

$$\frac{\partial E_p}{\partial \log r} = 0 \tag{7}$$

-high rate constant k_χ for the chemical reaction (2):

The overall kinetics of the system is influenced by the chemical reaction (pure kinetic conditions). The cathode potential