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Dielectric study of charge motion in DNA

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Abstract. The d.c. conductivity and dielectric properties of solid low-humidity NaDNA layers have been examined over frequency and temperature ranges up to 10^5 Hz and 80–330 K respectively. The results presented are basically consistent with a model in which the majority charge carriers are protons (H_3O^+, OH^-) moving on the surface of a NaDNA chain in the neighbourhood of the phosphate groups. The increasing hydration also increases the mobility of counterions (Na^+) and their contribution to a d.c. conductivity. The Arrhenius d.c. conductivity seems to be limited by electrochemical processes on the electrodes. Low-frequency dispersion is also caused by this effect. The local and long-range motion of charge carriers is limited below temperatures of a dipolar thermally stimulated depolarization current (TSDC) peak observed in the range 165–255 K. The amplitude and position of the peak depend strongly on the water content in the sample.

Key words: DNA – D.c. conductivity – Thermally stimulated relaxation – Proton transport

Introduction

Local and long range motion of electrons, holes, protons and other ions is of fundamental importance in biology. For example, the coupling of electron and proton transport in the membranes of mitochondria, bacteria and chloroplasts drives an ATP synthesis. Proton transfer processes are also widely implicated in the enzymatic activity of many proteins. The main research interest has been focused on proteins in the last decade and apparent progress has been made in the understanding of the response of solid samples to a d.c. or a low-frequency a.c. excitation signal (Pethig 1988, Pissis and Anagnostopoulou-Konsta 1990). In contrast, some uncertainties seem to exist in analogous research on nucleic acid materials, owing to the remarkable complexity of the system. Eley et al. (1979) interpreted the Arrhenius temperature dependence of the d.c. conductivity (also with an exponential hydration dependence) as the intrinsic conductivity with electrons and holes as majority charge carriers. They observed protonic conductivity on samples with a water content higher than 25 wt%. Van Lith et al. (1986) studied electron transport by measuring the microwave conductivity generated in hydrated DNA at low temperatures by nanosecond pulses of 3 MeV electrons. They observed electron transport only above 79 wt% water content. Nevertheless, the idea of intrinsic semiconductivity in DNA solid samples at low hydrations is now supported by the relaxation measurements of Bonicontro et al. (1988) over the range from 10 kHz to 10 MHz in a composite capacitor without electrode contact. Dielectric measurements at frequencies lower than 10^5 Hz exhibit two relaxation regions, this may be interpreted in terms of the motion of Na^+ counterions in sample volume (Neubert et al. 1985). Our previous experimental TSDC, low-frequency and d.c. conductivity measurements in NaDNA samples show the strong hydration dependence of the observed effects (dipolar TSDC relaxation above 160 K, low-frequency dispersion and Arrhenius d.c. conductivity) and their relative independence of the primary structure of DNA. Also many similarities with the published results obtained in other materials of both biological and non-biological origin containing water have led us to make proposals about the important role of protons in the charge dynamics in DNA (Jelínková et al. 1986; Laudát et al. 1987).

In this paper we summarize our new results of d.c. conductivity and low-frequency dielectric measurements in the frequency (10^{-3}–10^5 Hz) and temperature (80–330 K) domains, attempting to clarify the observed effects and to unify the various interpretations in a new model of charge dynamics in solid DNA. For this, new information about the nature of movable entities (charges), localization of charge carriers, transport path mechanism, relaxation and transport parameters, etc., is needed. The use of solid DNA samples with a low water content (but com-

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parable with water content in some anhydrobiotic plants, pollen, bacteria, corn seeds, etc.) gives us the possibility of studying the charge dynamics close to the sugar-phosphate backbone of DNA. The primary hydration shell strongly influences the physical and biological properties of DNA.

Materials and methods

Electrical measurements were performed on solid layers and pressed pellets (prepared under a pressure of 80 kp/cm) of NaDNA, disodium salt of adenosine 5′-monophosphate (Na_2AMP, Reanal Budapest), disodium salt of adenosine 5′-diphosphate (Na_2ADP, Reanal), adenosine (Calbiochem) and adenine (Lachema Brno). A large amount of the sodium salt of DNA was also isolated from calf thymus by a modified method of Marmur (1961). The solid layers were prepared at the end of the isolation procedure. During the precipitation of NaDNA in 0.1 × SSC buffer solution with ethanol, molecules of NaDNA were wound onto a glass rod covered with silicon rubber. After slow drying, typically 0.5×10^{-3} m thick samples (13×10^{-3} m in diameter, with a density of 0.9 g/cm^3) were cut. The dry samples were also doped by heavy water (98.4 vol% D_2O) in some experiments. In the following the water content, h(wt%), is defined as the weight of sorbed water divided by the sample weight during the electric measurement (obtained as the mean value of the weights before and after the electric measurement). The pressed pellets of Na_2AMP, Na_2ADP and adenosine were prepared without further treatment. Adenine was purified by recrystallization. The samples were placed in a measuring capacitor using a three electrode configuration.

The electrical properties of the samples have been studied in the temperature domain by methods of thermally stimulated depolarization currents (TSDC), thermally stimulated polarization currents (TSPC) and d.c. conductivity; and in the frequency domain by measurements of frequency-dependent permittivity. In order to obtain reproducible results in NaDNA samples (the samples swell upon hydration, change their dimensions, etc.), we have attempted to do all measurements under defined conditions (sample dimensions, humidity, temperature, electrode pressure, etc.). For example, in comparative studies we have measured the d.c. conductivity along with the TSDC and TSPC under given experimental conditions and for a particular state of the sample (Fig. 2).

We describe briefly the TSDC method (Bucci et al. 1966, Fig. 1): The sample is polarized by an applied electric field, E_p, at a temperature, T_p, for a time, t_p. This polarization is subsequently frozen-in by cooling the sample to a temperature, T_0, sufficiently low to prevent depolarization by thermal energy. The electric field is then switched off and the sample is warmed at a constant rate, b (typically $b = 3$ K/min), while the depolarization current is detected by an electrometer. In the case of a single relaxation process obeying the Arrhenius equation, $\tau(T) = \tau_0 \cdot \exp(W/kT)$, the depolarization current density, $J(T)$, is given by

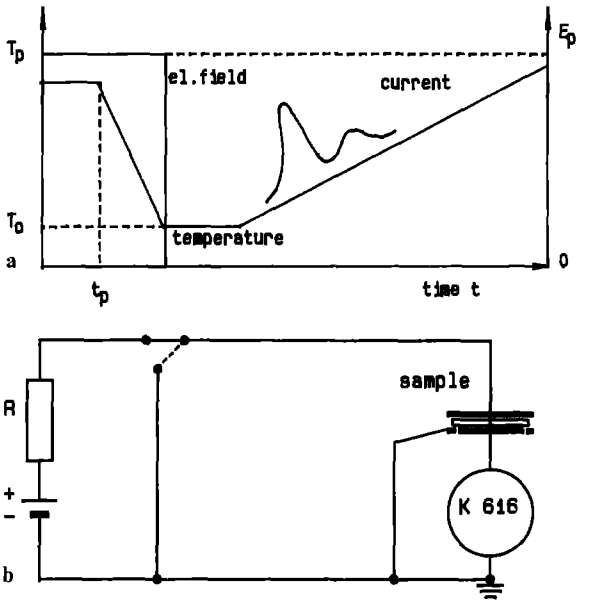

Fig. 1. **a** Principles of the TSDC measurements. **b** The basic electrical circuit used in TSDC, TSPC and d.c. conductivity measurements

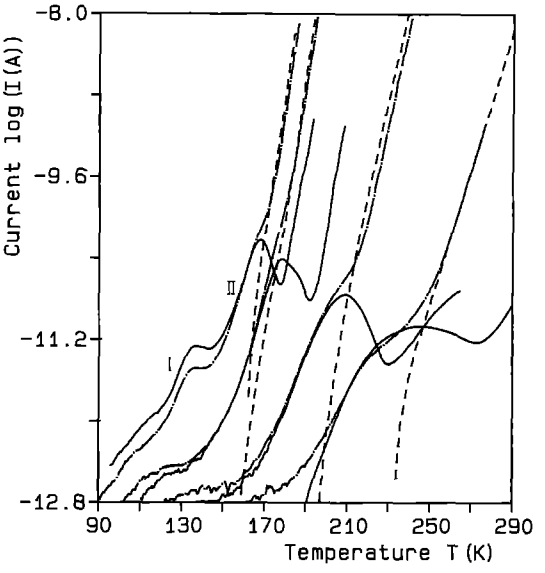

Fig. 2. TSDC (——), TSPC (— · —) spectra and d.c. conductivity (– – – –) of a NaDNA solid layer measured at four hydration contents (37.3 wt%, 28.5 wt%, 8.2 wt% and 6.4 wt% water). The samples were placed in a measuring capacitor with stainless steel electrodes. $T_p = 190-280$ K, $E_p = 10^5$ V/m, $t_p = 15$ min. The d.c. conductivity and TSPC were measured on the samples in the electric field, E, with an intensity of 10^5 V/m

$$J(T) = \frac{P_0}{\tau_0} \exp(-W/kT) \cdot \exp\left[-\frac{1}{b\,\tau_0} \int_{T_0}^{T} \exp(-W/kT')\,dT'\right], \quad (1)$$

where τ is the relaxation time, W the activation energy of the relaxation, τ_0 the pre-exponential factor, T the absolute temperature, k the Boltzmann constant, and P_0 the

initial polarization. The analysis of the shape of this curve makes it possible to obtain the activation energy, W, the pre-exponential factor, τ_0, and the contribution, $\Delta\varepsilon$, of a peak to the static permittivity.

In TSPC measurements the depolarized sample is cooled to low temperatures. The electric field is then switched on and the sample is warmed at a constant rate. The recorded TSPC currents consist of the contributions from both the relaxation effects and the d.c. conductivity. The method allows one to observe the dipole ordering, to determine the temperature range where the ohmic conductivity dominates, to state the optimal T_p, etc.

All measurements of the current TSDC, TSPC and d.c. conductivity were carried out with an automatic measuring apparatus, equipped with 8-bit microprocessor-controlled data acquisition (Laudát and Laudát 1991). Currents were measured by a Keithley 616 electrometer with a sensitivity of 10^{-15} A, the temperature of the sample was controlled by a Eurotherm 820 PID temperature controller and measured by means of a copper-constantan thermocouple placed inside the voltage electrode (Fig. 1 b). An apparatus for frequency-dependent permittivity measurements was constructed according to Boukamp (1984). This allows one to measure in the frequency range 10^{-4}–10^{4} Hz on samples with an impedance up to 10 Gohms.

Results

For the understanding of charge carrier dynamics in solid DNA the following results seem to be important: Figure 2 shows typical TSDC responses of solid DNA samples with different hydration, h, and their relation to the d.c. conductivity and the TSPC. The TSDC measurements revealed the existence of a dominant relaxation peak at temperatures 160–250 K – peak II (in some samples of lower humidity we observed another relaxation peak at higher temperatures – peak III; the peak is not apparent in Fig. 2). The solid samples with a water content higher than 25–30 wt% exhibit another complex relaxation band at temperatures below 150 K. The relaxation band consists of one or two dipolar relaxation peaks (peaks I).

The high temperature TSDC peak II is due to the relaxation in the sample volume. This is indicated by an experiment with totally blocking teflon electrodes, where the peak was apparent, but its amplitude was reduced owing to the reduced intensity of the electric field in the sample volume. The linear dependence of the released charge calculated from the area under the peak on polarizing the electric field, E_p, indicates its dipolar origin. Experimental analysis of the peak, utilizing the partial heating and thermal sampling methods (Turnhout 1975), shows that the peak is not single, but exhibits a distribution of activation energies and relaxation times. Both the position and the amplitude of the peak strongly depend on the amount of water in the sample. Drying the sample, the peak shifts from 166 K (37 wt% of water, $W = 0.58$ eV, $\log(\tau_0\,[\mathrm{s}]) = -16$, $\Delta\varepsilon = 125$) to higher temperatures up to 241 K (Fig. 3 a) – 255 K (< 6.4 wt% water, Fig. 2; $W =$

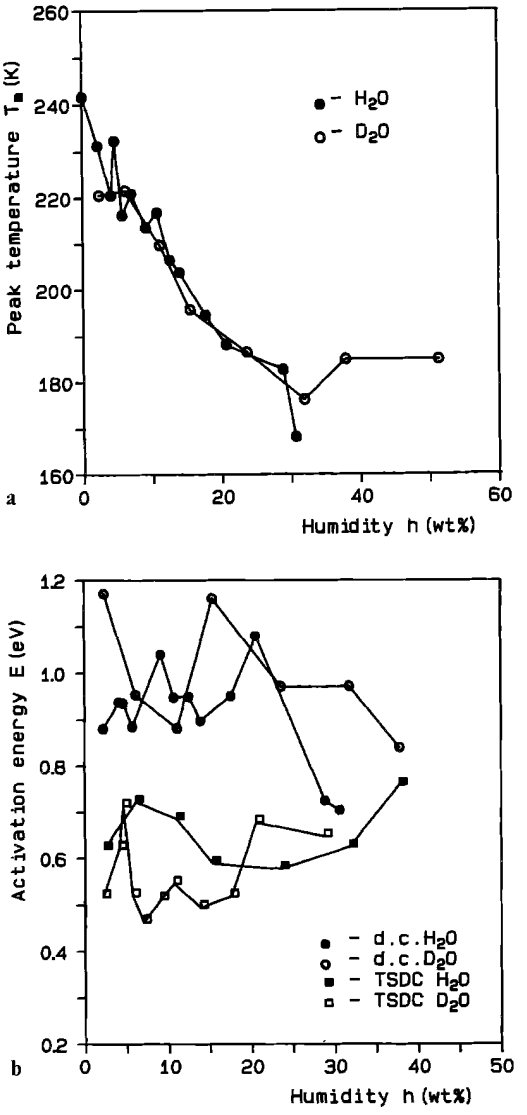

Fig. 3. **a** The hydration dependence of the peak II temperature, T_m, for NaDNA samples with H_2O and D_2O. **b** The hydration dependence of the peak II activation energies, W and E_{dc}. The measuring conditions were the same as in Fig. 2

0.6 eV, $\log(\tau_0\,[\mathrm{s}]) = -10$, $\Delta\varepsilon = 65$). The amplitude of the peak lowers, and its half width increases. The hydration dependence of the activation energy, W, calculated by the initial rise method is shown in Fig. 3 b. The curve of the Arrhenius temperature dependence of the d.c. conductivity, σ_{dc}, crosses the TSDC peak curve at the temperature, T_m, of the peak maximum. W (obviously ~0.6 eV) is much lower than the activation energy of the d.c. conductivity, E_{dc}, in the same temperature range and also at higher temperatures ($E_{dc} > 0.9$ eV, Fig. 3 b).

Similar TSDC and d.c. conductivity behavior has been observed in NaDNA samples doped with D_2O. As in Fig. 2 for H_2O, there are the same shapes of the TSDC spectra and their relations to the d.c. conductivity dependences. Within experimental error, for peak II we have observed nearly the same values of the W, E_{dc} (Fig. 3 b), the same shift of T_m (Fig. 3 a) and nearly the same value of σ_{dc} at different h (Fig. 4). There are some indications of higher

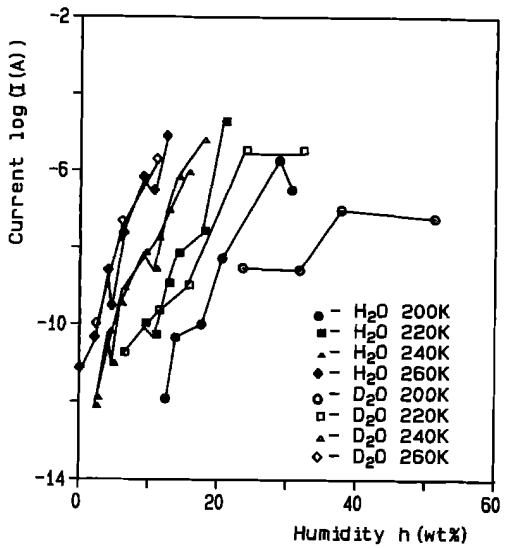

Fig. 4. The hydration dependence of the d.c. conductivity measured at several temperatures at the intensity of electric field 10^5 V/m

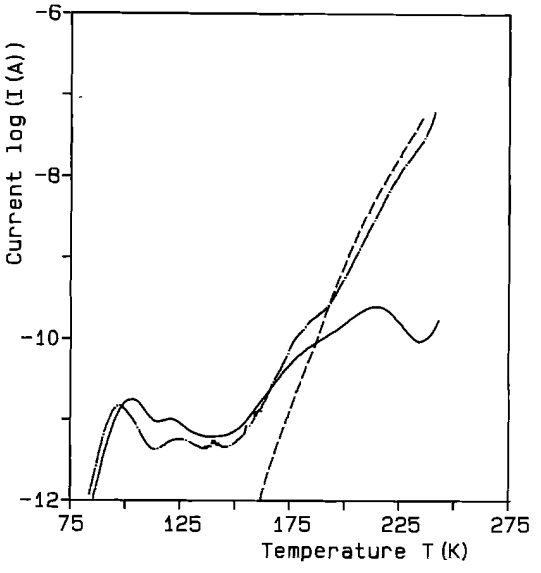

Fig. 5. TSDC (——), TSPC (— · —) spectra and d.c. conductivity (- - - -) in a frozen aqueous solution of 10^{-3} mol NaCl. The samples were cylinders of 1.0 mm height and 78.5 mm^2 cross-sectional area with stainless steel electrodes. T_p was 215 K, $E_p = 10^5$ V/m, $t_p =$ 15 min, $E = 10^5$ V/m

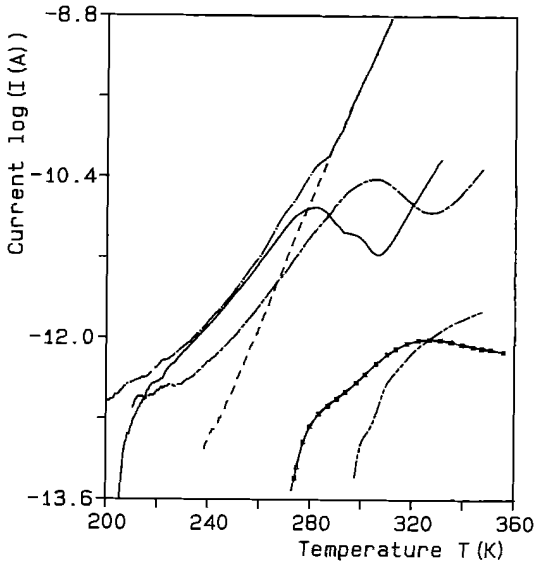

Fig. 6. TSDC spectra of adenine compounds of DNA: Na_2ADP (——), Na_2AMP (— - —), adenosine (×—×—×), and adenine (— - - —). (- - - -) represents the d.c. conductivity of ADP and (— —) the TSPC of ADP samples. $T_p = 310$ K (350 K for adenosine and adenine compounds), $t_p = 15$ min and $E_p = 10^5$ V/m. Measured with stainless steel electrodes

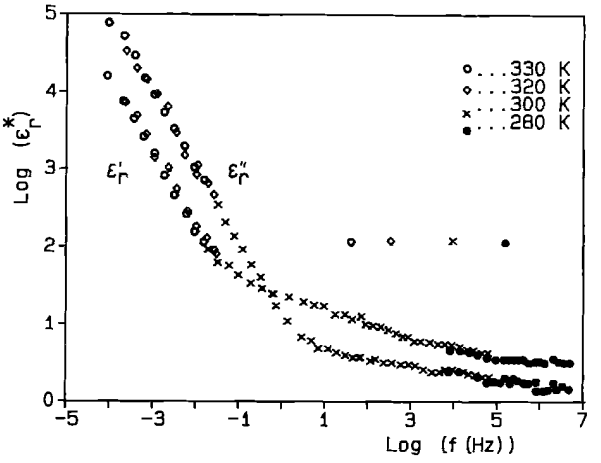

Fig. 7. The frequency dependence of the complex permittivity of dry solid NaDNA measured at different temperatures. The markers above the dispersion curves in the upper right of the diagram indicate the relative shift of the normalizing datum point required to give this plot

T_m and lowering of σ_{dc} in D_2O NaDNA at higher hydration (>25 wt%, Fig. 3 a, Fig. 4).

The nature of the effects in the temperature region 160–180 K have been probed in the model system for the DNA ion-water shell, 10^{-3} mol frozen aqueous solution of NaCl. The TSDC spectrum in Fig. 5 exhibits the dipolar relaxation peak at 160–190 K associated with the d.c. conductivity of protons (H_3^+O, OH^-). The plot also shows the free and the bound water dipolar relaxation peaks at lower temperatures (<150 K) and the proton space charge relaxation peak at higher temperatures (>200 K) (Laudát and Laudát 1992).

Figure 6 shows the TSDC spectra and the temperature dependence of the d.c. conductivity for DNA adenine compounds measured on samples under comparable conditions (preparation, drying, etc.). There is a clear difference between the electrical behavior of materials with the polar $PO_4^-Na^+$ group (Na_2AMP, Na_2ADP which bind water much more strongly) and of materials without the phosphate group such as adenosine and adenine. The d.c. conductivity in the ionic material is higher by several orders of magnitude. Like DNA peak II they also exhibit dipolar TSDC relaxation. At temperatures higher than 300 K the TSDC peaks in adenine and adenosine are probably of a space-charge origin.

Figure 7 shows the frequency dependence of the complex permittivity at various temperatures. As there were no changes in the shape of the curves, the results are

presented in a normalized form, giving a much broader frequency range than the measured one (Jonscher 1983). The dependencies (Ω dispersion) obey the relations

$$\begin{aligned} \varepsilon'(\omega)-\varepsilon_\infty &\sim \varepsilon''(\omega)\sim\omega^{n-1} \qquad \omega>\omega_c\,, \\ \varepsilon'(\omega)-\varepsilon_\infty &\sim \varepsilon''(\omega)\sim\omega^{-p} \qquad \omega<\omega_c\,, \end{aligned} \tag{2}$$

where ω_c is a characteristic frequency and n and p are constants (Jonscher 1978). A limiting slope of practically -1 at low frequencies is apparent. A strong dispersion in both the real and the imaginary parts of the complex permittivity shows no d.c. conductivity. On samples with imperfect contacts to the electrodes an additional maximum (α dispersion) around 1 Hz–1 kHz was observed. A shift of the characteristic frequency to lower frequencies, as well as lower loss and lower capacity of the sample, is caused by lowering the electrode pressure on the sample. The low-frequency (Ω) dispersion is not observed with totally blocking electrodes. The shift of the characteristic frequency, ω_c, to higher frequencies was, on the other hand, observed in samples with a higher water content, as found in proteins (Shablakh et al. 1984). The characteristic frequency shift may be approximated by the Arrhenius relationship, $\omega_c=\omega_0\exp(-W_f/kT)$ and this gives the activation energy, $W_f=1.25\pm0.1$ eV.

Discussion

The experimental results of electrical measurements presented above show the effects associated with local and long range motion of water dipoles, protons (H_3^+O, OH^-) and counterions (Na^+). The possible motion of the whole NaDNA backbone, or part of it, and the previously reported dominance of long range motions of electrons and holes (Eley et al. 1979) have been not observed in the results presented. This statement is supported by the following arguments:

The relaxation TSDC peaks I below 150 K (Fig. 2) observed only in highly hydrated NaDNA samples ($h>25$ wt% water) are due to the relaxation of free and slightly bound water. Relaxation peaks of the same origin are typically observed in ice (Apekis 1983), frozen aqueous solutions of NaCl (Fig. 5), HCl (Laudát and Laudát 1992) and in other highly hydrated biological materials (Pissis 1987). At lower humidities, when each phosphate group contains <5 water molecules (Falk et al. 1963), all water is strongly bound and thus does not relax. The relaxation peaks of water dipoles are missing in this temperature region of the TSDC spectra (Fig. 2).

Nevertheless, our interest has been focused on the effects in the high temperature region above 150 K. They are important for the understanding of local and long range motion of charge carriers. It has been found that there is a close relation of dipolar TSDC relaxation (peak II) and d.c. conductivity. The d.c. conductivity curve crosses the curve of peak II at T_m (Fig. 2). These effects are also associated with water and ions, which confirm the experiment in the frozen aqueous solution of NaCl (Fig. 5). Peak III observed in some solid NaDNA samples in the temperature range of apparent d.c. conductivity is probably also due to the relaxation of space charges.

The increase of the d.c. conductivity above the T_m of peak II (Fig. 2) indicates the existence of some kind of phase transition. It is not a first-order transition with exothermic or endothermic effects, because the peak shifts to higher temperatures with increasing heating rate. Microcalorimetric measurements show a first order transition in DNA-water-ions at somewhat higher temperatures – above 200 K (60 wt%; Mrevlischvili 1984). We have also observed a TSDC peak with the same properties in mononucleotides (Na_2AMP, Na_2ADP – Fig. 6), human albumin and in a complex system of plant leaves (monstera deliciosa, etc.). We propose therefore, that peak II may be due to a glass transition in ion-water clusters adsorbed on the DNA surface. This interpretation corresponds with earlier proposals of glass transitions in biological systems (Bruni et al. 1990) and tissues (Careri et al. 1990). It is typical for solids that dipolar relaxations are observed at the lowest temperatures, the possible glass transitions at medium and space charges at high temperatures in the temperature region of intrinsic conductivity of the sample (Turnhout 1975). The decrease in amplitude and shift of peak II with decreasing h (Fig. 3a) is associated with the lower rotational mobility of water (lower dielectric constant) owing to the strong binding to $PO_4^-Na^+$ groups.

The same relation between the TSDC dipolar relaxation ($T_m>165$ K) and the d.c. conductivity of wet (37 wt% water) and nearly dry (<6 wt% water) samples (Fig. 2) suggests the same transport and relaxation mechanism, where electron and holes are minority charge carriers. The exponential dependence of the d.c. conductivity on the hydration observed in DNA samples (Burnel et al. 1972) is typical of protonic conductors. Also the values of $W\sim0.6$ eV (Fig. 3b) agree with the value of activation energy of the protonic d.c. conductivity, E_{pr} (Riehl 1965). Careri et al. (1990) used a dielectric method over the frequency range 10 kHz–10 MHz on samples of biological tissues placed in the measuring capacitor with insulated electrodes. Their results indicate that the temperature dependence of the d.c. conductivity in the region of the transition temperatures may be expressed by $\sigma_{dc}\sim\exp T^6$. Our results on NaDNA measured directly in the temperature region of peak II show the Arrhenius temperature dependence of the d.c. conductivity. The possible explanation of these discrepancies and the higher values of E_{dc} against E_{pr} lies in the role of electrodes in the d.c. conductivity measurements. A further search for supporting evidence for the hypothesis of the dominant role of the electronic transport in DNA using photoconductivity measurements gave no clear evidence either. The previous photoconductivity results in the infrared, visible and ultraviolet spectral regions were interpreted by a bolometric effect (Eley et al. 1975; Šubertová et al. 1983).

The role of protons and counterions in d.c. conductivity and relaxation responses was examined by doping the solid samples with D_2O. The expected T_m shift of the dipolar TSDC peak II to higher temperatures and lowering the σ_{dc} is indicated only at higher hydration (>25 wt%, Fig. 3a and Fig. 4). At lower water content

in the samples the strong $Na^+ - H_2O$ D_2O or $Na^+PO_4^- - H_2O$ (D_2O) interaction probably surmounts the effect of D_2O. The strong hydration dependence of both relaxation and d.c. conductivity phenomena support the idea of the dominant role of protons in these phenomena. The contribution of heavier counterions probably increases with increasing hydration of the samples, owing to their higher mobility. They are then excluded on the electrode surfaces. This was shown by a microprobe analysis of the electrode deposit. The surface layer, especially its blocking effect, influences the properties of the above phenomena. The additional effects also support the above interpretations.

The local motion of protons and counterions and their transport through the bulk of the solid sample takes place in the neighbourhood of the phosphate groups. The evidence is given in Fig. 5. There is a strong difference between the electrical properties of the DNA compound with the polar phosphate groups $PO_4^-Na^+$ and the ions (Na_2AMP, Na_2ADP) and the compounds without them (bases, nucleosides). The strong ion–water interaction causes a preferred hydration of $PO_4^-Na^+$ groups as is well known from the earlier studies of DNA hydration sites (Falk 1963). The possible hopping of H_3^+O or OH^- ions between the phosphate groups (P – P distance along the sugar-phosphate chain $s = 0.69$ nm) is equivalent to the rotation of a dipole with the dipole moment, $m = q \cdot s = 1.27 \times 10^{-28}$ C.m. For higher hydrations the hydrogen bond network may facilitate the charge transfer via the Grotthuss proton transfer mechanism.

The d.c. conductivity in the solid DNA layers seems to be limited by electrochemical reactions on the electrodes. These processes also cause the low-frequency dispersion which was not observed when employing totally blocking electrodes. Our interpretation of the low-frequency dispersion corresponds to a similar conclusion on proteins drawn by Morgan and Pethig (1986), but not to the previous interpretations in terms of the quasi-d.c. conductivity in the sample volume proposed by Shablakh et al. (1984). The hysteresis in the current-voltage characteristics (Laudát 1990) and the corrosion of electrodes also strongly suggest that the electrode processes rather than the bulk mobility of protons provide the transport parameters.

The above results of the electrical studies on solid DNA samples are important to the understanding of the biological function of DNA. There is an apparent mobility of protons and counterions in the close vicinity of the DNA backbone, i.e., in the first hydration shell. This must influence the local motion of the DNA molecule and its polarization properties. Bruni (1990) has recently proposed the idea that the cytoplasm of anhydrobiotic organisms (plant seeds, pollen, bacteria, and others) exist in a glassy state even at physiological temperatures. Our results indicate that the NaDNA molecule itself may be found fixed up to 255 K. The fixed structure of partially dehydrated DNA at relatively high temperatures is interesting also for the technique of preservation of functioning genetic material by cooling, because higher fixation temperatures lower the danger of damages. The TSDC technique gives the possibility to exactly determine the temperatures at which the material is fully fixed.

Conclusions

From above results and discussion of relaxation and d.c. conductivity measurements we suggest the following model of local and long range motion in solid DNA. In this model the protons (H_3^+O and OH^- ions) are the majority charge carriers moving in the neighbourhood of the phosphate groups by hopping or at higher hydrations by the Grotthuss proton transfer mechanism through the hydrogen bond network. Increasing hydration increases the mobility of counterions and their contribution to the d.c. conductivity. The d.c. conductivity is limited by processes on the electrodes, the low-frequency dispersion is also caused by this effect. The local and long-range motion of charge carriers is limited below temperatures of a dipolar thermally stimulated depolarization current (TSDC) peak II observed in the temperature range of 165–255 K. The observed effects are important for the understanding of biological properties of DNA as well as for the preservation techniques of biological materials.

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