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Redox interactions between dye 4-(E)-1-ethyl-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)quinolinium bromide and NAD^+/NADH

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An intrinsic property of the merocyanine dyes is the intramolecular charge transfer, which determines a variety of their applications in different fields like optical communication technology, molecular electronics, as optical chemosensors for analytical purposes and voltage-sensitive dyes for mapping membrane potential changes in excitable cells, etc. In this study, the electrochemical behavior of recently synthesized styrylquinolinium dye 4-(*E*)-1-ethyl-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)quinolinium bromide and its possible interaction with NAD^+/NADH redox couple have been investigated. It has been established that in neutral and alkaline buffer solutions the dye co-exists in benzenoid (reduced) and quinoid (oxidized) forms and the equilibrium between both forms can be shifted by change of pH. A quasi-reversible electrochemical behavior, assigned to consecutive electroreduction and electrooxidation of dye, has been observed by means of cyclic voltammetry. The redox coupled interaction between the dye and NAD in solution is evaluated by juxtaposing the results obtained by UV-Vis spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy.

Key words: styrylquinolinium dye, electrochemical activity, NAD+/NADH, UV-Vis spectroscopy, cyclic voltammetry, electrochemical impedance spectroscopy.

INTRODUCTION

Microbial fuel cells (MFCs) are devices capable of converting the chemical energy of available organic substrates directly into electricity by using different microorganisms as bio-micro reactors. The main drawback of MFC technology, which limits the broader application as power sources, is the low achieved power and generated current. One of the factors influencing the microbial fuel cells' performance is the electron transfer from the living cells to the anode surface, which might be overcome by the addition of the so called exogenous mediators (ExMs) of extracellular electron transfer (EET). Among the most explored artificial mediators are methylene blue [1, 2], thionine [3], neutral red [1, 4, 5], 2,6-dichloro phenolindophenol, safranine-O, phenothiazine, resurofin [6], etc. It is proven that the formal potential of every exogenous mediator determines the possibility for exchanging electrons with cellular redox molecules possessing close potential [7]. The highest increase of the current (1 $A.m^{-2}$) and power (640 $mW.m^{-2}$) generated by yeast-based biofuel cell has been achieved with the methylene blue [1], possessing formal potential Eo`= +0.055 V (vs. SHE). Exogenous mediators with positive formal potentials like thionine (Eo`=+0.064), methyl red (Eo`= +0.385), etc., act as electron acceptors beeing reduced by electrons originating from various metabolic pathways, while mediators with too negative formal potentials like bromocresol green (Eo`= -0.380 V) and neutral red (Eo`= -0.290 V) are capable of exchanging electrons only with redox molecules with more negative potentials (like NADH) in a way important for balancing levels for gain of biological and electrical energy [8]. Diverting electrons from different energetic levels, the exogenous mediators actually affect the metabolic pathways. It is demonstrated that bromocresol green and neutral red are capable of up-regulating alcoholic fermentation, while those with more positive potentials like methylene blue redirects the yeast catabolism to predominant aerobic respiration [2].

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Thus, the use of ExMs becomes a new appropriate approach for studying energy levels of metabolic pathways and their contribution to the EET. The mechanisms of acting of ExMs are still unclear and need more in vivo as well as in vitro investigations for explanation of the processes occurring within biocatalysts and the biofuel cell. Finding new redox active molecules as putative exogenous mediators will contribute to better understanding and elucidation of the reaction mechanisms between ExMs and cellular redox couples.

Recently, the influence of dye 4-{(*E*)-2-[4-(dimethylamino)naphthalen-1-yl]ethenyl}-1-methylquinolinium iodide (DANSQI) on the electrical outputs of *Candida melibiosica* 2491 yeast-based biofuel cell was investigated [9]. Exploring the possible mechanisms for the observed improved performance, it was suggested that the dye acts as subcellular shuttle on account of its specific intramolecular charge transfer properties and the transition between its basic forms - benzenoid and quinoid. The exchange of electrons/protons between DANSQI and subcellular electronophores was proved. It was also established that the presence of the dye affects the yeast metabolism. Subcellular studies showed that 1 μM dye increased 30-times the peroxisomal catalase activity (1.15 ± 0.06 Unit/mg protein) and twice the mitochondrial cytochrome *c* oxidase activity (92 ± 5 Unit/mg protein).

In this study, another, recently synthesized and characterized styrylquinolinium dye 4-(E)-1-ethyl-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)quinolinium bromide (shortly D3) [10, 11] was investigated in respect to establishment of its redox properties and possible interaction with NADH/NAD+ redox couple in solution. Like other styrylquinolinium dye [9], D3 contains 4-hydroxynaphthyl group and quinolinium moiety with quaternary nitrogen linked by conjugated bridge (−CH=CH–) [11]. Due to the conjugated structure, an intrinsic property of this class of dyes is the intramolecular charge transfer (ICT) from the phenol hydroxyl group (acting as an electron donor) through the π-conjugated bridge to the quinolinium moiety (acting as an electron acceptor). The results, obtained by means of electrochemical (EIS, CV) and spectrophotometric methods, are compared and discussed.

MATERIALS AND METHODS

Preparation of solutions

The styrylquinolinium dye 4-(E)-1-ethyl-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)quinolinium bromide (D3) was synthesized as previously described [10]. Freshly prepared 2.5 mM dye in DMSO was used as a stock solution for further dilution to 50 μM in the respective 0.1M buffer (phosphate buffered saline (PBS), pH 7; Tris-HCl, pH 8; acetate buffer, pH 4.6 and potassium phosphate, pH 10) or 10 mM NaOH.

1 mM nicotinamide adenine dinucleotide (NADH or NAD+) solutions were freshly prepared just before the experiments and mixed with the dye in proportion 10:1. 10 mM sodium hydroxide, pH 12, was used for stabilization of NADH in solution and preventing its non-controlled oxidation. Water alone should not be used to prepare NADH solutions since it is a proton-donor solvent and would decompose NADH.

Electrochemical studies

The electrochemical behavior of D3 alone and in mixtures with NAD+ or NADH was investigated by means of electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Both studies were performed in three-electrode mode by using platinum wires as working and counter electrodes and Ag/AgCl (3M KCl) as a reference electrode. The CV studies were carried out with different scan rates (from 10 mV/s to 1 V/s) by using PalmSens 2 potentiostat/galvanostat. The EIS measurements were conducted at frequency range varying from 50 kHz to 2 mHz, an ac signal of amplitude 10 mV and dc at a fixed potential module (vs. OCP). A PalmSence 3 potentiostat with EIS function was used for these analyses.

The capacitance of the double layer (C_{dl}) was estimated by formula (1):

$$C_{dl} = \frac{1}{\omega . R_{CT}} \quad (1)$$

where ω is the radial frequency (ω=2πf) and RCT is the charge transfer resistance determined from the impedance spectra.

The exchange current density (j0) was calculated using equation (2):

$$j_o = \frac{RT}{2FS} . \frac{1}{R_{CT}} \quad (2)$$

where R is the gas constant, T is the absolute temperature, F is the Faradaic constant, 2 is the number of exchanged electrons and S is electrode area in cm^2.

Spectrophotometric measurements

The spectrophotometric analyses for determination of the benzenoid (D3BF) and quinoid (D3QF) forms of the dye were performed in a wavelength scan mode between 200 nm and 800 nm, while the presence of the reduced or

oxidized form of NAD was traced up to 450 nm by using Hach-Lange UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

In our previous study [9], it was demonstrated that the hemicyanine dye DANSQI can undergo transformations from quinoid to benzenoid form and vice versa depending on the solvent. Taking into consideration that these reversible transformations are connected not only with ICT of electrons but also with processes of protonation/deprotonation [11], it can be expected that they are pH-dependent, i.e. the equilibrium between both forms can be shifted by changes of pH. To check this hypothesis, D3 was dissolved in buffers with different pH and the obtained solutions were analyzed spectrophotometrically. Two characteristic absorption bands can be distinguished on the recorded spectra (Fig. 1). The shorter-wave absorption band at 460 nm, corresponding to the SO–CT (where SO is the singlet state and CT is the charge transfer state) transition, is referred to the benzenoid structure of the dye (D3BF) and the longer wavelength band - to the quinoid form (D3QF) [12]. Normally, the absorption bands of the dye D3 are broad, having half-widths of about 5000 cm^{-1}. The broadness of the absorption bands may arise due to a contribution of more than one electronic state to the absorption spectrum or a broad distribution of conformers (solvent-solute or intramolecular) in the ground state. Analyzing the individual spectra, it can be concluded that in acidic medium only the benzenoid form exists, while in neutral and alkaline buffer solutions a co-existence of both forms of the dye is observed. It should also be noted that in alkaline media the characteristic absorption band for benzenoid form is sharpen, which is probably connected with deprotonation of the phenol hydroxyl group at high pH and formation of an anion [11, 13]. Such narrowing of the band was also observed with the addition of an organic base piperidine to the D3 solution [12, 14]. In anhydrous DMSO solution, D3 exists only in a quinoid form (Fig. 1, inner graph). The splitting of the absorption maximum into two bands with λmax at 680 nm and 650 nm is associated with aggregation phenomenon [11]. The maximum at 680 nm is assigned to a monomer, while the lower one at 650 nm - to the quinoid dimer. Though not so clearly expressed, a shoulder from shorter-wave side at 650 nm can be also distinguished in the spectra of the dye in alkaline buffer solutions.

The existence of D3 in reduced (benzenoid) and oxidized (quinoid) forms suggests that the dye could play the role of an electron-acceptor (oxidizer) as well as an electron-donor (reductant). Thus, it can be supposed that D3 may undergo a reversible electrochemical conversion and participate in a variety of processes with an exchange of electrons and/or protons.

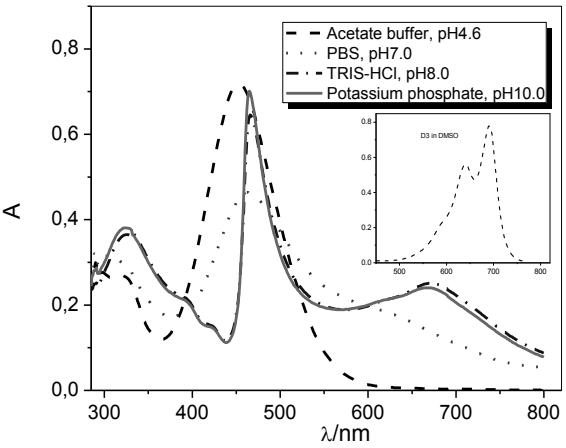

Fig. 1. UV-Vis spectra of dye D3 dissolved in buffers with different pH; inner graph – D3 in DMSO.

The electrochemical activity of D3 in alkaline buffer solution, where it exists in both reduced (D3BF) and oxidized (D3QF) forms, was examined by means of CV. When the potential was swept in negative direction, a well-defined cathodic peak appeared on the CVs, which shifted to more negative potentials with the increase of the scan rates (Fig. 2). At the lowest scan rate applied (50 mV/s), the cathodic peak potential in the presence of D3 (-54 mV vs. Ag/AgCl) significantly differs from that observed on the CV of the background NaOH electrolyte (-200 mV vs. Ag/AgCl), which supposes that the former one is attributed to the electroreduction of the dye on the electrode surface. After reversing the scan into positive direction, a big anodic peak is formed with a maximum at -540 mV vs. Ag/AgCl at 50 mV/s, shifting to more positive potentials with acceleration of the scan rate. It is worth noticing that at the same scan rate the position of this peak coincides with that of the anodic peak in the voltammogram of NaOH solution, which is firmly connected with the hydrogen desorption reaction. However, the much higher intensity of the corresponding anodic peak in the presence of D3 suggests a strong contribution of the dye to the formation of this peak. In a previous study [11], a two-step mechanism for oxidation of the reduced form of D3 was proposed, which first step includes a formation of negatively charged intermediate by deprotonation of the phenol hydroxyl group. Thus, it may be hypothesized that the enhanced anodic peak in the presence of D3 is due to the increased amount of protons as a product of dye deprotonation. Another evidence, supporting

such hypothesis, is the close intensity of the cathodic and anodic peaks at the same scan rates, supposing that the electroactive particles, participating in the oxidation reaction, originate from the reduced dye formed during the cathodic scan. At more positive potentials (above +400 mV vs. Ag/AgCl), an anodic hump (better distinguishable at higher scan rates) is observed, which could be assigned to the ICT and conversion of the intermediate dye anion into D3QF [11].

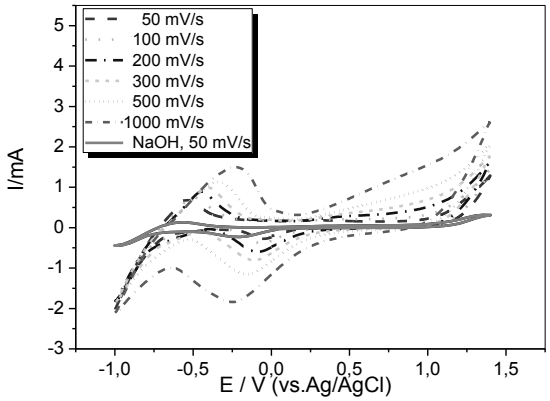

Fig. 2. Cyclic voltammograms of 50 μM 4-(E)-1-ethyl-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)quinolinium bromide (D3 dye) obtained with increasing scan rates.

The established electrochemical activity of D3 motivated the investigation of the putative interactions between the dye and reduced or oxidized form of NAD^+/NADH couple, which is widely explored as a model redox system because of its important role in the energetics of the living cells [15].

Distinguished differences were observed in the CV patterns obtained with NAD^+ and its mixture with D3 (Fig. 3a). While well-defined broad cathodic and anodic peaks, assigned to multistep electroreduction and re-oxidation, appeared in the CV of NAD^+, the CV of the mixture of NAD^+ and D3 is similar to that of NADH (Fig. 3b), suggesting that the predominant form of the dye D3BF reduced NAD^+ to NADH. Though the CVs of NADH and its mixture with D3 look similar, some differences in the patterns exist. First, in the presence of the dye the observed cathodic peak is shifted to more positive potentials, and second, a new oxidation peak at ca. +250 mV (vs. Ag/AgCl) appears, which is missing in the CV of NADH. The lack of pronounced anodic peak, corresponding to the NADH electrooxidation, may be attributed to different reasons such as electrode fouling, formation of electrochemically inactive intermediates, etc. Elving et al. [16] emphasized the impact of the experimental protocol on the results obtained in the electrochemical studies of the NAD system in aqueous media, especially as related to the effects of adsorption of the various NAD species, the mediation role of adsorbed and other surface species on the electrode, and the time-scale of the particular experimental approach used.

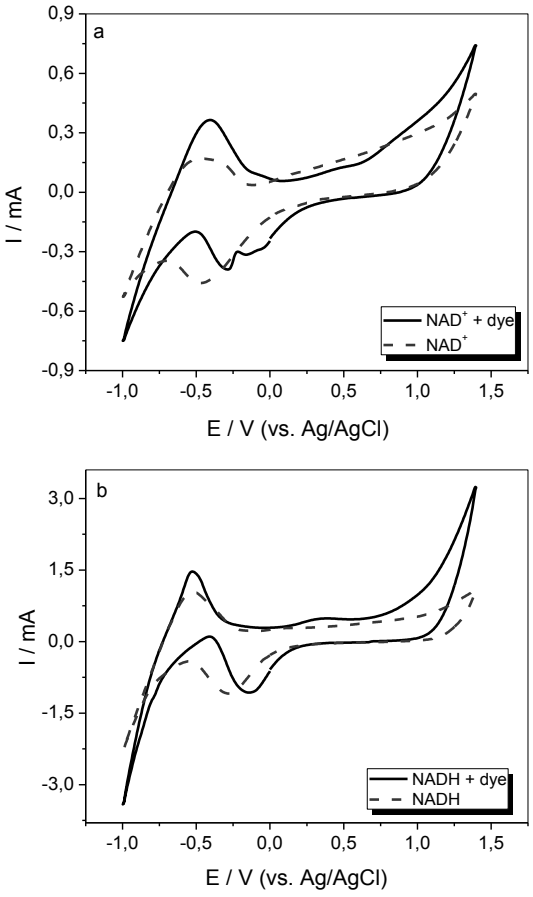

Fig. 3. Cyclic voltammograms of: a) 500 μM NAD+ (dashed line) and mixed solution of 500 μM NAD+ and 500 μM D3 (solid line); b) 500 μM NADH (dashed line) and mixed solution of 500 μM NADH and 500 μM D3 (solid line); Scan rate 200 mV/s.

It was supposed that in the case of Pt or Au electrodes, on which surface the adsorption of NAD^+ is negligible, the initial step in the NADH oxidation proceeds to at least some extent through mediator redox systems located close to the electrode surface such as OH^-_{ads}/H_2O, O_{ads}/OH^-_{ads} or other redox couples. It was also assumed that a key point in the NADH oxidation pattern is the deprotonation step and its relation to the initial electron-transfer step [16]. Thus, the appearance of the anodic peak at ca. +250 mV (vs. Ag/AgCl) in the CV of mixture of NADH and D3 could be related namely to the role of D3QF/D3BF redox couple as a mediator for initialization of NADH oxidation, probably associated with facilitated exchange of protons with the quinoid form of the dye.

Summarizing the results from the CV experiments, it can be concluded that due to the co-existence of both forms (D3QF and D3BF) in

alkaline buffer solutions the styrylquinolinium dye D3 may interact with NAD^+ as well as with NADH at appropriate conditions. Having in 3mind that the benzenoid form of the dye presents the reduced dye molecules, it is considered that the reduced dye donates electrons and a proton to the NAD^+, while the dye in its oxidized (quinoid) form may accept electrons/proton from NADH. In this way, the reduction of the dye occurs simultaneously with the oxidation of NADH and vice-versa in a non-enzymatic dynamic way (Fig. 4).

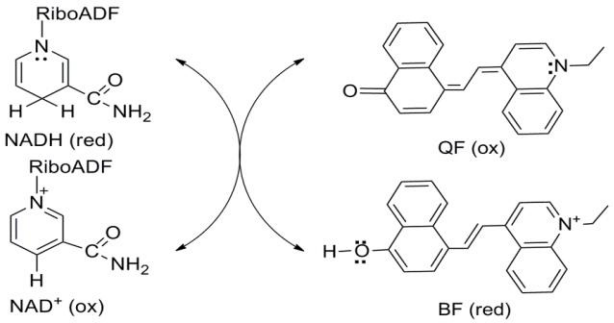

Fig. 4. Schematic presentation of the deductive reactions between D3 dye and NAD+/NADH.

The more evident differences in the CV patterns of NAD^+ and its mixture with D3 could be assigned to the predominance of the dye's reduced form (D3BF) in aqueous solutions, which interaction with the oxidized NAD is additionally forced by the applied electrochemical conditions. This hypothesis is supported by comparison of the UV-Vis spectra of mixture of NAD^+ and D3, recorded before and after the CV experiments (Fig. 5). The spectral data show that after electrochemical treatment of the mixture, the band of the benzenoid form decreases double, while the absorption band at higher wavelengths, representing the quinoid form, grows up, directing to a possible electrochemically forced coupled reaction between the dye and NAD.

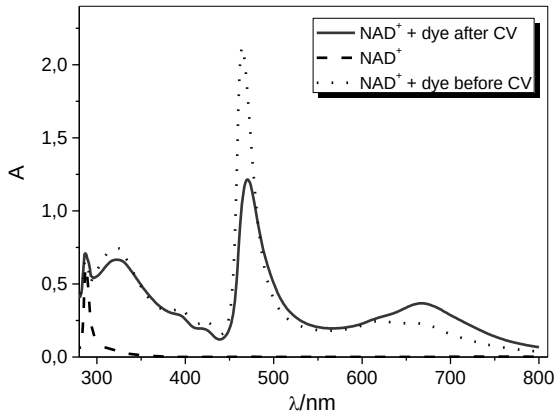

Fig. 5. UV-Vis spectra of 500 μM NAD+ and its mixture with 50 μM D3 before and after electrochemical experiments.

The interaction of the dye with NAD^+/NADH couple was additionally investigated by means of EIS. For the right interpretation of the obtained spectra, the data of the dye`s mixtures with NAD (Fig. 6a) have been compared with those of the substances alone (Fig. 6b). While all samples are diffusion limited at mid and low frequency range, the response to the applied sinusoidal signal in the high frequencies varied for the different substances (Fig. 6, insets; Table 1).

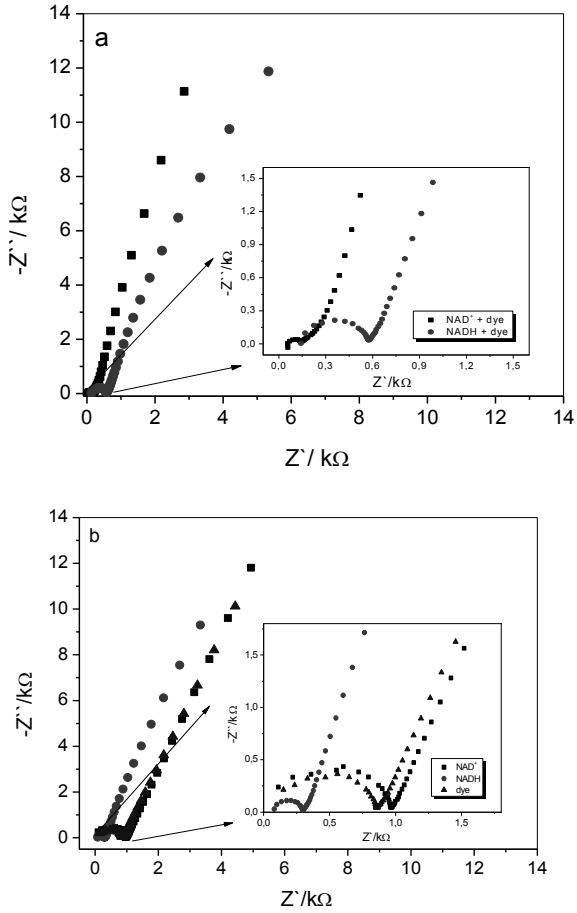

Fig. 6. Nyquist plots of: a) mixed solutions of 500 μM NAD+ + 50 μM D3 and 500 μM NADH + 50 μM D3; b) individual solutions of 50 μM D3; 500 μM NAD+ and 500 μM NADH, recorded at frequency range from 50 kHz to 2 mHz with sinus amplitude 10 mV. Insets - magnification of the impedance spectra at high frequencies.

It was assumed that the observed diverse parameters like ohmic (R_Ω) and charge transfer (R_{CT}) resistances as well as double layer capacitance (C_{dl}) are a consequence of occurred interaction in the case of mixed dye. For instance, the ohmic resistance of the dye itself remains identical in the presence of NADH (even when in excess), while the polarization resistance was twice lower and the capacitance – twice higher. Comparing the R_{CT} and C_{dl} of NADH alone to those of the mixture dye/NADH, it is seen that R_{CT} is

twice lower than that of the mixture but C_{dl} is twice higher. It was supposed that the capacitance of the mixed with NADH dye is lower because of their interaction in the solution and in the frame of the double layer exchanging electrons/protons, which would decrease their transfer to the electrode. In this way, although the smallest diameter was observed for NADH alone, showing the possible exchange of its 2 electrons and a proton with the electrode, the increasing arc diameter of the mixture indicates the exchange of NADH electrons and protons not with the electrode but with dye molecules instead. Having in mind, on the one hand, the intermediates formed and on the other one, the small surface of the Pt electrode, both could explain the increased resistances and bigger arc diameter. If we accept that a part of the NADH molecules are oxidized by the dye molecules (D3QF) we have to assume that NAD^+ is dynamically formed (thus D3BF, D3QF, NAD^+ and NADH are present in the sample). That is why the data obtained with NAD^+ alone and in mixture with the dye have been also compared. The presence of more reduced dye`s molecules in the sample, which might reduce NAD^+ molecules argues the lower ohmic resistance of the mixture dye/NAD^+ compared to NAD^+ alone. At the same time the R_{CT} of the mixture was 9-times lower than that of the NAD^+ and about 7-times lower than that of the dye alone. The highest capacitance of the dye/NAD^+ mixture could be due to the newly formed NADH, which itself shows the highest exchange current density among the pure explored substances. The similarity of the arc`s diameters of dye/NAD^+ and NADH itself supports this assumption.

Table 1. Extracted data from recorded electrochemical impedance spectra.

Sample	Ohmic resistance (R_Ω) Ω	Charge transfer resistance (R_{CT}) Ω	Double layer capacitance (C_{dl}) nF	Exchange current density (j_0) μA/cm^2
Dye D3 + NADH	145	431	25	37
Dye D3 + NAD^+	55	95	112	168
Dye D3	150	707	15	23
NADH	80	220	48	73
NAD^+	115	860	12	19

CONCLUSIONS

The dye 4-(*E*)-1-ethyl-4-(2-(4-hydro xynaphthalen-1-yl)vinyl)quinolinium bromide (D3), dissolved in neutral and alkaline buffer media, exists in benzenoid (reduced) and quinoid (oxidized) forms, which equilibrium is pH dependent. In alkaline buffers the dye can undergo reversible electrooxidation/electroreduction. It has been also established that dye D3 react with both oxidized and reduced forms of NAD, more pronounced with NAD^+, probably because of the predominance of benzenoid form (D3BF) at the explored experimental conditions. The coupled redox reactions can be detected by CV and EIS. The obtained results reveal a possibility for development of non-enzymatic method for detection of NAD *in vitro* as well as potential for utilization of the styrylquinolinium dye D3 as an exogenous mediator of electron transfer in bioelectrochemical systems as microbial fuel cells.

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Окислително- редукционни взаимодействия между багрилото 4- (E) -1-етил-4- (2- (4-хидроксинафтален-1-ил) винил) хинолиниев бромид и NAD+/NADH

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(Резюме)

Присъщо свойство на мероцианиновите багрила е вътрешномолекулния пренос на заряд, който определя приложенията им в различни области като оптично- комуникационна технология, молекулярна електроника, използването им като оптични хемосензори за аналитични цели и картографиране на измененията на мембранния потенциал във възбудими клетки. В настоящото изследване е анализирано електрохимичното поведение на синтезираното наскоро багрило 4- (E) -1-етил-4- (2- (4-хидроксинафтален-1 -ил) винил) хинолиниев бромид и възможното му взаимодействие с редокс двойката NAD^+/NADH. Установено е, че в неутрални и алкални буферни разтвори багрилото съществува в своята бензоеноидна (редуцирана) и хиноидна (окислена) форма и равновесието между двете форми може да се измести чрез промяна на pH. Квази-обратимо електрохимично поведение, отнесено към последователни електроредукция и електроокисление на багрилото, е наблюдавано с помощта на циклична волтамперометрия. Сдвоеното окислително-редукционно взаимодействие между багрилото и NAD в разтвора е оценено чрез съпоставяне на резултатите от UV-Vis спектроскопия, циклична волтамперометрия и електрохимична импедансна спектроскопия.