Short Communications and Preliminary Notes

SOME POLYELECTROLYTE PROPERTIES OF DESOXYRIBONUCLEATE

by

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It was pointed out by FUOSS in 1949[1] that desoxyribose nucleic acid (DNA) is a typical polyelectrolyte and the early experimental results in respect of viscosity, osmotic pressure, electrometric titration and electric conductivity obtained in 1924 by HAMMARSTEN[2], and interpreted then as an anomalous capture of sodium counter ions, may be looked upon today as typical polyelectrolyte properties. Many of the physico-chemical data obtained since, *e.g.*, the anomalous titration curves[3,4], may be explained by the present theory for polyelectrolytes[5–7]. It has been found by the study of various model substances[8–11] that this theory may also be applied to the dielectric properties of polyion solutions and thus to DNA solutions.

The dielectric properties of DNA solutions under varying conditions have been extensively studied at this laboratory[12–15] and the results have been interpreted along the lines of the DEBYE theory. The dipolar structure of DNA and an orientation polarization were assumed to be the cause of the dielectric increment and dispersion.

Most of the investigations have been carried out at pH 6–7 and the charge of the polyion must then arise mainly from the phosphoric acid groups, as the amino, imino and enolic groups are not ionized. The maximum negative charge will only be obtained at "infinite dilution", as the screening effect of the sodium counter ions in Na-DNA at other concentrations will decrease the negative charge considerably, especially with excess counter ions when sodium chloride or some other salt is added.

The dielectric increment may be assumed to be an expression of the net negative charge of the polyion. The results obtained[12,14], *i.e.* sharply increasing increment per gram per litre with increasing dilution of Na-DNA solutions, and a sharp drop of the increment with excess counter ions, are then in agreement with the changes of the net charge as stated above. Moreover the increment drops sharply on decrease of the ionization by addition of hydrochloric acid[14]. Similarly, on neutralizing the free DNA (obtained by treatment of Na-DNA with ion exchange resins) with sodium hydroxide, the increment increases from 1.7 dielectric constant (DC) units at pH 3.9 to 7.6 DC units at pH 7.3 (0.02 % w/v of "moisture-free" Na-DNA)[10].

In other experiments with deaminated Na-DNA (nitrous acid treatment which removed about 50 % of the amino groups and decreased the N/P ratio from 1.69 to 1.52) it was found that the dielectric dispersion was unchanged, *i.e.* the increment, the critical wavelength and the course of the curve were the same as for untreated Na-DNA (in 0.02 % aqueous solution)[10]. This is contrary to the dipolar concept of DNA as explaining dielectric data but it agrees with the importance of the acid groups assumed above. In this connection it may be pointed out that the increments per phosphoric acid group per unit volume for comparable Na-DNA and nucleohistone (DNHi) specimens at the same concentration (phosphoric acid groups per unit volume) are of the same order[15]. Also the increments for DNHi are dependent upon concentration and excess sodium ions in the same way as for Na-DNA. This seems to indicate that the phosphoric acid groups in DNHi are ionized, and thus the main linkages between DNA and histone in "native" DNHi would not comprise the phosphoric acid groups to any large extent. In "synthetic" nucleoproteins, however, this may be the case, which would explain, *e.g.*, the different solubilities.

When the dielectric increments of various DNA salts (obtained by neutralizing aliquots of deionized DNA with the proper hydroxides) were determined (at concentrations equivalent to 0.02 % Na-DNA and pH about 7.3) the following order for the increments was obtained[10]

$$\mathrm{Li^+} > \mathrm{Na^+} > \mathrm{K^+} \simeq \mathrm{NH_4^+} \gg \mathrm{Mg^{+2}}$$

Thus the screening effects of these ions are in inverse order, which is in agreement with the ion exchange affinities found for these ions. It favours the polyelectrolyte aspects given above for DNA. Also the effectiveness in decreasing the increment of Na-DNA of Na, K, and Mg chlorides is in agreement herewith, viz. Mg $\gg$ K $>$ Na[14]. Similarly, the influence of various amines on the osmotic pressure of DNA solutions[2], agrees with these aspects.

Some examples are given in the figure of the effects of substituting water as solvent for DNA with water–ethanol mixtures, *i.e.* solvents with lower DC's than water. The dielectric increment of Na-DNA (0.02 %, pH about 6.5) drops sharply as the DC of the solvent decreases, in conformity with the increasing electrostatic attraction and thus the increasing screening effect of the counter ions.

Concerning the changes of the dielectric dispersion obtained under varying conditions, these are at least qualitatively in accordance with the Wagner theory[16], which considers the anisotropy of the dielectric in respect of DC and electric conductivity. Three main effects have been obtained for DNA and similar polyions[8-15]: the critical frequency of the dispersion curve is displaced from high to low frequencies when (1) an added excess of salt is diminished at constant polyion concentration, (2) the polyion concentration decreases, and (3) when the DC of the solvent is diminished at constant polyion concentration (see Fig. 1). These changes all imply a decrease of the conductivity in the solvent regions between the polyions–mainly due to an absolute decrease of Na$^+$ ion concentration (1, 2) or an increased polyion–simple ion association (3).

The present approach seems capable of explaining a considerable part of the data for DNA solutions. There may, however, be other effects taking place parallel to those stated above. No account has been taken of any polyion–polyion interaction or change of shape of the polyions. It is possible that several theories must be correlated before all data can be explained.

Whether it would be necessary to postulate an ice-like, crystalline structure of water around the polyions[17], does not seem to have been definitely established by experiment.

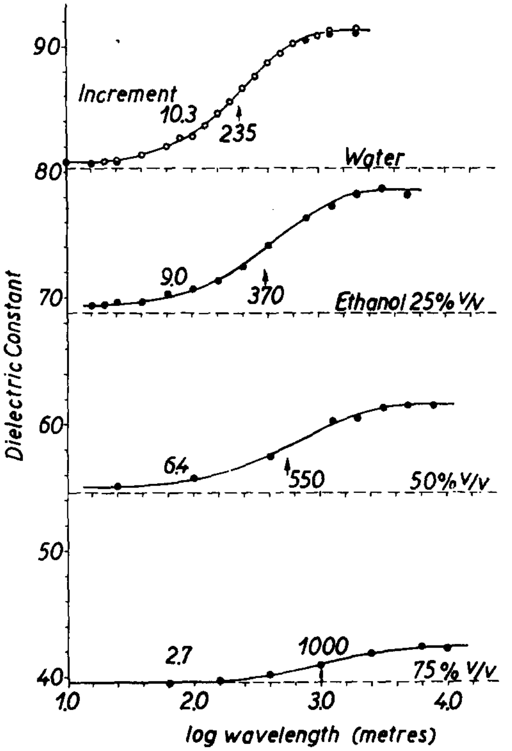

Fig. 1. Dielectric dispersion curves for 0.02 % solutions of Na-DNA in water and 25, 50 and 75 % ethanol. The arrows and attached figures indicate the critical wavelengths (metres). The dielectric increments of Na-DNA are given to the left (low frequency DC — high frequency DC). o denotes values taken from I. Jungner[14].

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