

ELECTRIC SATURATION OF DIELECTRIC PERMITTIVITY VARIATION
IN MACROMOLECULAR SOLUTIONS

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Complete dielectric saturation in solutions of prolate or oblate macromolecules aligned in an intense electric field is discussed quantitatively. A positive effect was measured in solutions of isotactic polystyrene in benzene and carbontetrachloride for Tween 80 and methyl-polymethacrylate in benzene.

Consider a macromolecular solution so dilute that correlations between the macromolecules and between them and the molecules of the solvent (dielectric constant ϵ_0) are negligible. It is our aim to find the differential change in the dielectric constant of the solution $\delta\epsilon(E)$ due to a very intense electric field E [1]. A macromolecule (effective dipole moment μ), when acted on the local electric field F undergoes a reorientation described by a Boltzmann distribution function of the dimensionless Langevin-Debye parameter

$$p = \mu F/kT. \quad (1)$$

The macromolecules are assumed to be so rigid that electron distortion is linear. For anisotropically polarizable macromolecules (with α_{\parallel} , α_{\perp} the electric polarizabilities parallel and perpendicular to the symmetry axis, which is that of the permanent dipole μ), a second (Langevin) parameter accounting for reorientation of the induced dipole of anisotropy

$$q = |\alpha_{\parallel} - \alpha_{\perp}| F^2/2kT \quad (2)$$

appears in the Boltzmann distribution function [1].

Let the weak field measuring the variation $\delta\epsilon$ act in the same direction as the intense polarizing field E . Then $\delta\epsilon(E)$ consists of two parts [2]:

$$\delta\epsilon_{\alpha}(p, \pm q) = \pm \frac{8\pi\rho}{3} \left(\frac{\epsilon_0 + 2}{3}\right)^2 |\alpha_{\parallel} - \alpha_{\perp}| R_{\alpha}(p, \pm q); \quad (3)$$

$$\delta\epsilon_{\mu}(p, \pm q) = -\frac{4\pi\rho}{3kT} \left(\frac{\epsilon_0 + 2}{3}\right)^2 \mu^2 R_{\mu}(p, \pm q), \quad (4)$$

with ρ the mean number density of macromolecules in solution. The functions R_{α} and R_{μ} define the degree of reorientation of macromolecules in the intense field E :

$$R_{\alpha}(p, \pm q) = \Phi(p, \pm q) + \frac{3}{2}p\{L_3(p, \pm q) - L_1(p, \pm q)L_2(p, \pm q)\} \pm 3q\{L_4(p, \pm q) - L_2^2(p, \pm q)\}; \quad (5)$$

$$R_{\mu}(p, \pm q) = 3L_1^2(p, \pm q) - 2\Phi(p, \pm q) \mp 6(q/p)\{L_3(p, \pm q) - L_1(p, \pm q)L_2(p, \pm q)\}. \quad (6)$$

The $L_n(p, \pm q)$ are generalized Langevin functions, known explicitly [1, 2]. The reorientation function

$$\Phi(p, \pm q) = \frac{1}{2}\{3L_2(p, \pm q) - 1\} \quad (7)$$

describes electric saturation of the Kerr effect [3]. The sign "plus" in eqs. (3) - (7) is for prolate macromolecules (positive electric anisotropy, $\alpha_{\parallel} - \alpha_{\perp} > 0$) whereas the sign "minus" applies for oblate ones (negative electric anisotropy, $\alpha_{\parallel} - \alpha_{\perp} < 0$).

In particular, for non-dipolar macromolecules we have $\mu = p = 0$ and the only nonzero variation is that given by eq. (3) with reorientation function $R_{\alpha}(\pm q)$ (plotted in fig. 1). Since prolate macromolecules tend to align with their long polarizability ellipsoid axis in the field direction, the variation $\delta\epsilon_{\alpha}(+q)$ grows steeply to the limiting value:

$$\delta\epsilon_{\alpha}(+\infty) = \frac{8\pi\rho}{3} \left(\frac{\epsilon_0 + 2}{3}\right)^2 |\alpha_{\parallel} - \alpha_{\perp}| \quad (3a)$$

at reorientation saturation, when $R_{\alpha}(+q) = 1$, with $q \rightarrow \infty$.

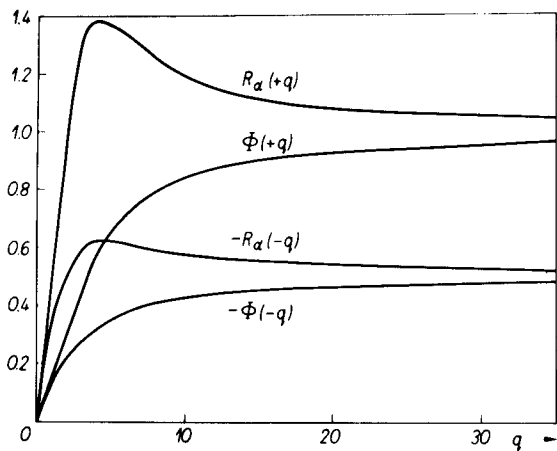


Fig. 1. Graphs of reorientation functions $R_\alpha(0, \pm q)$ and $\Phi(0, \pm q)$ (defined by eqs. (5) and (7) with $p = 0$), for prolate and oblate macromolecules, respectively.

Oblate macromolecules are reoriented at saturation in a manner to bring their shorter symmetry axes into line with the field direction; by (3) and (5), we now have:

$$\delta\epsilon_\alpha(-\infty) = \frac{1}{2}\delta\epsilon_\alpha(+\infty), \quad (3b)$$

since now $R_\alpha(-q) = -1/2$, at $q \rightarrow \infty$.

For non-dipolar macromolecules, the variations $\delta\epsilon_\alpha(\pm q)$ are positive irrespective of shape, leading, at electric saturation, to the relation (3b), the same as for electric saturation of the Kerr effect [3]. Moreover, from fig. 1 one sees that in regions of arbitrary reorientation far from complete saturation the functions $R_\alpha(\pm q)$ and $\Phi(\pm q)$ differ strongly in shape owing to the fact that, whereas in dielectric measurements the reorientation due to the intense field has, superimposed upon it, a reorientation due to the measuring field (if the latter varies at a rate sufficiently slow for the macromolecules to keep pace), in optical measurements the changes in refractive index which we measure are caused by reorientation in the intense dc electric field alone. Because of this difference between electric and optical measurements, $R_\alpha(\pm q)$ grows initially much more steeply than $\Phi(\pm q)$.

For dipolar anisotropically polarizable macromolecules, the reorientation functions (5) and (6) are plotted in figs. 2 and 3 ($\Phi(p, \pm q)$ of eq. (7) is shown in refs. [3, 4]). Since for prolate macromolecules the permanent and induced dipoles reorient concordantly into the field direction, $R_\alpha(p, +q)$ grows steeply with increasing ratio q/p^2 . The oblate case is different: at first, the permanent dipole μ tends to alignment with

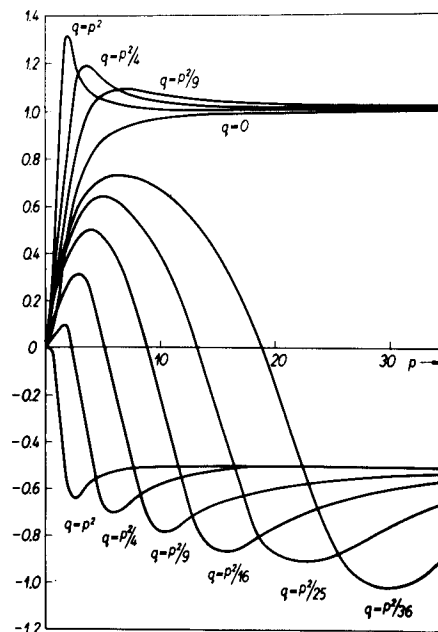


Fig. 2. Shape of the reorientation function (5) for prolate macromolecules (curves $R_\alpha(p, +q)$ lying above the curve for $q = 0$) and oblate macromolecules (curves $R_\alpha(p, -q)$ lying beneath the curve for $q = 0$).

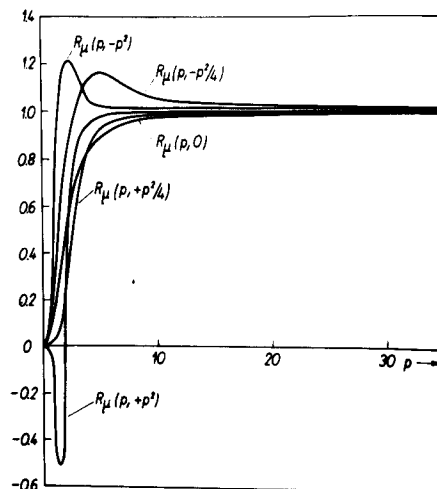


Fig. 3. Shape of the reorientation function (6) for dipolar non-polarizable macromolecules ($q = 0$) and ones having positive and negative anisotropy of polarizability, respectively.

the field, but with increasing field strengths the induced dipole takes the overhand, thus reorienting the macromolecule into a position with μ perpendicular and the shorter polarizability axes parallel to the field. This change of tendency leads first to an increase and then to a decrease in positive values of $R_\alpha(p, -q)$ followed by an inversion of sign at some well-defined value of q/p^2 .

Thus, at $p \rightarrow \infty$ and $q \rightarrow \infty$, $R_\alpha(p, +q)$ tends to 1 and $R_\alpha(p, -q)$ to $-1/2$, so at saturation we again have eqs. (3a) and (3b). The other function $R_\mu(p, \pm q)$ tends to 1 at $p \rightarrow \infty$ and $q \rightarrow \infty$ in either case, so at complete saturation the dipolar part of (4) is always negative and field-independent. From Graph 3, the functions $R_\mu(p, \pm q)$ are seen to be always positive for either kind of macromolecules, except at $p = 2$, $q = 1$, where $R_\mu(p, +q)$ for the prolate case becomes 0 and then, at $q > p^2/4$, inverts its sign and remains negative.

For weak reorientation, eqs. (5) and (6) can be written, with sufficient accuracy, as:

$$R_\alpha(p, \pm q) = (p^2 \pm 2q)/5; \quad (5a)$$

$$R_\mu(p, \pm q) = (p^2 \mp 4q)/5, \quad (6a)$$

yielding with eqs. (3) and (4) a total variation $\delta\epsilon_\alpha + \delta\epsilon_\mu$ quadratic in the field strength as given by the wellknown Langevin-Debye formula [1].

Recently, Parry Jones et al. [5] made the first measurements of complete dielectric saturation in solutions of poly- γ -benzyl-L-glutamate (μ as high as 2700 debyes [3]) in dioxane and found a variation $\delta\epsilon$ negative in the whole range of E . Their curve lies between our curves $R_\mu(p, +q)$ for $0 \leq q < p^2/4$ (Graph 3), in good accordance with the values [3] $p = 0.1E$, $q = 10^{-5}E^2$, which yield $q/p^2 \approx 10^{-3}$. Hence, in this case, reorientation of polarizability ellipsoids need not be considered.

The method of measuring $\delta\epsilon$ in this investigation was that of ref. [6]. Total capacitance in the measuring generator circuit at empty liquid condenser was about 55 pF. With this capacitance, the generator operated at about 6.5 MHz. A change of capacitance by 9.24×10^{-4} pF (the last readable amount on the scale of the high-accuracy condenser) entailed a change in frequency by about 24.9 Hz. Hence, $\Delta\nu/\nu \approx 4 \times 10^{-6}$ Hz. The solutions had a conductivity $< 10^{-12}$

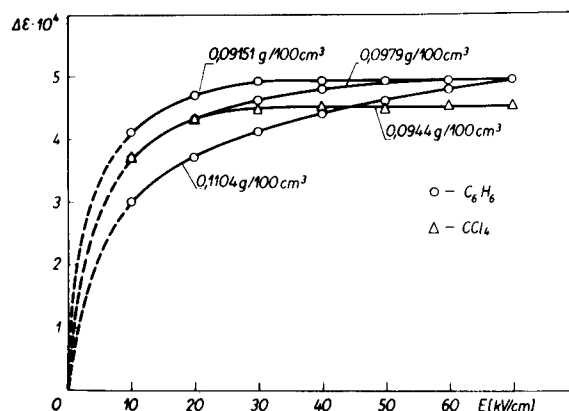


Fig. 4. Positive electric saturation $\delta\epsilon(E)$ as observed in solutions of polystyrene in C_6H_6 and in CCl_4 .

$\Omega^{-1} \text{ cm}^{-1}$. Measurements were made at $20 \pm 0.5^\circ\text{C}$. The variations $\delta\epsilon(E)$ measured in solutions of (isotactic) polystyrene in benzene and carbon tetrachloride are plotted in fig. 4. A shape of $\delta\epsilon(E)$ similar to that for polystyrene in CCl_4 was found for Tween 80 in C_6H_6 (at a concentration of 0.0864 g/100 cm^3). Positive variations $\delta\epsilon(E)$ were found also in atactic polymethacrylate methyl in benzene. In all cases, a positive saturation effect was observed which, in accordance with eqs. (3) and (4) and the reorientation functions as they run in Graphs 1 - 3, is due essentially to reorientation of the electric dipoles induced in the anisotropic macromolecules.

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