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 Anagnostopoulos-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-
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 kPa/cm) of NaDNA, disodium salt of adenosine 5’-monophosphate (Na₂AMP, Reanal Budapest), disodium salt of adenosine 5’-diphosphate (Na₂ADP, 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 x SSC buffer solution with ethanol, molecules of NaDNA were wound onto a glass rod covered with silicon rubber. After slow drying, typically 0.5 x 10⁻³ m thick samples (13 x 10⁻³ m in diameter, with a density of 0.9 g/cm³) were cut. The dry samples were also doped by heavy water (98.4 vol% D₂O) 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 Na₂AMP, Na₂ADP 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, \[ \tau (T) = \tau_0 \cdot \exp \left( \frac{W}{kT} \right), \] the depolarization current density, \( J(T) \), is given by

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

where \( \tau \) is the relaxation time, \( W \) the activation energy of the relaxation, \( \tau_0 \) the pre-exponential factor, \( T \) the absolute temperature, \( k \) the Boltzmann constant, and \( P_0 \) the