Modeling the Characteristics of a Polyaniline–DNA Film from the Voltammetric Response of the Product of Electropolymerization[1]

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Abstract—The article studies the anodic voltammetric response of polyaniline obtained by electropolymerization of aniline from a 3.7 M sulfuric acid solution in the presence of two DNA samples differing in source and molecular weight. Electropolymerization was carried out in the cyclic voltammetry mode with varying the number of potential sweep cycles and concentrations of DNA samples. The voltammetric response data of polyaniline, obtained in the voltammetry mode with a linear potential sweep to the anode region, were analyzed using a theoretical model that takes into account capacitive currents, electrochemically reversible Faraday currents, and the interaction between the redox centers of polyaniline. An analysis of the data obtained showed a significant nonlinear effect of the number of polymerization cycles, concentration, and nature of the DNA samples on the energy of interaction between the redox centers of polyaniline.

Keywords: electropolymerization, polyaniline, DNA, voltammetry, polymer redox center interactions model

INTRODUCTION

The combination of polyaniline (PANI) and DNA is successfully used as part of highly sensitive electrochemical sensors and biosensors. In particular, the use of PANI obtained by electropolymerization of aniline in oxalic acid in the presence of native DNA made it possible to create a sensor for determining DNA intercalators of the anthracycline series [1]. In a similar sensor for the determination of doxorubicin based on the electrochemical parameters of the PANI–DNA layer, it was proposed to update the DNA layer, which made it possible to perform multiple analyte determination [2]. Incorporation of DNA between two layers of electropolymerized PANI in a sensor with impedimetric signal recording reduced the doxorubicin detection limit to 0.6 pM [3]. In these biosensors, PANI served simultaneously as a signal-forming component and a matrix for DNA physical immobilization based on non-covalent binding of native DNA due to electrostatic interactions between negatively charged phosphate groups of the DNA backbone and positively charged PANI chains. Similar interactions were used to extract DNA from aqueous solutions using PANI-coated magnetic particles [4].

Single stranded DNA molecules aggregate with PANI due to $\pi-\pi$ interactions between nucleic bases and PANI [5]. Upon hybridization of single stranded DNA located on the PANI surface, with a complementary succession, desorption of the hybridization product occurs. In this case, the properties of PANI change, in particular, its reaction with a fluorescent dye [6, 7]. DNA aggregation can also be carried out using bridging metal ions and a PANI derivative bearing sulfate groups [8]. Sorption of biomolecules on the PANI surface can be used to separate and isolate single- and double-stranded DNA molecules from complex biological matrices [9]. A detailed study of the processes of DNA sorption on the PANI surface by the methods of spectral correlation interferometry and chromatography using spin columns was carried out in [10, 11].

The formation of DNA–PANI complexes changes both the conformation of the biopolymer [12] and the properties of PANI. This has found application in the formation of nanostructured materials containing both components [13–16]. In them, DNA spatially orients PANI polymer chains, simultaneously doping them. The latter process increases the upper pH limit of the manifestation of the electrical conductivity of the polymer.

To characterize DNA–PANI complexes, a large set of physicochemical methods of analysis is used,

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[1] A tribute to outstanding electrochemist Oleg Aleksandrovich Petrii (1937–2021).

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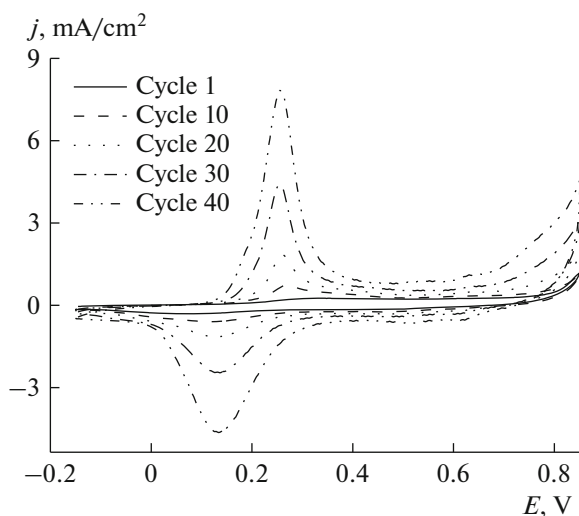
Fig. 1. An example of voltammograms recorded during the electropolymerization of a 0.5 M solution of aniline in 3.7 M H_2SO_4 containing 1 mg/mL of DNA1. The voltammograms recorded on the 1st, 10th, 20th, and 40th cycles of the potential sweep are shown.

among which are spectrophotometry in the visible and UV light regions, IR Fourier spectroscopy, circular dichroism spectroscopy, atomic force microscopy [17], MALDI mass spectrometry, and scanning electron microscopy [18]. Due to the electrochemical activity of PANI, electrochemical impedance spectroscopy [19] and cyclic voltammetry [20] are effective methods for analyzing DNA−PANI complexes. The latter is the most accessible. An analysis of the data obtained by this method provides important information about the properties of the polymer and the nature of the effects of various factors.

Previously, a theoretical model of the electrochemical oxidation of a PANI film was proposed, which can be used to analyze voltammograms and obtain information about the parameters of the electropolymerization product [21]. This was demonstrated by the voltammetric evaluation of the aging of PANI [22, 23], the study of the effect of pH on it [24], and the nature of anions [25], as well as the study of the nature of the electrical conductivity and capacitance of PANI [26, 27].

In this work, this approach is extended to describe the effect of the concentration and nature of DNA in solution during the electropolymerization of aniline on the thermodynamic characteristics of the resulting PANI.

1. EXPERIMENTAL

In this work, we used low-molecular DNA from salmon milt (DNA1, Sigma, USA, Cat. No. 31149, average molecular weight 4.6 kDa) and DNA from fish milt (DNA2, Sigma, USA, Cat. No. 74782, molecular

weight 40−1000 kDa). The rest of the reagents were qualified as "reagent grade."

Voltammetric measurements were carried out in a non-thermostated cell with a volume of 5 mL at room temperature. Voltammograms were recorded using an AUTOLAB PGSTAT 302N potentiostat-galvanostat with a SCAN250 linear potential sweep module and NOVA 1.11 software (Metrohm Autolab B.V., Netherlands). The working electrodes were glassy carbon electrodes (GCE) made from glassy carbon SU 2000 (NIIGrafit, Moscow) in the form of 20-mm-long rods with a cross section of 2.8 mm^2, inserted into polytetrafluoroethylene insulating tubes. Electrical contact was provided by a stainless steel current collector attached to the glassy carbon rod on the opposite side from the working surface by means of an electrically conductive adhesive based on epoxy resin and carbon black. A silver chloride electrode (Ag/AgCl/3 M KCl) (Metrohm Autolab B.V., Netherlands) was used as a reference electrode. A platinum rod 2 mm in diameter served as an auxiliary electrode.

Immediately before use, the GCE was mechanically polished with alumina powder and washed with ethyl alcohol and distilled water. After that, the electrode was electrochemically cleaned in a 0.2 M H_2SO_4 solution 10 times by potential cycling in the range from −0.2 to 1.0 V at a scanning rate of 0.1 V/s.

PANI on the GCE surface was obtained at room temperature by multiple potential cycling in the range from −0.15 to 0.85 V at a scanning rate of 0.1 V/s in an aqueous solution containing 0.5 M aniline, 3.7 M H_2SO_4, and the required DNA concentration. It should be noted that, in a solution with such an acid concentration, DNA molecules partially undergo apurinization, as a result of which damaged DNA molecules may occur in the reaction mixture during aniline polymerization [28]. An example of voltammograms recorded during the electropolymerization of aniline is shown in Fig. 1. After electropolymerization, the electrode was removed from the reaction mixture with an open circuit, washed with a 3.7 M H_2SO_4 solution, and placed in a cell with a 3.7 M H_2SO_4 solution for the voltammetric characterization of PANI.

The voltammetric characteristic of the electropolymerized PANI was carried out by linear potential sweeping from 0 to 0.85 V at a sweep rate of 0.1 V/s in a 3.7 M H_2SO_4 solution; in this case, the electrode was kept at a potential of 0 V for 5 s before the start of recording the voltammogram. In the voltammogram obtained, the peak current (j_p) and peak potential (E_p) of PANI oxidation were determined. An example of recorded voltammograms is shown in Fig. 2. The dependence of the charge consumed during the oxidation of PANI on the electrode potential was calculated by integrating the dependence of the current density on the potential in the range from 0 to 0.85 V.

2. RESULTS AND DISCUSSION

The effect of DNA on the electrochemical polymerization of aniline was characterized using a formal representation of the electrochemical oxidation of PANI described in [21]. For this, using the experimental data obtained in the reversible electrochemical oxidation of PANI films, a mathematical model was constructed that describes the interactions between PANI redox centers, taking into account the capacitive and Faraday current components in the voltammogram.

2.1. Theoretical Model of Electrochemical Oxidation of a PANI Film

The process involving a PANI film on the electrode surface can be represented in general form as

$$\text{Red} \rightleftarrows \text{Ox}^{n+} + ne. \qquad (1)$$
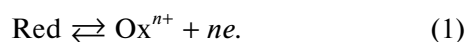
The charge transfer inside the film is accompanied by a counter ion flow to maintain the overall electrical neutrality of the polymer layer. To simplify the analysis, it was assumed that these processes are sufficiently fast and the state of the polymer at each electrode potential value can be considered equilibrium. The total charge Q_T consumed in the electrochemical oxidation of PANI, which is a function of the electrode potential E, can be represented as the sum of the capacitive charge Q_C of the PANI film and the charge Q_F corresponding to the Faraday current during charge transfer from the polymer to the electrode:

$$Q_T(E) = Q_C(E) + Q_F(E). \qquad (2)$$

It is assumed that the integral electrical capacity of the polymer film is proportional to the Faraday charge arising during the PANI oxidation and is determined by the product aQ_F, where a is the proportionality coefficient, which is a characteristic of a particular PANI film.

When PANI completely transforms into the oxidized form at high potentials ($E > E_L$), the Faraday current tends to 0. In this case, the recorded current is determined only by the capacitive component and Q_F stops changing, reaching the asymptotic value Q^0, which is the maximum charge of the Faraday process spent on the oxidation of all PANI redox centers.

Thus, the product aQ^0 is a characteristic of a particular PANI film, is constant, and does not depend on the applied potential and sweep rate. Performing the mathematical transformations presented in [21], we can obtain Eq. (3), in which E_z is the zero-charge potential of the polymer:

$$Q_T(E > E_L) = Q^0(1 - aE_z) + aQ^0E. \qquad (3)$$

At sufficiently high potentials ($E > E_L$), the dependence of Q_T on E acquires a linear form (Fig. 3). In the linear dependence region, linear regression is con-
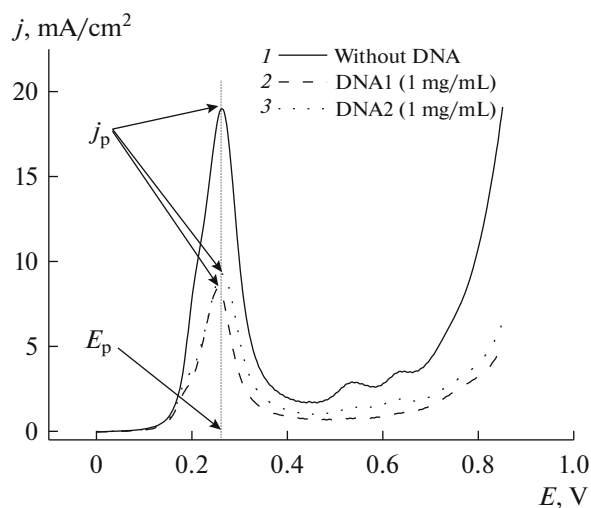
Fig. 2. An example of voltammograms recorded with electropolymerized PANI in 3.7 M H_2SO_4. The number of electropolymerization cycles is 40; (*1*) in a solution without DNA, (*2*) in a solution with DNA1 1 mg/mL, and (*3*) in a solution with DNA2 1 mg/mL.
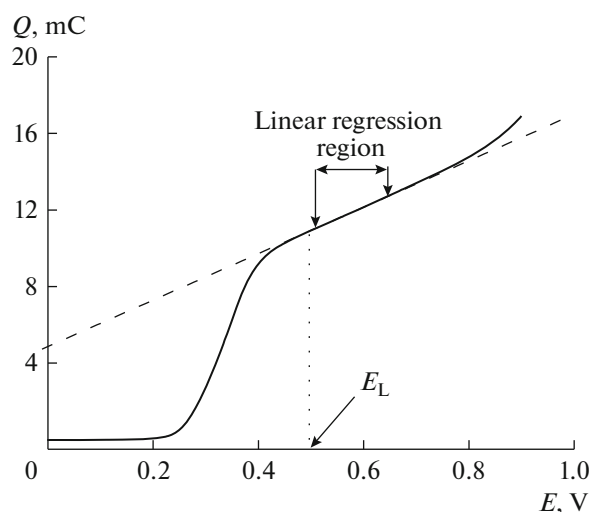
Fig. 3. An example of the dependence of the measured charge in the oxidation of PANI on the applied potential; (dotted line) the line obtained by linear regression in the specified region of dependence using the least squares method; E_L is the potential at which the Faraday current becomes 0.

structed using the least squares method, the parameters of which are the coefficients of the line defined by Eq. (3). The slope of this line is aQ^0, and its intersection with the *y*-axis ($E = 0$) allows one to get the value of $Q^0(1 - aE_z)$, which gives $(E_z - a^{-1})$.

Thus, for each PANI film sample obtained with a certain combination of DNA concentration and the number of aniline polymerization cycles, the PANI

voltammetric response was recorded, presented in the form of the initial voltammogram (Fig. 2) and in its integrated form (Fig. 3), according to which the parameter values j_p, E_p, aQ^0, and $(E_z - a^{-1})$ were determined and used in further calculations. It should be noted that none of the parameter values (a, Q^0) can be obtained from the voltammogram data separately.

2.2. Voltammetric Response in the Presence of Interactions between PANI Redox Centers

Let the polymer film contain N_{Red} reduced and N_{Ox} oxidized redox centers, the sum of which $N = N_{Red} + N_{Ox}$ is a constant. The mutual transition of these centers is governed by Eq. (1). It is assumed that each redox center can interact with a certain number of neighboring polymer redox centers, equal to c_{neighb}. When considering the interactions of pairwise neighboring centers, three types can be distinguished: interaction between a pair of oxidized centers with an average energy ε_{OO}, interaction between a pair of reduced centers with an average energy ε_{RR}, and interaction between an oxidized and a reduced center with an average energy ε_{RO}.

Using the self-consistent field method [21], one can obtain Eqs. (4)–(8), in which ξ_R and ξ_O are dimensionless interaction parameters, N_{Av} is the Avogadro number, R is the universal gas constant, F is the Faraday constant, T is absolute temperature, x_p is the fraction of oxidized sites at the peak potential, and E^0 is the standard redox potential of PANI:

$$\xi_R = -\frac{c_{neighb}N_{Av}(\varepsilon_{RR} - \varepsilon_{RO})}{RT} \quad (4)$$

$$\xi_O = -\frac{c_{neighb}N_{Av}(\varepsilon_{OO} - \varepsilon_{RO})}{RT}, \quad (5)$$

$$E_p = E^0 - \frac{RT}{nF}[(\xi_R + \xi_O)x_p - \xi_R] - \frac{RT}{nF}\ln\left(\frac{1 - x_p}{x_p}\right), (6)$$

$$\frac{j_p}{avQ^0} = \frac{nF}{RT}\frac{(E_p - E_z + a^{-1})(1 - x_p)x_p}{[1 - (\xi_R + \xi_O)(1 - x_p)x_p]} + x_p, \quad (7)$$

$$x_p = \frac{1}{2} + \frac{RT}{nF}\frac{[1 - (\xi_R + \xi_O)(1 - x_p)x_p]^2}{(E_p - E_z + a^{-1})}. \quad (8)$$

Using numerical methods for solving the system of nonlinear equations (7) and (8) at $T = 298$ K, $n = 2$, with the initial approximation $x_p = 0.5$ and other parameters determined from experimental data, we can obtain the values of x_p and $(\xi_O + \xi_R)$. Having obtained the value of $(\xi_R + \xi_O)$ and using Eq. (6) at $E_0 = 0.225$ V [21], separate values of ξ_R and ξ_O are calculated.

2.3. Determining the Parameters of the Voltammetric Response of PANI Oxidation

Using the section of linear dependence of the charge spent on PANI oxidation on the electrode potential (see Fig. 3), the parameters of the line were obtained using the least squares method, from which aQ^0 and $(E_z - a^{-1})$ for each PANI film were calculated.

The parameters obtained were used to solve the system of nonlinear equations (7) and (8) in the R version 3.6.2 software package for statistical calculations. Solving the system of equations makes it possible to obtain the values of x_p and $(\xi_R + \xi_O)$ and, solving Eq. (6), the individual values of ξ_R and ξ_O. In particular, the indicators $(\xi_R - \xi_O)$ and $(\xi_R + \xi_O)$ are of interest. According to Eqs. (4) and (5), the difference $(\xi_R - \xi_O)$ is directly proportional to the difference between ε_{OO} and ε_{RR} $((\xi_R - \xi_O) \sim (\varepsilon_{OO} - \varepsilon_{RR}))$, which makes it possible to estimate the effect of external factors on the change in the Helmholtz free energy of the oxidized and reduced forms of PANI. The sum $(\xi_R + \xi_O)$ is proportional to $(2\varepsilon_{RO} - \varepsilon_{OO} - \varepsilon_{RR})$, which, at negative values of $(\xi_R + \xi_O)$, implies $(\varepsilon_{OO} + \varepsilon_{RR} > 2\varepsilon_{RO})$. A decrease in this sum indicates that, for a partially oxidized polymer and a fixed oxidation state, the equilibrium between the existence of a system of pairs of reduced−oxidized structural elements, as well as an equivalent system consisting of reduced−reduced and oxidized−oxidized pairs, shifts towards systems with reduced−oxidized elements.

2.4. Effect of DNA Concentration and Type on the Thermodynamic Parameters of PANI

PANI polymerization was carried out in the absence of DNA, as well as in the presence of DNA1 and DNA2 samples with concentrations of 0.2, 0.5, and 1.0 mg/mL. The interaction parameters of PANI redox centers were determined for the 10th, 20th, 30th, and 40th polymerization cycles. To obtain statistically significant results, the experiment was repeated using different electrodes from 3 to 6 times under the same conditions.

To assess the effect of the number of polymerization cycles and the concentration of DNA in solution on ξ_R, ξ_O, $(\xi_R - \xi_O)$, and $(\xi_R + \xi_O)$ for two DNA samples, generalized additive models (GAM) were built, which are regression models with a nonlinear transformation of the original features [29]. The models were built in the R version 3.6.2 software package using the mgcv package version 1.8-31. The models had the form (9):

$$y = b + f1(N_{Cycl}) + f2(C_{DNA}) + e, \quad (9)$$

where y is one of the parameters E_p, x_p, ξ_R, ξ_O, $(\xi_R - \xi_O)$, and $(\xi_R + \xi_O)$; N_{Cycl} is the number of polymerization cycles; C_{DNA} is the DNA concentration (mol/L) in solution upon polymerization; b is a free term; ε is a
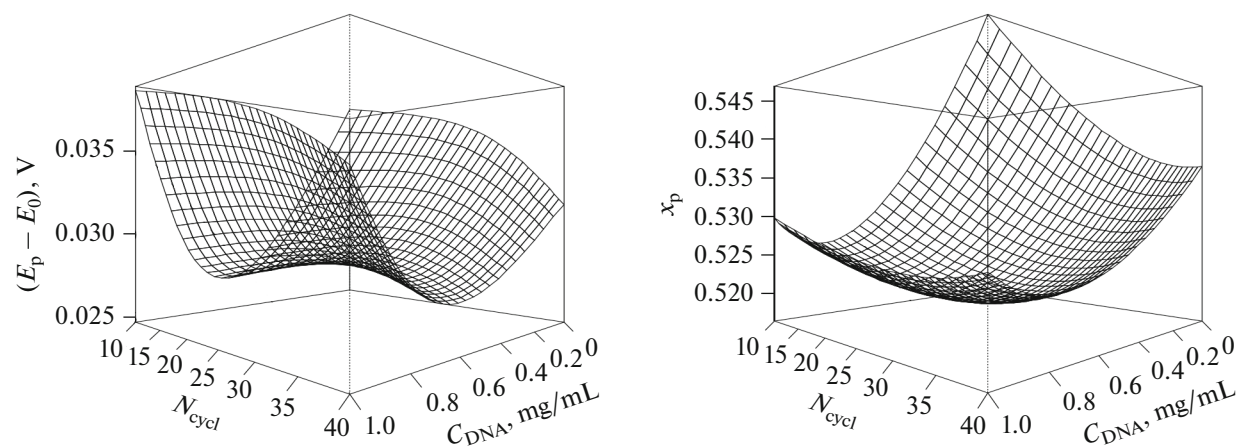
Fig. 4. Graphical representation of the models of dependence $(E_p - E_0)$ and x_p on the number of PANI polymerization cycles and DNA concentration.

term containing random errors not taken into account by the model (residuals); and $f1$ and $f2$ are nonlinear smooth spline functions (thin plate regression splines).

Table 1 presents the characteristics of the models obtained. The effect of the DNA source on the parameters E_p and x_p is statistically insignificant; therefore, these parameters were simulated using the generalized data for DNA1 and DNA2. For the rest of parameters, in the case of DNA1, both the number of polymerization cycles and the DNA1 concentration are significant factors in all the models obtained and the functions of the corresponding dependences are nonlinear (the effective number of degrees of freedom is greater than one). When using DNA2, the number of polymerization cycles is also a significant factor and its

dependences of the simulated parameters are nonlinear. For the DNA2 concentration, all dependences are linear (the number of degrees of freedom is 1). It should be noted that the significance level of the DNA2 concentration parameter for ξo is 0.96, which indicates that there is no relationship between the DNA2 concentration and ξo.

The resulting models are presented in graphical form in Figs. 4–6. It can be seen in Fig. 4 that the peak potential depends nonlinearly on the number of polymerization cycles with a minimum located about 25 cycles, while the potential changes within 15 mV. Increasing the DNA concentration increases the peak potential only slightly. The proportion of oxidized centers at the peak potential also varies nonlinearly with an increase in the number of polymerization

Table 1. Characteristics of the generalized additive models of dependences of x_p, ξ_R, ξ_O, $(\xi_R - \xi_O)$, and $(\xi_R + \xi_O)$ on the number of polymerization cycles and DNA concentration

| Model		Effective number of degrees of freedom (p is the significance level)		Percentage of explained data variability, %
		$f1(N_{Cycl})$	$f2(C_{DNA})$	
DNA	E_p	2.78 ($<2 \times 10^{-16}$)	1.88 (1.9×10^{-5})	66.8
DNA	x_p	1.96 (8.8×10^{-11})	1.74 (7.4×10^{-7})	43.3
DNA1	ξ_R	2.94 ($<2 \times 10^{-16}$)	2.38 (4.8×10^{-7})	85.5
	ξ_O	2.79 ($<2 \times 10^{-16}$)	2.54 (6.2×10^{-6})	84.8
	$(\xi_R - \xi_O)$	2.80 ($<2 \times 10^{-16}$)	2.70 (8.8×10^{-9})	84.8
	$(\xi_R + \xi_O)$	2.91 ($<2 \times 10^{-16}$)	1.38 (1.7×10^{-4})	85.2
DNA2	ξ_R	2.86 ($<2 \times 10^{-16}$)	1.00 (1.3×10^{-7})	81.1
	ξ_O	2.88 ($<2 \times 10^{-16}$)	1.00 (0.96)	88.2
	$(\xi_R - \xi_O)$	2.73 ($<2 \times 10^{-16}$)	1.00 (7.3×10^{-5})	78.3
	$(\xi_R + \xi_O)$	2.93 ($<2 \times 10^{-16}$)	1.00 (3.6×10^{-5})	89.1
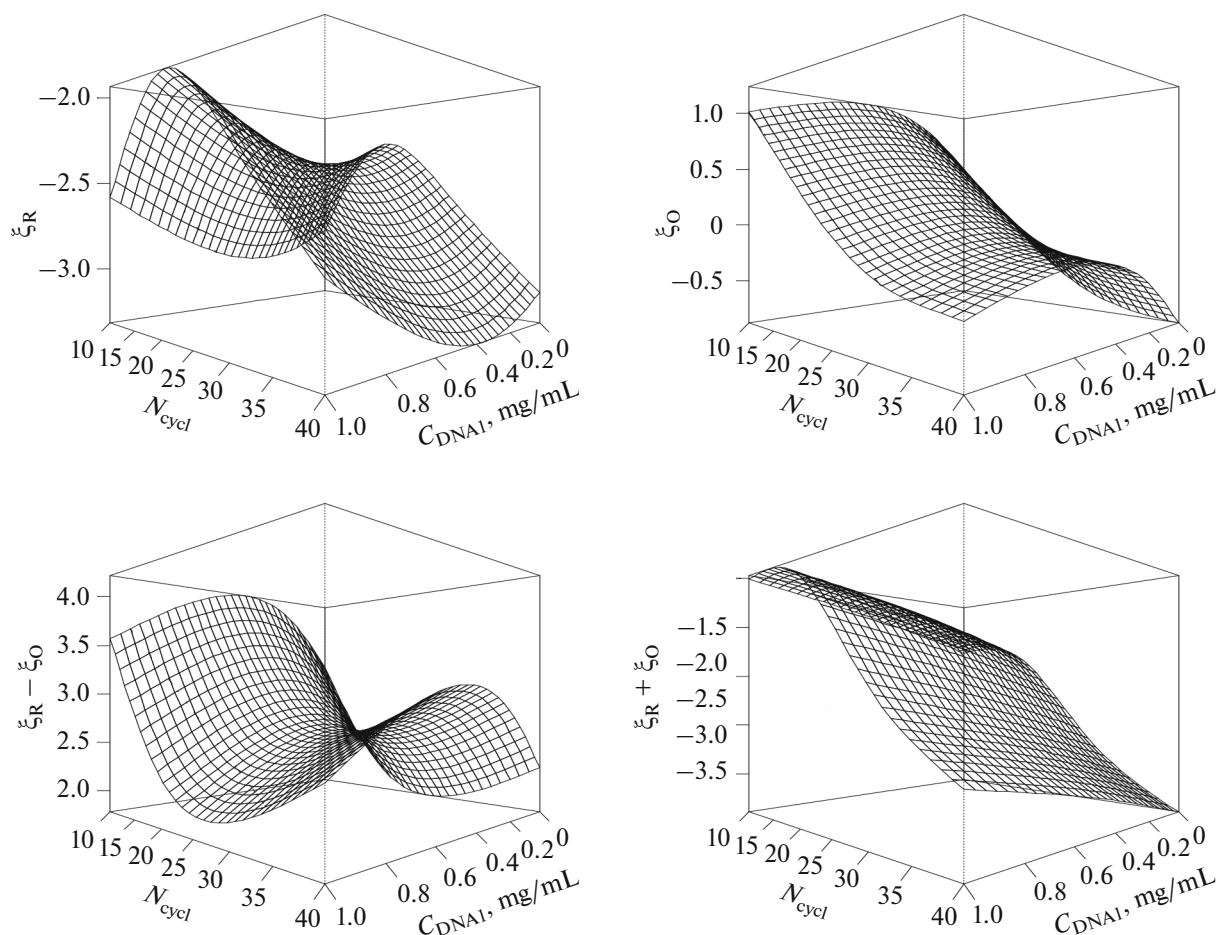
Fig. 5. Graphical representation of models of dependences of ξ_R, ξ_O, $(\xi_R - \xi_O)$, and $(\xi_R + \xi_O)$ on the number of PANI polymerization cycles and DNA1 concentration.

cycles, decreasing slightly in the range up to 20 cycles and increasing with a further increase in the number of cycles within 0.015 units. Increasing the DNA concentration slightly increases x_p by 0.010 units. Positive values of $(\xi_R - \xi_O)$ indicate that the energy of interactions between oxidized centers is greater than that between reduced ones. A decrease in $(\xi_R - \xi_O)$ indicates a decrease in the free energy of the oxidized form or an increase in the free energy of the reduced form of PANI. The minimum values of $(\xi_R - \xi_O)$ upon varying the number of polymerization cycles for both DNA1 and DNA2 are observed at about 25 cycles. The addition of any of the used DNA samples to the polymerization to the solution leads to an increase in $(\xi_R - \xi_O)$. This suggests that an increase in the DNA concentration leads to an increase in the free energy for the oxidized form of PANI or a decrease in the free energy for the reduced form of the polymer. Moreover, in the case of DNA1, the effect is leveled at a DNA1 concentration greater than 0.5 mg/mL. When using DNA2, an increase in its concentration does not have a statis-

tically significant effect on the parameter ξ_O. Thus, all changes in $(\xi_R - \xi_O)$ are entirely related to ξ_R, which indicates a significantly greater effect of DNA2 on the reduced form of the polymer, which is expressed in a decrease in the interaction energy between reduced centers.

An increase in the number of polymerization cycles reduces $(\xi_R + \xi_O)$ for both DNA samples, which indicates a shift in equilibrium towards the existence of reduced–oxidized structural elements compared to the separate existence of reduced–reduced and oxidized–oxidized pairs. This may indicate that the distributed lattice of polarons is preferred over bipolaron structures [26, 30]. The structural elements of the distributed polaron lattice, according to [26], are responsible for the charge transfer in PANI. The effect of DNA concentration on $(\xi_R + \xi_O)$ is linear, but the effect of different DNA samples is multidirectional. Low-molecular DNA1 increases this parameter, stabilizing bipolaron structures, while DNA2 reduces it, contributing to the existence of a distributed polaron
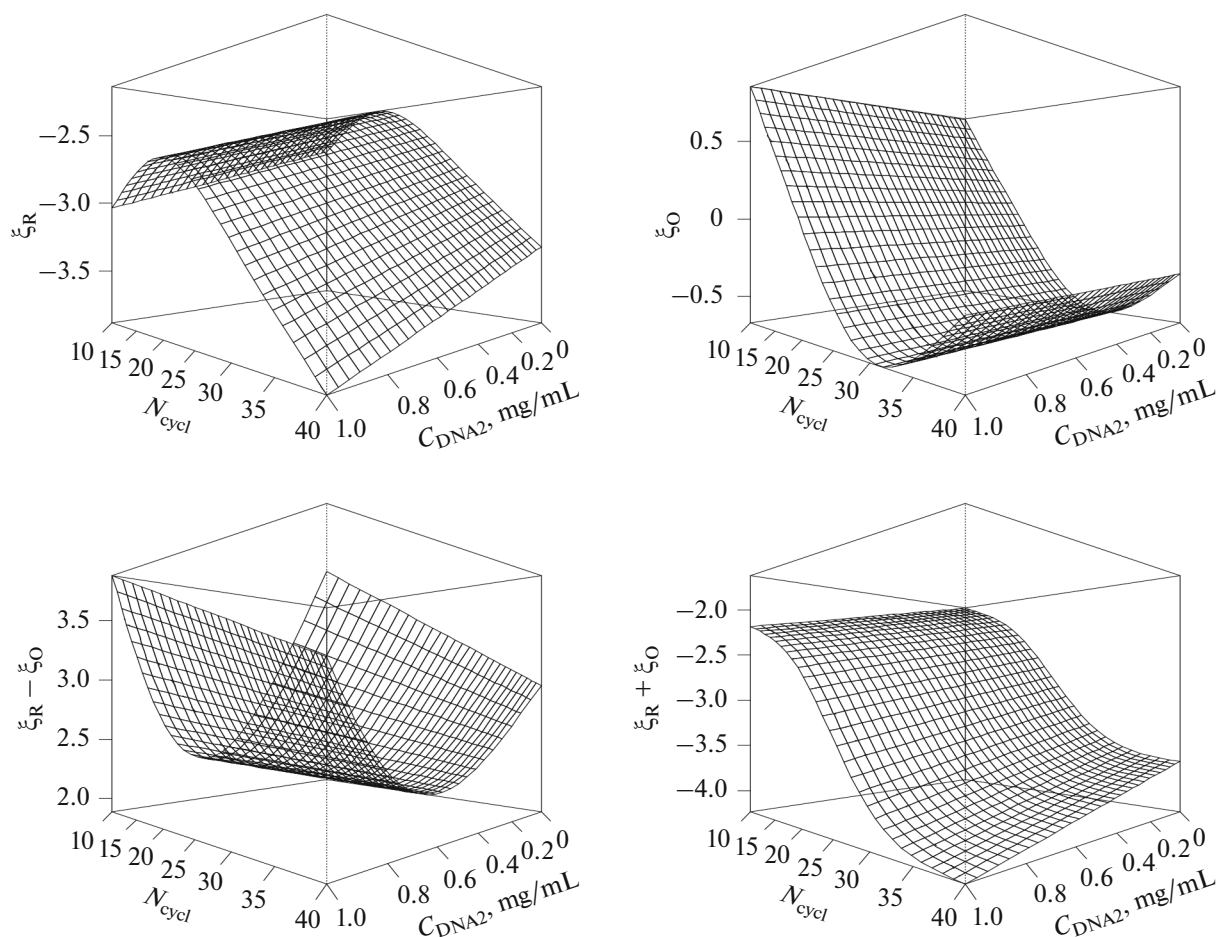
Fig. 6. Graphical representation of models of dependences ξ_R, ξ_O, $(\xi_R - \xi_O)$, and $(\xi_R + \xi_O)$ on the number of PANI polymerization cycles and DNA2 concentration.

lattice. Given the independence of ξ_O from the DNA2 concentration, the changes in $(\xi_R + \xi_O)$ are determined by ξ_R and indicate a greater effect of the DNA2 sample on the reduced form of the polymer.

CONCLUSIONS

An analysis of the voltammetric response of PANI obtained by electropolymerization from 3.7 M sulfuric acid in the presence of DNA from salmon and fish milk with different molecular weights using a theoretical model of the electrochemical oxidation of PANI made it possible to estimate the parameters of interaction between PANI redox centers. Estimates of changes in the energy of interaction between PANI redox centers were obtained by varying the number of electropolymerization cycles from 10 to 40 and the DNA concentration from 0 to 1.0 mg/mL. Using the data obtained, regression models with a nonlinear transformation of the original features were built. The observed positive values of $(\xi_R - \xi_O)$ allow us to con-

clude that the energy of interactions between oxidized PANI centers is greater than that between reduced ones. The minimum values of $(\xi_R - \xi_O)$ upon varying the number of polymerization cycles are observed at about 25 polymerization cycles. The addition to the polymerization solution of any of the used DNA samples leads to an increase in the free energy for the oxidized form of PANI or a decrease in the free energy for the reduced form of the polymer. However, while, in the case of DNA2, the dependence of changes on the DNA concentration is linear, in the case of DNA1, a maximum is observed near a DNA1 concentration of 0.5 mg/mL. With an increase in the number of polymerization cycles, a change in the parameters $(\xi_R + \xi_O)$ of PANI indicates a shift in equilibrium towards the existence of reduced–oxidized structural elements in comparison with the separate existence of reduced–reduced and oxidized–oxidized pairs. This indicates the preference for a distributed polaron lattice over bipolaron structures. The effect of DNA concentration on $(\xi_R + \xi_O)$ is linear, but the effect of different

DNA samples is multidirectional. Low-molecular DNA1 increases this parameter, stabilizing bipolaron structures, and DNA2 reduces it, contributing to the existence of a distributed polaron lattice, while it can be noted that DNA2 has a greater effect on the reduced form of the polymer.

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CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest.

REFERENCES

1. Shamagsumova, R., Porfireva, A., Stepanova, V., Osin, Y., Evtugyn, G., and Hianik, T., Polyaniline-DNA based sensor for the detection of anthracycline drugs, *Sens. Actuators, B*, 2015, vol. 220, p. 573.

2. Kulikova, T.N., Porfireva, A.V., Shamagsumova, R.V., and Evtugyn, G.A., Voltammetric Sensor with replaceable polyaniline-DNA layer for doxorubicin determination, *Electroanalysis*, 2018, vol. 30, no. 10, p. 2284.

3. Kulikova, T., Porfireva, A., Evtugyn, G., and Hianik, T., Electrochemical DNA sensors with layered polyaniline−DNA coating for detection of specific DNA interactions, *Sensors*, 2019, vol. 19, no. 3, p. 469.

4. Medina-Llamas, J.C., Chávez-Guajardo, A.E., Andrade, C.A.S., Alves, K.G.B., and de Melo, C.P., Use of magnetic polyaniline/maghemite nanocomposite for DNA retrieval from aqueous solutions, *J. Colloid Interface Sci.*, 2014, vol. 434, p. 167.

5. Liu, S., Wang, L., Luo, Y., Tian, J., Li, H., and Sun, X., Polyaniline nanofibres for fluorescent nucleic acid detection, *Nanoscale*, 2011, vol. 3, no. 3, p. 967.

6. Sengupta, P.P., Gloria, J.N., Amato, D.N., Amato, D.V., Patton, D.L., Murali, B., and Flynt, A.S., Utilizing intrinsic properties of polyaniline to detect nucleic acid hybridization through UV-enhanced electrostatic interaction, *Biomacromolecules*, 2015, vol. 16, no. 10, p. 3217.

7. Sengupta, P.P., Gloria, J.N., Parker, M.K., and Flynt, A.S., A polyaniline-based sensor of nucleic acids, *J. Visualized Exp.*, 2016, vol. 117, p. e54590.

8. Hu, Y., Yang, T., Li, Q., Guan, Q., and Jiao, K., Conjugated self-doped polyaniline−DNA hybrid as trigger for highly sensitive reagentless and electrochemical self-signal amplifying DNA hybridization sensing, *Analyst*, 2013, vol. 138, no. 4, p. 1067.

9. Kapustin, D., Prostyakova, A., Bryk, Ya., Yagudaeva, E., and Zubov, V., New composite materials modified with nano-layers of functionalized polymers for bioanalysis and medical diagnostics, p. 83−106, in: *Nanocomposites and polymers with analytical methods*. Ed. Cuppoletti, J. Croatia: Intech, 2011.

10. Yagudaeva, E., Zybin, D., Vikhrov, A., Prostyakova, A., Ischenko, A., Zubov, V., and Kapustin, D., Sorption of nucleic acids and proteins on polyaniline and polyaramide nano-coatings as studied by spectral-correlation interferometry in a real time mode, *Colloid Surface B*, 2018, vol. 163, p. 83.

11. Liaw, D.-J., Zybin, D.I., Prostyakova, A.I., Yagudaeva, E.Y., Vikhrov, A.A., Ishchenko, A.A., Zubov, V.P., and Kapustin, D.V. Statistical and dynamic sorption of nuclear acids on the sorbent surfaces modified with nano-thick polymer layers, *Chem. Chem. Tech.*, 2018, vol. 61, no. 1, p. 4.

12. Nagarajan, R., Liu, W., Kumar, J., Tripathy, S.K., Bruno, F.F., and Samuelson, L.A., Manipulating DNA conformation using intertwined conducting polymer chains, *Macromolecules*, 2001, vol. 34, no. 12, p. 3921.

13. Ma, Y., Zhang, J., Zhang, G., and He, H., Polyaniline nanowires on Si surfaces fabricated with DNA templates, *J. Am. Chem. Soc.*, 2004, vol. 126, no. 22, p. 7097.

14. Nickels, P., Dittmer, W.U., Beyer, S., Kotthaus, J.P., and Simmel, F.C., Polyaniline nanowire synthesis templated by DNA, *Nanotechnology*, 2004, vol. 15, no. 11, p. 1524.

15. Bardavid, Y., Ghabboun, J., Porath, D., Kotylar, A.B., and Yitzchaik, S., Formation of polyaniline layer on DNA by electrochemical polymerization, *Polymer*, 2008, vol. 49, no. 9, p. 2217.

16. Bardavid, Y., Kotlyar, A.B., and Yitzchaik, S., Conducting polymer coated DNA, *Macromol. Symp.*, 2006, vol. 240, no. 1, p. 102

17. Zeifman, Y.S., Maiboroda, I.O., Grishchenko, Y.V., Morozova, O.V., Vasil'eva, I.S., Shumakovich, G.P., and Yaropolov, A.I., Enzymatic synthesis of electroconductive biocomposites based on DNA and optically active polyaniline, *Appl. Biochem. Microbiol.*, 2012, vol. 48, no. 2, p. 145.

18. Giacobbe, S., Pezzella, C., Della Ventura, B., Giacobelli, V.G., Rossi, M., Fontanarosa, C., and Piscitelli, A., Green synthesis of conductive polyaniline by Trametes versicolor laccase using a DNA template, *Eng. Life Sci.*, 2019, vol. 19, no. 9, p. 631.

19. Abdullin, T.I., Nikitina, I.I., Evtugin, G.A., Budnikov, G.K., and Manapova, L.Z., Electrochemical properties of a two-component DNA-polyaniline film at the surface of glassy carbon electrode, *Russ. J. Electrochem.*, 2007, vol. 43, p. 1284.

20. Yano, J., Kohno, T., and Kitani, A., Electrochemical preparation of polyaniline microspheres incorporated with DNA, *J. Appl. Electrochem.*, 2009, vol. 39, no. 5, p. 747.

21. Marmisollé, W.A., Florit, M.I., and Posadas, D., A formal representation of the anodic voltammetric response of polyaniline, *J. Electroanal. Chem.*, 2011, vol. 655, no. 1, p. 17.

22. Marmisollé, W.A., Florit, M.I., and Posadas, D., Electrochemically induced ageing of polyaniline monitored by the changes in its voltammetric response, *J. Electroanal. Chem.*, 2011, vol. 660, no. 1, p. 26.

23. Marmisollé, W.A., Florit, M.I., and Posadas, D., Effect of the potential on the electrochemically induced

ageing of polyaniline films, *J. Electroanal. Chem.*, 2012, vol. 669, p. 42.

24. Scotto, J., Florit, M.I., and Posadas, D., pH dependence of the voltammetric response of Polyaniline, *J. Electroanal. Chem.*, 2017, vol. 785, p. 14.

25. Scotto, J., Florit, M.I., and Posadas, D., Redox commuting properties of polyaniline in hydrochloric, sulphuric and perchloric acid solutions, *J. Electroanal. Chem.*, 2018, vol. 817, p. 160.

26. Scotto, J., Florit, M.I., and Posadas, D., About the species formed during the electrochemical half oxidation of polyaniline: Polaron-bipolaron equilibrium, *Electrochim. Acta*, 2018, vol. 268, p. 187.

27. Scotto, J., Marmisollé, W.A., and Posadas, D., About the capacitive currents in conducting polymers: the case of polyaniline, *J. Solid State Electrochem.*, 2019, vol. 23, no. 7, p. 1947.

28. An, R., Jia, Y., Wan, B., Zhang, Y., Dong, P., Li, J., and Liang, X., Non-enzymatic depurination of nucleic acids: factors and mechanisms, *PloS one*, vol. 9, no. 12, p. e115950.

29. Wood, S.N., *Generalized additive models: an introduction with R.* CRC press, 2017. 496 p.

30. Stafström, S., Bredas, J.L., Epstein, A.J., Woo, H.S., Tanner, D.B., Huang, W.S., and MacDiarmid, A.G., Polaron lattice in highly conducting polyaniline: theoretical and optical studies, *Phys. Rev. Lett.*, 1987, vol. 59, no. 13, p. 1464.

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