Water-induced dc conductivity of DNA: A dielectric-gravimetric study

A. Bonincontro, G. Careri, A. Giansanti, and F. Pedone*
Dipartimento di Fisica, Prima Università degli Studi di Roma, La Sapienza, I-00185 Roma, Italy
(Received 29 June 1988)

The dc conductivity of hydrated Li-DNA and Na-DNA powdered samples has been detected in a composite capacitor without electrode contacts. In all slightly hydrated samples the conductivity increases exponentially along with the water content with the same exponential factor, confirming initial suggestions of an intrinsic semiconductivity. Above about 25% water content, capillary condensation produces an additional relaxation effect.

DNA (deoxyribose nucleic acid) hydration is a subject of current experimental interest[1] in view of the well-known role of water in determining the structure[2] of this biopolymer. The nature of the dc conductivity of hydrated DNA seems to be still controversial, both from the theoretical[3,4] and the experimental[5,6] side. The early experimental work, reviewed by Pethig,[5] revealed an exponential increase of the intrinsic semiconductivity with increasing water content up to 25%, followed by a region dominated by protonic conductivity. However, more recently Van Lith *et al.*,[6] by using pulsed ionization in order to avoid electrodes in contact with samples, detected mobile charges only above 79% water content, at variance with previous findings.

In the past years a sensitive dielectric-gravimetric technique[7] has been developed in this laboratory to detect water-induced dielectric properties of biomaterials by avoiding direct electrode contacts, which are known[8] to be a source of dielectric relaxation at low frequencies. This technique has been applied to detect protonic conductivity[9] and percolation in lysozyme[10] and in purple membrane.[11] The hydrated sample is placed in a glass dish, which is part of a two parallel-plate capacitor, set on the pan of a balance, and both the sample weight and dielectric data in the range from 10 kHz to 10 MHz are contemporaneously measured and stored during slow dehydration by a constant dry air flux, at a temperature of 27.5±0.1 °C.

Na-DNA from herring sperm was from Boheringer. RNA (ribonucleic acid) and protein contaminations were found to be less than 1% as determined by the orcinol method[12] and 0.3% as determined by the method of Lowry *et al.*,[13] respectively. The size distribution of DNA molecules ranged from 300 to 1100 nucleotide pairs, as determined by agarose gel electrophoresis.[14] DNA was dissolved in water at a concentration of 2 mg/ml and extensively dyalized against water. The dyalized solution was made 0.4 *M* in counterion (Na and Li) by addition of ethanol up to 70% of final concentration, the precipitated DNA was recovered by centrifugation at 20 000 g for 15 min. The DNA pellet obtained was washed twice with 70% ethanol to remove excess salt, and finally lyophilized and ground to powder. In the following *h* is the hydration level of the powdered sample in grams of water per gram of dry DNA; the dry weight was determined by oven drying samples at 80 °C.

More than 20 different samples have been tested after variable durations of isopiestic hydration. It was soon realized that hydration at 5 °C and even prolonged hydration at 25 °C produced an additional dielectric relaxation, likely due to capillary water condensation on the DNA powdered sample. Capillary condensation is known to occur when samples are hydrated at relative humidities higher than 30%; specifically it has been observed in DNA samples,[15] but it does not seem to have been considered when measuring dielectric properties of DNA,[5,6]

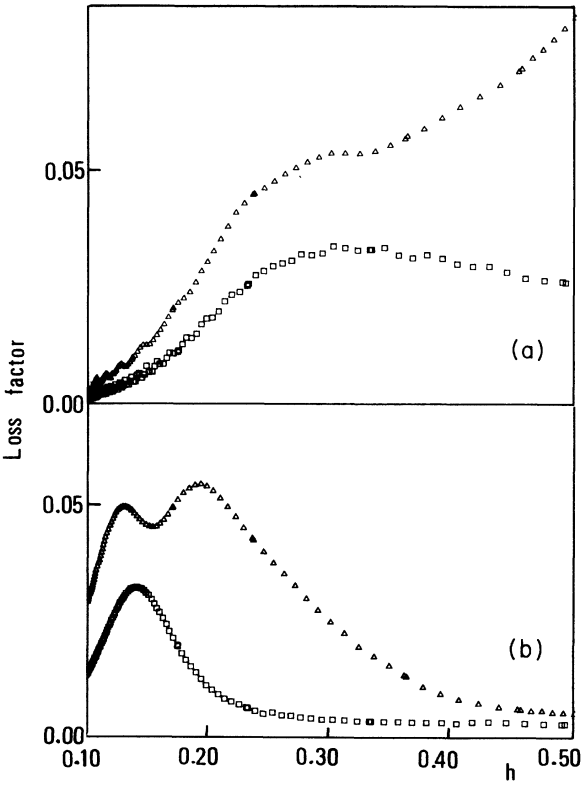

FIG. 1. Loss factor vs hydration *h* at (a) 10 MHz and (b) 10 kHz. Triangles are for Na-DNA hydrated at 5 °C: squares for a similar sample, hydrated at 20 °C. At high hydration a larger contribution by capillary water is clearly detectable in the sample hydrated at the lower temperature.

in spite of the known high dielectric relaxation displayed by capillary water.[16] The presence in our data of two different types of dielectric relaxation is shown in Figs. 1(a) and 1(b), one type being characteristic of the Maxwell-Wagner effect of our composite capacitor,[7,9] and the other superimposed on the previous one, which is easily attributed to water clusters of different sizes contributing to capillary water.[16] The contribution of this second relaxation proved to be dependent on the sample hydration history and was out of our control; therefore, in the following we shall be concerned with samples where the effect of this second type of relaxation was negligible in comparison to the first one.

In Fig. 2 we show the water-induced change of the frequency at which maximum dissipation takes place. As we have previously discussed[9] this quantity f_m is related to the dc conductivity σ of the sample by a simple equation: $f_m=(2\pi\epsilon_0)^{-1}(1+\varepsilon)^{-1/2}\sigma$ where ϵ_0 is the vacuum permittivity and ε is the relative dielectric constant. Although our results are displayed in Fig. 2 as $\log_{10}f_m$ versus h curves, since $\log_{10}f_m \propto \log_{10}\sigma$, these data will be discussed as if they represented $\log_{10}\sigma$ versus h curves. The assumption underlying the use of this last approximation is that hydration dependence of the dielectric constant can be neglected. This assumption is justified, because in the hydration range from $h=0.15$ to $h=0.20$ the capacitance increases only by 10%, while f_m increases by more than 1 order of magnitude.

Inspection of Fig. 2 shows that at low hydration the conductivity follows the typical exponential increase with increasing hydration already detected in most biopolymers;[5] $\sigma \propto \exp(\alpha h)$, where $\alpha=27.1\pm0.2$ in Li-DNA and Na-DNA, the latter hydrated with D_2O or H_2O. We note, incidentally, that the inferred conductivity reported here in DNA samples is of the same order of magnitude as the protonic conductivity observed in this laboratory with the same apparatus and in the same hydration range for protein powders.[9-11]

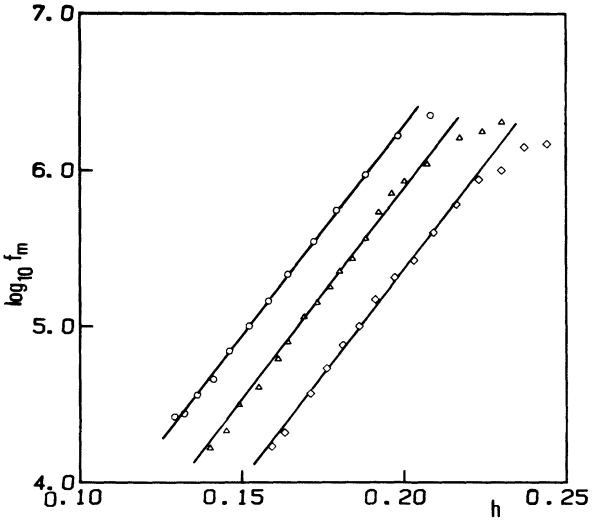

FIG. 2. $\text{Log}_{10}f_m$ vs hydration h. △, H_2O hydrated Na-DNA; ○, D_2O hydrated Na-DNA; ◇, H_2O hydrated Li-DNA. Solid lines represent the best fit through data with a slope of 27.1 (reciprocal hydration).

Our data confirm the previously detected exponential increase of the dc conductivity at low hydration,[5] but we believe our value to be more reliable because of the absence of electrode effects[8] and of the larger number of experimental data. The apparent disagreement with the recent findings by Van Lith *et al.*[6] can be understood if in this latter work only the motion of free electrons produced by ionization was measured at high hydration, while an intrinsic semiconductivity of the DNA backbone was observed in our slightly hydrated samples with different counterions. We believe this confirmation of the previous suggestion[5] to be relevant in view of the uncertainties in recent theoretical treatments.[4]

---

*Also at Dipartimento di Genetica e Biologia Molecolare, Prima Università degli Studi di Roma, La Sapienza, I-00185 Roma, Italy.

[1]C. Demarco, S. M. Lindsay, M. Pokorny, and J. Powell, Biopolymers **24**, 2035 (1985); A. Bonincontro, A. Di Biasio, and F. Pedone, *ibid.* **25**, 241 (1986); S. A. Lee, S. M. Lindsay, J. W. Powell, T. Weidlich, N. J. Tao, and G. D. Lewen, *ibid.* **26**, 1637 (1987); L. J. Schreiner, M. M. Pintar, A. J. Dianoux, F. Volino, and A. Rupprecht, Biophys. J. **53**, 119 (1988).

[2]E. Clementi, in *Structure and Dynamics: Nucleic Acids and Proteins*, edited by E. Clementi and R. H. Sharma (Adenine, New York, 1983); M. L. Kopka, A. V. Fratini, H. F. Drew, and R. E. Dickerson, J. Mol. Biol. **163**, 129 (1983); W. Saenger, W. N. Hunter, and O. Kennard, Nature **324**, 385 (1986).

[3]S. Suhai, Biopolymers **13**, 1739 (1974).

[4]A. K. Bakhshi, P. Otto, J. Ladik, and M. Seel, Chem. Phys. **108**, 215 (1986).

[5]R. Pethig, *Dielectric and Electronic Properties of Biological Materials* (Wiley, New York, 1979).

[6]D. Van Lith, J. M. Warman, M.P. de Haas, and A. Hummel, J. Chem. Soc. Faraday Trans. I **82**, 2933 (1986).

[7]G. Careri and A. Giansanti, in *Membranes, Metabolism and Dry Organisms*, edited by A. C. Leopold (Cornell University Press, Ithaca, 1986).

[8]H. Morgan and R. Pethig, J. Chem. Soc. Faraday Trans. I **82**, 143 (1986).

[9]G. Careri, M. Geraci, A. Giansanti, and J. A. Rupley, Proc. Natl. Acad. Sci. USA **82**, 5342 (1985).

[10]G. Careri, A. Giansanti, and J. A. Rupley, Proc. Natl. Acad. Sci. USA **83**, 6810 (1986).

[11]G. Careri, F. Bruni, L. Szimanowski, and J. A. Rupley, Proc. Natl. Acad. Sci. USA (to be published).

[12]W. C. Schneider, Methods Enzymol. **3**, 680 (1957).

[13]O. M. Lowry, M. J. Rosenbrough, A. L. Farr, and R. J. Randall, J. Biol. Chem. **193**, 265 (1951).

[14]J. Sudgen, B. De Troy, R. J. Roberts, and J. Sambrook, Anal. Biochem. **68**, 36 (1975).

[15]A. D. McLaren and J. P. Kirwan, J. Gen. Virol. **33**, 155 (1976).

[16]J. B. Hasted, *Aqueous Dielectrics* (Chapman and Hall, London, 1973).