

Dielectric Increments and Dispersions in Aqueous Solutions of a Dextran Ester Sulphate

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The sodium salts of a number of acid polyelectrolytes containing carboxylic or phosphoric acid groups have been shown to give high dielectric increments in aqueous solutions, and also to give dielectric dispersions at radio frequencies¹⁻⁵. The dielectric properties of these polyelectrolytes also show anomalous concentration effects as compared with globular proteins and simple dipolar ions. Recently it has been found that chondroitin sulphate much resembles the other acid polyelectrolytes in respect of dielectric increment and dispersion⁶. It was to obtain more information concerning the influence of sulphate groups in the molecule on the dielectric properties that this investigation of the sodium salt of a dextran sulphuric acid⁷ was carried out.

Table 1. Dielectric increments and critical wavelengths of dextran sulphate.

Concn. %	ϵ_l	ϵ_h	Increment ($\epsilon_l - \epsilon_w$)	I_g	λ_c (meters)
0.10	87.0	82.3	6.7	6.7	25
0.10	86.8	—	6.5	6.5	—
0.08	86.2	—	5.9	7.4	—
0.06	85.2	—	4.9	8.2	—
0.05	84.7	81.7	4.4	8.8	39
0.04	84.0	—	3.7	9.3	—
0.03	83.3	—	3.0	10	—
0.025	83.3	80.8	3.0	12	51
0.02	82.7	—	2.4	12	—

Symbols: ϵ_l = DC at frequencies low in relation to those of the dispersion region.
 ϵ_h = DC at frequencies high in relation to those of the dispersion region.
 ϵ_w = DC of solvent (80.3 for water at 20° C).
 λ_c = critical wavelength, obtained graphically.

EXPERIMENTAL

The dextran sulphate * used (abbreviated to DS hereafter) contained 17.3 % sulphur. The molecular weight of the specimen was about 40 000 (calculated from the sulphur content and the molecular weight of the dextran starting material — about 19 000 — determined viscometrically). The sulphur content corresponds to about two ester sulphate groups per glucose unit in the macromolecule.

The dielectric measurements were carried out by the ellipsoid method as modified by G. Jungner and coworkers^{2, 3} for measurements at various radio frequencies between 30 Mc/s and 30 kc/s. All measurements were made at 20.0° C. Fresh aqueous solutions below 0.1 % (w/v) were investigated. pH about 6.0.

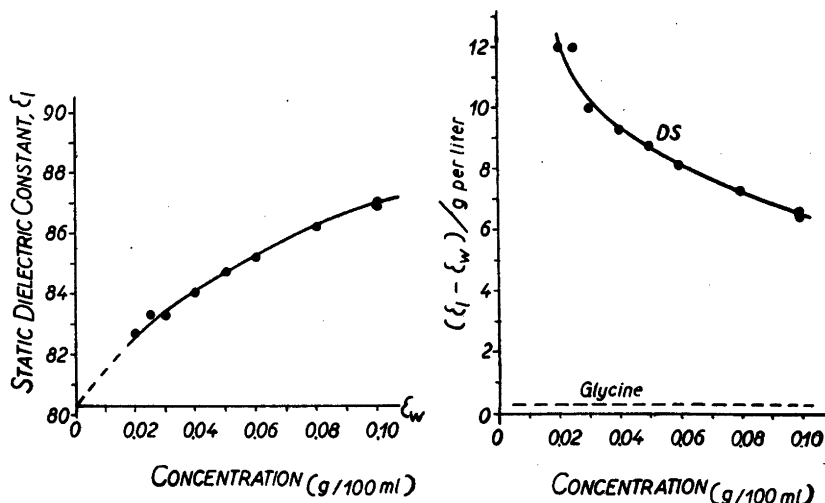


Fig. 1A (left), static dielectric constant and, Fig. 1B (right), increment per gram per liter as a function of concentration for DS in aqueous solutions.

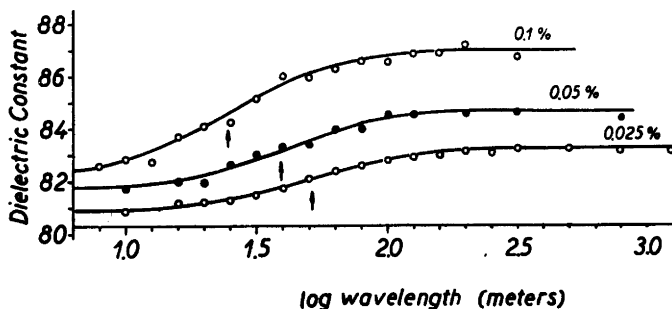


Fig. 2. Dielectric dispersion curves of dextran sulphate in aqueous solution at various concentrations.

The arrows indicate the critical wavelengths. The full-drawn curves are the theoretical curves according to the Debye theory fitting the experimental points.

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RESULTS

A dielectric increment was obtained for DS in dilute aqueous solution. The increment per gram per liter (I_g) was of the order of 10 dielectric constant (DC) units at the lowest concentrations studied, corresponding to a molar increment of about $4 \cdot 10^5$.

As is shown in Figs. 1A and B and Table 1, the increments are not linear functions of concentration. I_g increases as concentration decreases (Fig. 1B).

Dielectric dispersions were obtained in the frequency range used. The dispersions approached theoretical dispersions according to Debye (for a solute with a single relaxation time). The critical wavelengths (Fig. 2 and Table 1) varied considerably with concentration, being longer at lower concentrations. The relaxation times calculated according to the Debye theory and assuming that the DS molecule orientates in the electric field around its long axis, were $1.3 \cdot 10^{-8}$ sec. at 0.1 % and $2.6 \cdot 10^{-8}$ sec. at 0.025 % concentration.

DISCUSSION

A specimen of the neutral polyglucose dextran has been shown previously to give *no* dielectric increment in aqueous solution at 0.5 % concentration⁵. It is therefore natural to assume that the high dielectric increment obtained with DS in this study is closely connected with the presence of charged groups, $-\text{SO}_3^-$, in this molecule.

DS is an elongated molecule with side chains, which gives it a large surface compared with, *e. g.*, globular proteins in the same molecular weight class. DS will then have a high "surface charge" compared with such proteins, in which the charges — positive and negative — will be internally compensated to a large extent. This might be the explanation of the much higher dielectric increments obtained for DS and similar polyions (I_g about 10 for DS and less than 2 for globular proteins).

The cause of the dielectric increment in the case of proteins and simple dipolar ions is assumed to be an orientation polarization due to orientation of dipoles in the electric field in accordance with the Debye theory. Such an orientation effect implies a more or less asymmetric distribution of the charges in the molecule. It is, however, difficult to assume such an electric asymmetry for the DS molecule, and thus it is doubtful whether the Debye theory will apply to this case. Fuoss⁹ has suggested that a modified Wagner theory^{10, 11} will explain the polarization phenomena in the case of polyelectrolytes, and thus for DS.

Qualitatively there is no difference between the dielectric properties in aqueous solution of DS and other polyelectrolytes studied. All give, *e. g.*, nonlinear increment *vs.* concentration curves and displacement of the dispersion curves to longer wavelengths with lower concentrations. Quantitatively there are considerable differences, however. Thus the dielectric increments show large variations between different substances (and in some cases different molecular weights of one substance) even if comparisons are made at corresponding concentrations on an equivalents per unit volume basis, in pure aqueous solutions.

The course of the I_g vs. concentration curve (Fig. 1B) has previously been interpreted in similar cases¹⁻⁵ as being due to a prevalence of free polar macromolecules or polar aggregates in the solution at very low concentrations and of aggregates less polar at higher concentrations, *i. e.* association-dissociation phenomena on a macromolecular scale. It might, however, also be interpreted as being due to an increasing "dissociation" of counter ions (Na^+) from the macromolecule with increasing dilution, *i. e.* a lessening of the screening effect of the counter ions. Thus the net charge of the polyion increases with increasing dilution, giving rise to higher I_g values. This is well compatible with the dependence of viscosity and d.c. conductivity of polyelectrolyte solutions on concentration¹²⁻¹⁵ and does not seem to be influenced by the theory chosen for the dielectric polarization and relaxation phenomena.

Finally it may be mentioned that two other polysaccharide ester sulphates with relatively low molecular weights — a cellulose sulphate and the above-mentioned chondroitin sulphate — have been shown⁶ to have similar dielectric properties in aqueous solution to DS.

SUMMARY

The dielectric properties of DS in aqueous solution are similar to those of other acid polyelectrolytes studied, containing $-\text{COOH}$, $=\text{PO}_4\text{H}$ or $-\text{SO}_3\text{H}$ groups. As might be expected the dielectric increments seem to be mainly dependent upon the actual charge of the molecules.

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