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# EFFECT OF IONIC ORDERING IN CONDUCTIVITY EXPERIMENTS OF DNA AQUEOUS SOLUTIONS

The effects of ionic ordering in DNA water solutions are studied by conductivity experiments. The conductivity measurements are performed for the solutions of DNA with KCl salt in the temperature interval from 28 to 70  $^{\circ}$  C. The salt concentration varied from 0 to 2 M. The measurements of the conductivity of solutions without DNA but with the same concentration of KCl salt are also performed. The results show that, in the case of a salt-free solution of DNA, the melting process of the double helix is observed, while, in the case of the DNA solution with added salt, the macromolecule denaturation is not featured. For salt concentrations lower than some critical one (0.4 M), the DNA solution conductivity is higher than the conductivity of a KCl water solution without DNA. Starting from the critical concentration, the conductivity of a KCl solution is higher than the conductivity of a DNA solution with added salt. For the description of the experimental data, a phenomenological model is elaborated basing on electrolyte theory. In the framework of the developed model, a mechanism of counterion ordering is introduced. According to this mechanism the electrical conductivity of the system at low salt concentrations is caused by counterions of the DNA ion-hydrate shell. At an increasing the amount of salt to the critical concentration, counterions condense on the DNA polyanion. A further increase of the salt concentration leads to the formation of DNA-salt complexes, which decreases the conductivity of the system.

Keywords: effects of ionic ordering, DNA water solutions, conductivity, electrolyte theory, mechanism of counterion ordering, DNA-salt complexes.

### 1. Introduction

The DNA double helix is a strong polyelectrolyte, which dissociates in aqueous solutions into the macromolecular polyanion and mobile cations (counterions) [1, 2]. Under the natural conditions, the counterions are positively charged metal ions (usually Na<sup>+</sup> or K<sup>+</sup>) that neutralize negatively charged phosphate groups of the macromolecule backbone. The counterions and water molecules form an ion-hydrate shell around DNA, by stabilizing the structure of the double helix [3–8]. In spite of the significant mobility of counterions, they are organized as a dynamical structure around the macromolecule. This structure may be rather regular due to the homogeneity of the DNA backbone [9, 10]. The ordering of counterions around a DNA macromolecule determines the elastic properties of the double helix (bending, twisting, denaturation), DNA interaction with biologically active compounds (proteins, drugs), and mechanisms of compaction of the macromolecule in small volumes (chromosomes, viral capsids) [11–16]. The study of the dynamical ordering of DNA counterions is of paramount importance for understanding the mechanisms of DNA biological functioning.

Effects of the dynamical ordering of counterions around the DNA double helix may become apparent in conductivity experiments due to the interac-

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tion of charged particles of a solution with the electric field. As is known, the electric current in DNA water solutions is caused by the motion of counterions and DNA macromolecules [17–23]. In the case of DNA solutions without added salt (salt-free solution), the conductivity increases with the concentration of DNA because of the counterion dynamics in the ion-hydrate shell of the macromolecule [17,18]. At the heating of the system, the conductivity gradually increases. Near the temperature of the double helix melting, there is a sudden change of the conductivity, which is caused by the intense ejection of counterions from the DNA ion-hydrate shell [18]. In the case of a DNA solution with added salt, the conductivity of the system depends on both counterion type and salt concentration [17, 18]. The dependence on the counterion type is caused mostly by different electrophoretic mobilities of ions [17], while the dependence on the salt concentration may reflect the ordering of ions in a solution. The experimental data show that, at low concentrations of the added NaCl salt, the conductivity of a DNA solution is higher than that of a NaCl electrolyte solution. But, starting from some defined concentration, the DNA solution conductivity becomes lower than the electrolyte conductivity [19]. The reason for such concentration dependence of the DNA solution conductivity is not clear yet.

To elucidate the microscopic picture of the conductivity process in a DNA solution, the phenomenological approaches have been developed, and the atomatom calculations have been performed [24–27]. The results showed that the dynamics of counterions in a close vicinity to the DNA surface is modulated by the charged atomic groups of the double helix backbone. The counterions spend a part of the time in a complex with DNA (about 1 ns) and another part in the free state [28–31]. Free counterions determine the conductivity of a DNA solution in many respects, which was taken into consideration in phenomenological models [24, 26]. At the same time, the counterions tethered to phosphate groups form an ordered dynamical structure along the DNA backbone, which may be considered as a lattice of the ionic type (ionphosphate lattice) [9, 10]. The existence of the ionphosphate lattice is confirmed by observing the modes of ion-phosphate vibrations in the low-frequency Raman spectra of DNA ( $< 200 \text{ cm}^{-1}$ ) [32–35]. The ordering of counterions around the double helix and the formation of the ion-phosphate lattice should affect the conductivity of DNA water solutions.

The goal of the present work is to study the manifestations of a counterion ordering around the DNA double helix in conductivity experiments of DNA water solutions with added salt. To solve this problem, the conductivity of DNA water solutions with KCl salt is studied experimentally (see Section 2). The concentration dependence  $(0 \div 2M)$  of the conductivity of DNA solutions is obtained at the temperature interval from 28 to 70 °C (Section 3). For the interpretation of experimental data, the phenomenological model basing on electrolyte theory is developed (Section 4). In Section 5, a possible mechanism of ionic ordering around the DNA double helix is discussed.

### 2. Materials and Methods

The samples have been prepared using sodium salt of DNA from salmon testes purchased from Sigma-Aldrich Company (product number D1626). The average length of DNA macromolecules is about 2000 base pairs [36]. To prepare the samples of DNA water solutions, the powder of DNA has been diluted in deionized water to a concentration of 10 mg/ml. To decrease the DNA solution viscosity, it has been treated by a laboratory automatic mixer and then cooled to the 0 °C without the freezing of water. Then the initial solution has been diluted so that the concentration of DNA becomes 2 mg/ml, and KCl salt has been added to this solution. The concentrations of added salt in the obtained solutions are as follows: 0.4, 0.8, 1.2, 1.6, and 2 M. Water solutions without DNA but with the same concentrations of KCl salt have been also prepared. As a result, two series of the samples have been prepared: KCl electrolyte solutions and water solutions of DNA with KCl salt.

To measure the resistance of the sample, the solution (about 0.3 ml) is poured into a cylindrical capillary made of quartz glass with two platinum electrodes (electrode 1 and electrode 2) and one tungsten electrode (electrode 3) incorporated into the capillary walls (Fig. 1). The experimental cell is placed into a thermostat. The resistance has been determined with the use of an alternating current at a frequency of 80 KHz.

The measured resistance has the contributions from the polarizations of the sample and electrodes. To exclude the electrode contribution, the measurements have been performed for different pairs of electrodes:

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1 and 3, 2 and 3 (Fig. 1). In this case, the resistance can be presented as follows:

$$R_{13} = \frac{l_{13}}{\pi r^2 \sigma} + R_{\rm Pt} + R_{\rm W}; \tag{1}$$

$$R_{23} = \frac{l_{23}}{\pi r^2 \sigma} + R_{\rm Pt} + R_{\rm W}.$$
 (2)

Here,  $R_{13}$  and  $R_{23}$  are measured resistances between electrodes 1 and 3 and 2 and 3, respectively;  $l_{13}$  and  $l_{23}$  are the distances between electrodes 1–3 and 2–3, respectively; r is the capillary radius;  $\sigma$  is the specific conductance, and  $R_{\rm Pt}$  and  $R_{\rm W}$  are the resistances of platinum and tungsten electrodes, respectively. The first terms in relations (1) and (2) describe the resistance of the sample, while the second and third terms describe the polarization resistance of electrodes. The difference of formulae (1) and (2) gives the following formula for the conductivity of the sample:

$$\sigma = \frac{l_{12}}{\pi r^2 (R_{13} - R_{23})},\tag{3}$$

where  $l_{12}$  is the distance between electrodes 1– 2. Formula (3) allows us to determine the conductivity of the samples.

### 3. Results

We have determined the temperature dependences of the electrical conductivity of the salt solution ( $\sigma_{\rm KCl}$ ) and the solutions of DNA with added salt ( $\sigma_{\rm DNA+salt}$ ) (Fig. 2). The results show that the conductivity of the samples increases with the temperature for all considered samples.

According to the activation mechanism of ion motion in a solution, the temperature dependence of the conductivity of the system may be considered analogously to the Arrhenius equation for the temperature dependence of a chemical reaction rate [37]:

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{k_{\rm B}T}\right).\tag{4}$$

Here,  $\sigma_0$  is a coefficient;  $\Delta E$  is the potential barrier;  $k_{\rm B}$  is the Boltzmann constant; and T is the temperature. The exponent describes the probability of the ionic jumping over the potential barrier due to thermal fluctuations. To analyze the temperature dependence of the electrical conductivity, let us use the Arrhenius coordinates describing the logarithm

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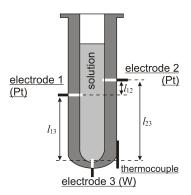


Fig. 1. Scheme of the experimental capillary cell

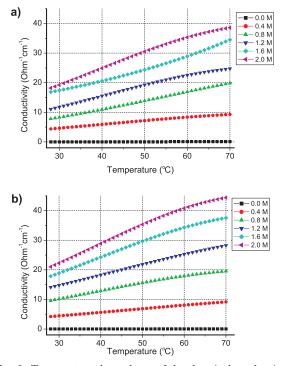
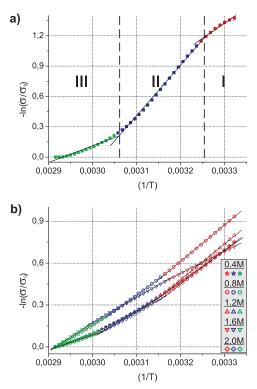


Fig. 2. Temperature dependence of the electrical conductivity of the samples: a) DNA solution with added KCl salt; b) KCl solution

of conductivity as a function of the transverse temperature. From formula (4), it is seen that the temperature dependence of the conductivity in Arrhenius coordinates should be linear.

The Arrhenius plot for a salt-free solution of DNA (Fig. 3, a) shows that there are two breaking points separating the distinguishable linear ranges. The linear ranges in the Arrhenius plot characterize the melting of a DNA double helix [18]. Ranges I (28÷37 °C) and III (54÷70 °C) correspond to the



**Fig. 3.** Arrhenius plot for DNA water solutions. a – salt-free solution. Range I corresponds to a double-stranded DNA (red points); II is the transition range of the double helix melting (blue points); Range III corresponds to a single-stranded DNA (green points). b) – solution of DNA with added salt. Solid black lines is the linear approximation

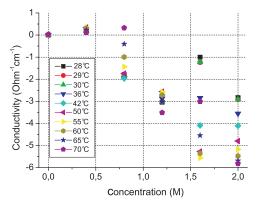


Fig. 4. Concentration dependence of the difference between the conductivities of DNA and electrolyte solutions

double stranded and single-stranded DNA, respectively. Range II  $(37 \div 54 \text{ °C})$  characterizes the denaturation of DNA macromolecules. In the case of DNA with added salt, the difference between linear ranges in the Arrhenius plot is not prominent, and the breaking points are hardly distinguishable (Fig. 3, b). The influence of added salt may be explained by the additional neutralization of the negatively charged atomic groups of the double helix by salt ions.

Different ranges in the Arrhenius plot characterizes different activation energies of the ionic motion in a solution. The values of potential barrier  $\Delta E$  are determined as a slope of the lines in Fig. 3 (Table). The results show that, in a salt-free solution of DNA before the melting temperature (range I), the activation energy is rather large comparing to the electrolyte solution (about 25 kJ/mole). In the transition range (range II), the activation energy (about 43 kJ/mole) increases almost twice comparing to range I, which is effectively caused by the ejection of counterions from the DNA ion-hydrate shell [9]. Under the melting temperature (range III),  $\Delta E$  values decrease.

In the solutions of DNA with added salt, the potential barriers  $\Delta E$  of different ranges are rather close. Comparing to the salt-free solution,  $\Delta E$  values only slightly decrease in ranges I and III, while, in the case of range II, they decrease more than twice. The fact of a comparatively low activation barrier in range II indicates that the added salt increases the melting temperature of the DNA double helix, which was also observed in calorimetric experiments [2].

Increasing the added salt concentration, the conductivities of the both DNA solution and electrolyte increase (Fig. 2). To compare the conductivity of a DNA solution with added salt and the conductivity of a KCl electrolyte solution, the difference  $\Delta \sigma =$  $= \sigma_{\text{DNA+KCl}} - \sigma_{\text{KCl}}$  is analyzed (Fig. 4). The results show that, at concentrations lower than some critical one (about  $c_{\text{cr}} \approx 0.4$  M), the DNA solution conductivity is higher than that of a salt solution  $(\sigma_{\text{DNA+salt}} > \sigma_{\text{salt}})$ . Under the critical concentration  $(c = c_{\text{cr}})$ , the conductivities of the DNA solution and the KCl solution are identical ( $\Delta \sigma = 0$ ). Starting

Values of potential barrier  $\Delta E$  for the ion motion in a DNA solution (kJ/mole)

	0 M	0.4 M	0.8 M	1.2 M	1.6 M	2.0 M	Mean
I II III		$     18.55 \\     14.07 \\     9.98 $	21.71 18.99 15.65	21.33 15.78 9.36	13.15 14.90 16.83	20.10 14.74 8.61	$19 \pm 4$ $16 \pm 2$ $12 \pm 4$ $16 \pm 4$

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from the critical concentration ( $c > c_{\rm cr}$ ), the DNA solution conductivity becomes lower than that of the respective electrolyte ( $\sigma_{\rm DNA+salt} < \sigma_{\rm salt}$ ). The dependence of the DNA solution conductivity on the salt concentration in the interval from 0 to  $c_{\rm cr}$  is almost the same for different temperatures, while, at concentrations from  $c_{\rm cr}$  to 2 M, it is different for different temperatures. The changes of  $\Delta \sigma$  values should reflect the structure changes in the DNA solution.

#### 4. Model

To understand the mechanism of electrical conductance of a DNA water solution, let us analyze the state of a DNA macromolecule in the solution. Due to the large contour length, the DNA macromolecules are coil-shaped. The size of DNA coils may be estimated with the use of the persistence model [2,38]. In framework of this model, the root-mean-square distance between the ends of a macromolecule is determined as follows:

$$\bar{D^2} = 2P^2(L/P - 1 + e^{-L/P}), \tag{5}$$

where L and P are the contour and persistence lengths of a macromolecule, respectively. The contour length for DNA from salmon testes is  $L \approx 0.68 \ \mu m$ [36]. The persistence length of DNA is  $P \approx 500$  Å [3, 36]. Using such parameters, the average volume of DNA coils is estimated to be  $0.02 \ \mu m^3$ . Taking into consideration that the average number of DNA macromolecules in 1 ml of the experimental solution is  $10^{15}$ , the total volume of DNA coils should be about 20 ml. One can conclude that the macromolecule coils overlap in the considered solution, and the conductivity may be determined by mobile ions only, because the migration of single DNA macromolecules is labored.

The number of mobile ions involved in the conductivity is determined by the concentration of DNA counterions and ions of added salt. Taking this into consideration, the conductivity of a DNA solution may be presented as follows:

$$\sigma_{\text{DNA+salt}}(c) = \sigma_1(c) + \sigma_2(c), \tag{6}$$

where  $\sigma_1(c)$  is the conductivity determined by the motion of salt ions (bulk ions);  $\sigma_2(c)$  is the conductivity determined by the mobility of counterions in the ion-hydrate shell of DNA; and c is the equivalent concentration of added salt.

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Taking into consideration that salt ions may condense on a DNA macromolecule, the conductivity of bulk ions may be considered as follows:

$$\sigma_1(c) = \sigma_{\text{salt}}(c) - A_1(c)(\lambda^+ + \lambda^-), \tag{7}$$

where  $\sigma_{\text{salt}}(c)$  is the contribution of salt ions to the conductivity of the system;  $A_1(c)$  is the concentration of salt ions condensed on a DNA macromolecule;  $\lambda^+$  and  $\lambda^-$  are the equivalent mobilities of positively and negatively charged ions, respectively. The second term in (7) describes a decrease in the conductivity caused by the association of positively and negatively charged ions with DNA. Note that the negatively charged ions may associate with the positively charged ions that are already tethered to the phosphate groups of the DNA backbone.

The contribution from DNA counterions to the conductivity of the system may be taken into consideration as follows:

$$\sigma_2(c) = c_{\rm p}\lambda^+ - A_2(c)\lambda^+,\tag{8}$$

where  $c_{\rm p}$  is the concentration of DNA counterions, which approximately equals the number of DNA phosphate groups; and  $A_2(c)$  is the concentration of counterions associated with the negatively charged atomic groups of a DNA macromolecule. The first term in (8) describes the contribution from DNA counterions to the conductivity of the system. The second term in (8) describes a decrease in the conductivity caused by the association of counterions with the phosphate groups of a DNA macromolecule. Taking the formulae (6), (7), and (8) into account, the contribution of DNA to the polyelectrolyte solution conductivity ( $\Delta \sigma = \sigma_{\rm DNA+salt} - \sigma_{\rm salt}$ ) can be determined as follows:

$$\Delta \sigma = c_{\rm p} \lambda^+ - A_2(c) \lambda^+ - A_1(c) (\lambda^+ + \lambda^-).$$
(9)

The concentration of condensed ions may be considered proportional to the concentration of salt and the concentration of DNA phosphate groups, respectively:  $A_1(c) = \beta(c)c$  and  $A_2(c) = \alpha(c)c_p$ . The coefficients  $\alpha(c)$  and  $\beta(c)$  depend on the concentration of added salt and describe the part of ions condensed on the macromolecule surface. Let us consider the functions  $\alpha(c)$  and  $\beta(c)$  in the linear approximation:

$$\alpha(c) = \alpha_0 + \alpha_1 c; \quad \beta(c) = \beta_0 + \beta_1 c, \tag{10}$$

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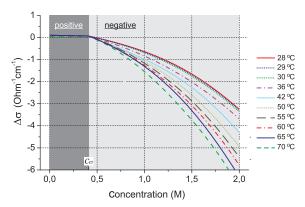


Fig. 5. Dependence of the difference between the conductivity of DNA and that of the electrolyte solution on the salt concentration calculated by formula (12)

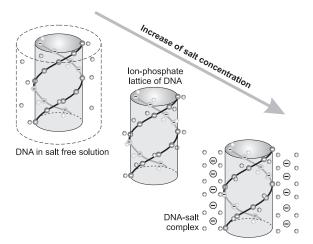


Fig. 6. Scheme of the process of ionic structuring around a DNA double helix at different concentrations of added salt

where  $\alpha_0$ ,  $\alpha_1$ ,  $\beta_0$ , and  $\beta_1$  are the parameters that can be determined from the following conditions.

In the case of a salt-free solution (c = 0), the conductivity is determined by the free counterions of DNA, and  $\alpha|_{c=0} = 0$ , thus,  $\alpha_0 = 0$ . The degree of neutralization of the DNA surface increases with the salt concentration. At some concentration  $(c = c_{\rm cr})$ , all phosphate groups of the double helix become neutralized. Since the counterions attached to a DNA macromolecule are not involved in the conductivity, the condition  $\alpha|_{c\geq c_{\rm cr}}=1$  should be valid, thus,  $\alpha_1 =$  $= 1/c_{\rm cr}$ . The ions of added salt condense on counterions that are already tethered to the phosphate groups of the DNA backbone. Therefore,  $\beta|_{c\leq c_{\rm cr}} = 0$ , and  $\beta_0 = -\beta_1 c_{\rm cr}$ . A further increase of the salt concentration leads to the crystallization of salt ions. At some definite concentration ( $c = c_{\max}$ ), the crystallization will be maximal, which corresponds to the condition  $\beta|_{c=c_{\max}} = 1$ , and  $\beta_1 = 1/(c_{\max} - c_{cr})$ . Taking these conditions into account, formulae (10) can be written in the form

$$\alpha(c) = \frac{c}{c_{\rm cr}}; \quad \beta(c) = \frac{c - c_{\rm cr}}{c_{\rm max} - c_{\rm cr}}.$$
 (11)

The temperature dependence of the ion mobility can be taken into consideration analogously to relation (4):  $\lambda = \lambda_0 \exp(-\Delta E/k_{\rm B}T)$ , where  $\lambda_0$  is the characteristic equivalent mobility. The value of  $\lambda_0$ can be determined, by using the known values of ion mobility at some definite temperature  $T_0$ :  $\lambda_0 =$  $= \lambda(T_0) \exp(\Delta E/k_{\rm B}T_0)$ . Taking this into consideration and substituting formulae (11) to relation (9), we can write the formula for  $\Delta \sigma$  in the following form:

 $\Delta \sigma =$ 

$$= \begin{cases} \frac{(c_{\rm cr} - c)c_{\rm p}\lambda_0^+}{c_{\rm cr}} \exp\left[-\frac{\Delta E(1 - T/T_0)}{k_{\rm B}T}\right], \ c \le c_{\rm cr}; \\ -\frac{(c - c_{\rm cr})c(\lambda_0^+ + \lambda_0^-)}{c_{\rm max} - c_{\rm cr}} \exp\left[-\frac{\Delta E(1 - T/T_0)}{k_{\rm B}T}\right], \ c > c_{\rm cr}. \end{cases}$$
(12)

In relation (12),  $\lambda_0^+$  and  $\lambda_0^-$  are the mobilities of positively and negatively charged ions at the characteristic temperature  $T_0$ .

It is seen that  $\Delta \sigma$  values are positive in the salt concentration range  $c \leq c_{\rm cr}$ . In the case of high concentrations of added salt ( $c > c_{\rm cr}$ ), the values  $\Delta \sigma$  are negative. The contribution of DNA to the conductivity of a polyelectrolyte is inessential ( $\Delta \sigma = 0$ ), when all phosphate groups of the DNA backbone are neutralized ( $c = c_{\rm cr}$ ). Note the developed model does not consider the degradation of DNA macromolecules at the melting temperatures.

#### 5. Discussion

To characterize the influence of DNA macromolecules on the conductivity of the system, let us estimate  $\Delta\sigma$  by formula (12). The parameters necessary for the calculations are determined as follows. The concentration of phosphate groups in a solution is determined according to the concentration of DNA in the experimental samples (2 mg/ml)  $c_{\rm p} = 6.35$  M. The maximal salt concentration is taken the same as the

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solubility limit of KCl  $c_{\rm max} = 4.6$  M [39]. The value of critical concentration of added salt  $c_{\rm cr} = 0.4$  M is determined from the condition  $\Delta \sigma = 0$ . The characteristic mobilities  $\lambda_0^+$  and  $\lambda_0^-$  for K<sup>+</sup> and Cl<sup>-</sup> ions are taken the same as those in the electrolyte solution  $\lambda_0^+ = 55.1 \text{ cm}^2 \Omega^{-1} \text{mole}^{-1}$  and  $\lambda_0^- =$  $= 55.8 \text{ cm}^2 \Omega^{-1} \text{mole}^{-1}$  at a temperature of 25 °C [37]. The potential barrier  $\Delta E \approx 16 \text{ kJ/mole}$  is taken as the average value of activation energies (Table). As a result, the concentration dependences of  $\Delta \sigma$  are shown in Figure 5.

It is seen that the conductivity of a DNA solution in the concentration range  $c < c_{\rm cr}$  is practically the same as the conductivity of the respective electrolyte solution, and  $\Delta \sigma$  is positive. At higher concentrations ( $c > c_{\rm cr}$ ), the obtained difference between the conductivities of the DNA solution and the electrolyte solution is negative. As the temperature increases, the values of  $\Delta \sigma$  decrease in this concentration range. The calculated results (Figure 5) qualitatively agree with the experimental data (Figure 4). However, in the concentration range  $c < c_{\rm cr}$ , the experimentally observed values of  $\Delta \sigma$  are larger, which may be caused by the complexity of the mechanism of counterion condensation on DNA.

According to the results of estimations, the following mechanism of counterion ordering around DNA macromolecules may be introduced. At a low concentration of added salt, the degree of phosphate group neutralization is about the same as that in the case of a salt-free solution (Figure 6, a). The counterions come off the ion-hydrate shell of a macromolecule and determine the conductivity of the system. The number of neutralized phosphate groups increases with the salt concentration. At the critical concentration, the phosphate groups should be completely neutralized (Figure 6, b). The counterions with the phosphate groups form an electrically neutral system resembling the lattice of an ionic crystal (ionphosphate lattice) [30–33]. The formation of the DNA ion-phosphate lattice induces a decrease of the conductivity of the system. After the formation of the ion-phosphate lattice, salt ions condense on counterions tethered to the phosphate groups of the macromolecule, and DNA-salt complexes are formed (Figure 6, c). Such complexes may be observed as the textures on a surface after the evaporation of the solution [16]. The formation of DNA-salt complexes reduces the conductivity of the system due to a decrease of

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the number of positively and negatively charged ions involved in the electric current.

#### 6. Conclusions

In the present work, the ordering of ions in DNA water solutions is studied by conductivity experiments. As a result, the temperature dependence (from 28 to 70  $^{\circ}$ C) of the conductivity for a DNA solution with KCl salt (the concentration from 0 to 2 M) is obtained. In the case of a salt-free solution, there exist three characteristic temperature ranges describing the stages of the melting of the DNA double helix. In the case of DNA with added salt, the characteristic stages of DNA melting are hardly distinguishable, that may be due to the stabilization of the double helix by the ions of added salt. The comparison between the conductivity of a DNA solution with added salt and the electrolyte solution shows that, at concentrations lower than 0.4 M (critical concentration), the conductivity of the DNA solution is higher than the conductivity of the respective electrolyte. Starting from the critical concentration, the conductivity of the electrolyte is higher than the conductivity of the DNA solution.

Basing on the developed phenomenological model for the conductivity of a DNA solution, the mechanism of ionic ordering in the DNA solution is introduced. It is considered that, at low concentrations of added salt, the DNA counterions contribute essentially to the electrical conductivity of the system. As the salt concentration increases to the critical one, the counterions condense on a DNA macromolecule, and the ion-phosphate lattice is formed. A further increase of the salt concentration leads to the condensation of anions on cations attached to the phosphate groups of the DNA backbone, and the DNA-salt complexes are formed. The growth of DNA-salt complexes decreases the conductivity of the system. The introduced mechanism qualitatively describes the experimentally observed changes of the conductivity of DNA solutions.

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#### ЕФЕКТ ІОННОГО ВПОРЯДКУВАННЯ В ЕКСПЕРИМЕНТАХ ПО ЕЛЕКТРОПРОВІДНОСТІ ВОДНИХ РОЗЧИНІВ ДНК

Резюме

Прояви впорядкування іонів у водних розчинах ДНК досліджувалися за допомогою методу кондуктометрії. Вимірювання електропровідності проводилися для водних розчинів ДНК з додаванням солі KCl в температурному діапазоні від 28 до 70 °С. Концентрація солі змінювалася від 0 до 2 М. Також вимірювалася електропровідність розчинів без ДНК з таким самим вмістом солі. Результати показали, що у випадку безсольового розчину ДНК спостерігають стадії плавлення подвійної спіралі, тоді як у випадку розчину ДНК з додаванням солі, денатурація макромолекули не спостерігалася. Для концентрації солі, нижчої від критичної (0.4 M), електропровідність розчину з ДНК виша за електропровідність відповідного електроліту. Починаючи з критичної концентрації, електропровідність електроліту вища за електропровідність розчину ДНК. Для опису експериментальних даних була розроблена феноменологічна модель, що базується на теорії електролітів. В рамках побудованої моделі запропоновано механізм впорядкування протиіонів. Відповідно до запропонованого механізму за низьких концентрацій солі електропровідність системи зумовлена протиіонами іон-гідратної оболонки ДНК. При підвищенні кількості іонів до критичної концентрації протијони починають конденсуватися на полјанјоні ДНК. Подальше підвищення концентрації солі індукує формування ДНК-сольових комплексів, поява яких приводить до зменшення електропровідності системи.

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