

## COMPLETE DIELECTRIC SATURATION IN DILUTE SOLUTIONS OF ASYMMETRIC MACROMOLECULES

by

B. KASPROWICZ, S. KIELICH AND Z. PRZENICZNY

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**Summary.** A classical theory of complete dielectric saturation in dilute solutions of prolate and oblate macromolecules is proposed, taking into account the reorientation of permanent and induced electric dipoles by an applied DC electric field of arbitrary strength up to field strengths causing, in the limiting case, complete alignment of all the macromolecules in solution. Graphs of electric reorientation saturation functions are plotted for non-dipolar, weakly dipolar, and strongly dipolar macromolecules. It is shown that, depending on the electric and geometrical structure of the microsystems, not only monotonously positive or negative saturation can occur but also new saturation processes which change their sign from positive to negative or inversely as the field increases. The theory is tentatively applied to a qualitative interpretation of experimental results.

### 1. INTRODUCTION

To O'Konski and co-workers [1 - 3] are due the earliest experiments on electric saturation of optical birefringence in polymer solutions. The theory of this phenomenon is based essentially on the Langevin-Debye theory [4 - 6] of electric reorientation of the dipoles and polarizability ellipsoids of the macromolecules in a strong DC electric field.

Complete electric saturation of the change in dielectric permittivity has been observed but recently in solutions of dipolar macromolecules (where saturation was negative [7]) and in solutions of nondipolar and weakly dipolar ones (where saturation was found to be positive in the entire range of variations of the electric field strength [8, 9]). A theory of complete dielectric saturation was put forward already by Booth [10], who applied the Onsager model [11] to dipolar water molecules. Applying the semi-macroscopic Kirkwood [12] - Fröhlich [13] method for dielectrics, Kielich [14] proposed a theory of complete dielectric saturation in dipolar liquids taking into consideration statistical molecular correlations.

In this paper, we shall develop the recently announced [15] theory of complete dielectric saturation in solutions of macromolecules and colloid particles. We assume, fo-

simplicity, the macromolecules as sufficiently rigid, prolate or oblate in shape, and presenting or not presenting a permanent dipole moment. Particular stress will be laid on molecules which are dipolar and, moreover, anisotropically polarizable, since here a strong DC electric field causes a reorientation of the permanent and induced dipoles, leading to the following two cases: (a) If the macromolecules (or colloid particles) are prolate, with dipole moment lying in the direction of maximal electric polarizability, the two reorientation processes (that of reorientation of the permanent dipoles and that of reorientation of the induced ones) enhance one another, making saturation easier; (b) Inversely, if the microsystems are oblate, so that their permanent dipole moment is perpendicular to the direction of maximal polarizability, the two reorientational processes compete, leading to a lesser degree of ordering (field-alignment).

## 2. FUNDAMENTALS OF THE THEORY OF ELECTRIC REORIENTATION

Let us consider a polymer or colloid solution so dilute as to render interactions between the macromolecules or colloid particles negligible. Neither can there be any direct interaction between these macrosystems and the molecules of the solvent, which is assumed as not affecting their properties. Let  $\epsilon_1, \epsilon_2, \epsilon_3$  denote the principal electric permittivities of a microsystem in solution in an isotropic solvent of permittivity  $\epsilon_0$ . The linear electric polarizabilities of the microsystem (macromolecule, colloid particle) are now given as [16, 17]:

$$\alpha_s = \frac{V(\epsilon_s - \epsilon_0)\epsilon_0}{4\pi[\epsilon_0 + (\epsilon_s - \epsilon_0)L_s]} \quad (1)$$

Above,  $s=1, 2, 3$ , and  $V$  is a volume the geometrical shape of which is described by the parameters

$$L_s = \frac{1}{2}r_1 r_2 r_3 \int_0^\infty \frac{dS}{(S+r_s^2)\sqrt{(S+r_1^2)(S+r_2^2)(S+r_3^2)}}; \quad (2)$$

$r_1, r_2, r_3$ , denoting the semi-axes of the dielectric ellipsoid. For the sphere we have  $L_1 = L_2 = L_3 = \frac{1}{3}$ ; for a cylinder with axis directed along the principal 1-axis  $L_1 = 0, L_2 = L_3 = \frac{1}{2}$ ; for a flat circular disc  $L_1 = L_2 = 0, L_3 = 1$ .

We assume the microsystem to possess the permanent electric dipole moment  $\mu$  and to be linearly polarizable. The total electric moment in an externally applied electric field  $\mathbf{E}$  is now:

$$m_i = \mu_i + \alpha_{ij} F_j \quad (3)$$

with  $\alpha_{ij}$  – the tensor of its linear polarizability the principal elements in which are given by (1). The electric field  $\mathbf{F}$  is the field effectively acting on the microsystem in solution; in general, it is not identical with the external field  $\mathbf{E}$  [17].

The potential energy of a microsystem in the external electric field is, to within the second power of the field strength [18]:

$$u(\Omega, \mathbf{E}) = -\mu_i F_i - \frac{1}{2}\alpha_{ij} F_i F_j. \quad (4)$$

On the simplifying assumption that the microsystems are rotation-symmetric about their principal 3-axis along which the dipole moment  $\mu_3$  is directed (we shall define this axis by the unit vector  $\mathbf{k}$ ), we have [19]:

$$\mu_i = \mu_3 k_i, \quad \alpha_{ij} = \alpha \delta_{ij} + (\alpha_3 - \alpha_1)(k_i k_j - \frac{1}{3} \delta_{ij}), \quad (5)$$

$\delta_{ij}$  denoting Kronecker's unit tensor with diagonal elements equalling 1 and non-diagonal elements equalling 0, and  $\alpha = \frac{(\alpha_3 + 2\alpha_1)}{3}$  the mean polarizability.

Let  $\mathbf{e}$  be a unit vector pointing in the direction of the externally applied electric field; with regard to eqs. (5), we can now write (3) and (4) more simply in the form:

$$m_i e_i = \mathbf{m} \cdot \mathbf{e} = \mu_3 \cos \vartheta + \left\{ \alpha + (\alpha_3 - \alpha_1)(\cos^2 \vartheta - \frac{1}{3}) \right\} F, \quad (6)$$

$$u(\Omega, \mathbf{E}) = -\mu_3 F \cos \vartheta - \frac{1}{2} \left\{ \alpha + (\alpha_3 - \alpha_1)(\cos^2 \vartheta - \frac{1}{3}) \right\} F^2; \quad (7)$$

$\vartheta$  is the angle between the symmetry axis of the microsystem and the direction in which the field acts ( $e_i k_i = \mathbf{e} \cdot \mathbf{k} = \cos \vartheta$ ).

In the absence of an electric field, the axes of the microsystems point randomly, and no direction is privileged. When an electric field is applied to the solution, the microsystems undergo orientation by the field. As a result of this reorientational process, and after the system as a whole has attained thermodynamical equilibrium, the symmetry axes of the microsystems are directionally distributed in accordance with a Maxwell-Boltzmann statistical distribution function:

$$f(\Omega, \mathbf{E}) = \frac{\exp \left\{ -\frac{u(\Omega, \mathbf{E})}{kT} \right\}}{\int \exp \left\{ -\frac{u(\Omega, \mathbf{E})}{kT} \right\} d\Omega}, \quad (8)$$

where the integral in the denominator extends over all orientations  $\Omega$  with respect to the field  $\mathbf{E}$ . The differential body angle  $d\Omega = \sin \vartheta d\vartheta d\varphi$ , with  $\varphi$  the azimuth of the symmetry axis.

If, in particular, the potential energy of a microsystem is of the form (7), the distribution function depends explicitly on  $\vartheta$  only, and can be written as follows [20]:

$$f(\vartheta, \mathbf{E}) = \frac{\exp(p \cos \vartheta \pm q \cos^2 \vartheta)}{2\pi \int_0^\pi \exp(p \cos \vartheta \pm q \cos^2 \vartheta) \sin \vartheta d\vartheta} \quad (9)$$

with

$$p = \frac{\mu_3 F}{kT} \quad (10)$$

denoting a dimensionless parameter of reorientation of the permanent electric dipoles  $\mu_3$ , and

$$q = \frac{|\alpha_3 - \alpha_1|}{2kT} F^2 \quad (11)$$

a parameter of reorientation of the induced electric dipoles, whose anisotropy of polarizability is defined as  $|\alpha_3 - \alpha_1|$ .

In the distribution function (9), the upper sign „+” has to be used in the case of prolate (cigar-like) microsystems, whose anisotropy of polarizability is positive:  $\alpha_3 - \alpha_1 > 0$ . This, e. g., is the case of the  $\text{CS}_2$  molecule. The lower sign „-” is for oblate (disc-shaped) microsystems, whose polarizability anisotropy is negative,  $\alpha_3 - \alpha_1 < 0$ , as in the case of the  $\text{C}_6\text{H}_6$  molecule.

With the explicit form of the distribution function (9) known, we are now able to calculate the statistical mean value of the projection of the dipole moment (6) into the field direction, from the well-known definition:

$$\langle \mathbf{m} \cdot \mathbf{e} \rangle_E = \int \mathbf{m} \cdot \mathbf{e} f(\Omega, \mathbf{E}) d\Omega, \quad (12)$$

This leads to the result:

$$\langle \mathbf{m} \cdot \mathbf{e} \rangle_E = \alpha F + \mu_3 \langle \cos \vartheta \rangle_E + (\alpha_3 - \alpha_1) (\langle \cos^2 \vartheta \rangle_E - \frac{1}{3}) F \quad (13)$$

where [20]:

$$\langle \cos^n \vartheta \rangle_E = L_n(p, \pm q) = \frac{\int_0^\pi \cos^n \vartheta \exp(p \cos \vartheta \pm q \cos^2 \vartheta) \sin \vartheta d\vartheta}{\int_0^\pi \exp(p \cos \vartheta \pm q \cos^2 \vartheta) \sin \vartheta d\vartheta}. \quad (14)$$

Above, we have introduced generalized Langevin functions  $L_n$ .

When the mean statistical projection of the electric moment into the direction of the field is known, we can proceed to calculate the electric polarization  $\mathbf{P}$  of the medium as a whole. In the present case (in the absence of correlations), this polarization is of the form:

$$P_E = \rho \langle \mathbf{m} \cdot \mathbf{e} \rangle_E \quad (15)$$

with  $\rho$  – the number density of macromolecules per volume  $V$  of the solution.

On inserting (13) and (14) into eq. (15), we obtain a generalized Debye-Langevin expression for the polarization of a solution of macromolecules or colloid particles in an externally applied electric field of arbitrary field strength:

$$P_E = \rho \{ \alpha F + \mu_3 L_1(p, \pm q) + (\alpha_3 - \alpha_1) [L_2(p, \pm q) - \frac{1}{3}] F \}. \quad (16)$$

### 3. CALCULATION OF COMPLETE DIELECTRIC SATURATION

We define the dielectric permittivity of a medium immersed in an intense electric field, after Debye [5], as follows:

$$\varepsilon(E) = \frac{\partial D}{\partial E} = 1 + 4\pi \frac{\partial P_E}{\partial E}, \quad (17)$$

where  $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$  is the electric induction vector.

In experimental determinations of variations in electric permittivity due to an intense DC electric field  $E$ , these variations are measured by means of another electric field  $E_m$  which, in general, is slowly variable in time. A diagram of the generator used in measuring

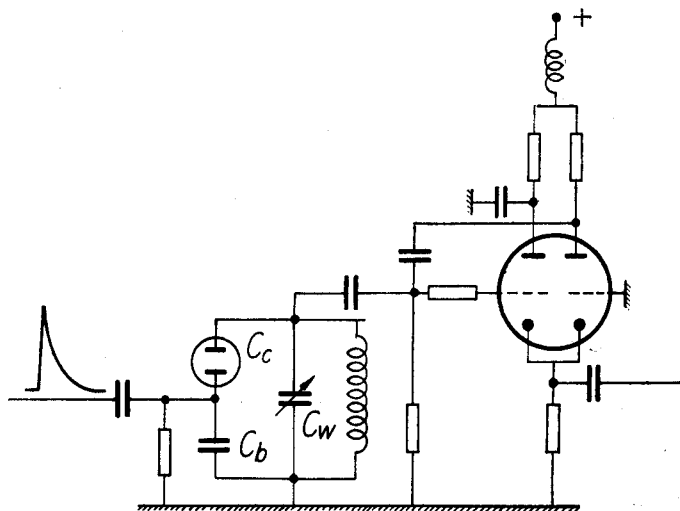


Fig. 1. Block diagram of the generator for measuring the electric permittivity  $\delta\epsilon$  and changes in permittivity  $\epsilon_0$  due to a strong DC electric field

$C$  - capacitance over which the pulse voltage is applied to the liquid condenser  $C_c$ ;  
 $C_b$  - 0,25  $\mu\text{F}$  blocking condenser;  $C_w$  - standard condenser for measuring changes in electric permittivity

the dielectric permittivity  $\epsilon_0$  and its variations  $\delta\epsilon$  in a strong DC electric field  $E$  is shown in Fig. 1. Here, we are interested in the difference between the permittivity  $\epsilon(E)$  measured in the presence of the external field and the dielectric constant  $\epsilon(0)$  measured in its absence:

$$\delta\epsilon(E) = \epsilon(E) - \epsilon(0) = \left( \frac{\partial D}{\partial E_m} \right)_{E_m=0} - \left( \frac{\partial D}{\partial E_m} \right)_{E_m=0} \quad (18)$$

The electric polarization measured with the weak field  $E_m$  alone is a linear function of the field strength  $E_m$ . By eq. (16), it is given by the well-known formula of Debye [5]:

$$P_{E_m} = \rho \left( \alpha + \frac{\mu_3^2}{3kT} \right) F_m, \quad (19)$$

since with regard to (14) we have, in a first approximation:

$$L_1(p, \pm q) = \frac{p}{3} = \frac{\mu_3 F_m}{3kT}, \quad L_2(p, \pm q) = \frac{1}{3}, \quad (20)$$

with  $F_m$  - the internal field existing in the presence of the measuring field  $E_m$  alone; ta-

king into account only the contribution due to the solvent, we can approximate  $F_m$  by resorting to Lorentz's model:

$$F_m = \frac{\epsilon_0 + 2}{3} E_m. \quad (21)$$

By eqs. (17) and (18) we obtain, as done previously [18], the following expression for the differential variation in electric permittivity (assuming that the measuring field  $E_m$  and the strong polarizing field  $E$  both act in the same direction):

$$\delta\epsilon(E) = 4\pi Q(\epsilon) \left\{ \left( \frac{\partial P_E}{\partial F_m} \right)_{E_m=0} - \left( \frac{\partial P_E}{\partial F_m} \right)_{E_m=0}^{E=0} \right\}. \quad (22)$$

In eq. (22), we have introduced the quantity

$$Q(\epsilon) = \left\{ 1 - 4\pi \frac{\partial}{\partial \epsilon} \left( \frac{\partial P_E}{\partial E_m} \right)_{E_m=0} \right\}^{-1} \left( \frac{\partial F_m}{\partial E_m} \right)_{E=0}. \quad (23)$$

With regard to the expression (16) for the total electric polarisation, we can re-write eq. (22) in the form:

$$\delta\epsilon(E) = \frac{4\pi}{3} Q(\epsilon) \left\{ \pm 2 |\alpha_3 - \alpha_1| R_\alpha(p, \pm q) - \frac{\mu_3^2}{kT} R_\mu(p, \pm q) \right\}, \quad (24)$$

where we have introduced the reorientation function for macromolecules in the phenomenon of dielectric saturation:

$$R_\alpha(p, \pm q) = \frac{1}{2} \left\{ \frac{\partial}{\partial F_m} [3L_2(p^*, \pm q^*) - 1] (F_m + F) \right\}_{E_m=0}, \quad (25)$$

$$R_\mu(p, \pm q) = 1 - 3 \frac{kT}{\mu_3} \left\{ \frac{\partial}{\partial F_m} L_1(p^*, \pm q^*) \right\}_{E_m=0}. \quad (26)$$

Above, the reorientation parameters  $p^*$  and  $q^*$  (with asterisks) depend simultaneously on the measuring field  $F_m$  and the polarizing field  $F$  (the total internal field acting on a microsystem is  $F_m + F$ ).

Taking the derivative of the generalized Langevin functions (14) with respect to the measuring field (keeping in mind that the reorientation parameters depend on the total internal field  $F_m + F$ ), we obtain:

$$\left\{ \frac{\partial L_n(p^*, \pm q^*)}{\partial E_m} \right\}_{E_m=0} = \{ L_{n+1}(p, \pm q) - L_n(p, \pm q) L_1(p, \pm q) \} \left( \frac{\partial p^*}{\partial E_m} \right)_{E_m=0} \pm \{ L_{n+2}(p, \pm q) - L_n(p, \pm q) L_2(p, \pm q) \} \left( \frac{\partial q^*}{\partial E_m} \right)_{E_m=0} \quad (27)$$

as a result of which the reorientation functions (25) and (26) reduce to the form given in Refs [9, 15]:

$$R_\alpha(p, \pm q) = \Phi(p, \pm q) + \frac{3}{21} p \{ L_3(p, \pm q) - L_1(p, \pm q) L_2(p, \pm q) \} \pm$$

$$\pm 3q \{L_4(p, \pm q) - L_2^2(p, \pm q)\}, \quad (28)$$

$$R_\mu(p, \pm q) = 3L_1^2(p, \pm q) - 2\Phi(p, \pm q) \pm$$

$$\mp 6 \left( \frac{q}{p} \right) \{L_3(p, \pm q) - L_1(p, \pm q) L_2(p, \pm q)\}. \quad (29)$$

These expressions contain the reorientation function for macromolecules introduced by O'Konski *et al.* [1] for describing electric saturation of Kerr's effect:

$$\frac{n_{\parallel} - n_{\perp}}{n} = \pm 2\pi\rho |\alpha_3^{\omega} - \alpha_1^{\omega}| \Phi(p, \pm q); \quad (30)$$

$n_{\parallel}$  and  $n_{\perp}$  denoting the light refractive indices for oscillations respectively parallel and perpendicular to the direction of the field  $\mathbf{E}$ , and  $n$  – the refractive index in the absence of an electric field;  $\alpha_1^{\omega}$  and  $\alpha_3^{\omega}$  are principal optical polarizabilities of the macromolecule for the light oscillation frequency  $\omega$ . By using the substitution [1]  $t = \sqrt{q} \cos \vartheta \pm \frac{p}{2\sqrt{q}}$  for  $q \neq 0$ , we reduce the generalized Langevin functions (14) to a form well-adapted to direct numerical computations [20]:

$$L_n(p, \pm q) = \frac{\exp \left\{ \mp \left[ \left( \frac{p^2}{4q} \right) + q \right] \right\}}{2q^{n/2} I(p, \pm q)} \int_{-\sqrt{q} \pm \frac{p}{2\sqrt{q}}}^{\sqrt{q} \pm \frac{p}{2\sqrt{q}}} \left( t \mp \frac{p}{2\sqrt{q}} \right)^n \exp(\pm t^2) dt \quad (31)$$

where we have introduced the integrals:

$$I(p, \pm q) = \frac{1}{2} \exp \left\{ \mp \left[ \left( \frac{p^2}{4q} \right) + q \right] \right\} \int_{-\sqrt{q} \pm \frac{p}{2\sqrt{q}}}^{\sqrt{q} \pm \frac{p}{2\sqrt{q}}} \exp(\pm t^2) dt, \quad (32)$$

which reduce to tabulated integrals. In fact, the integrals  $\int_0^x \exp(t^2) dt$  up to  $x=10$  are to be found in tabulated form in Ref. [21], whereas the integrals  $\int_0^x \exp(-t^2) dt = \left( \frac{\sqrt{\pi}}{2} \right) \operatorname{erf} x$  are expressed directly in terms of the tabulated error function  $\operatorname{erf} x$ .

With regard to eq. (31), we obtain explicitly for  $n=1, 2, 3, 4$  the following Langevin functions [15]:

$$L_1(p, \pm q) = \mp \frac{p}{2q} \pm \frac{e^p - e^{-p}}{4q^{1/2} I(p, \pm q)},$$

$$L_2(p, \pm q) = \frac{p^2 \mp 2q}{4q^2} \mp \frac{e^p + e^{-p}}{4q^{1/2} I(p, \pm q)} - \frac{p(e^p - e^{-p})}{8q^{3/2} I(p, \pm q)},$$

$$\begin{aligned}
 L_3(p, \pm q) &= \mp \frac{p(p^2 \mp 6q)}{8q^3} - \frac{p(e^p + e^{-p})}{8q^{3/2}I(p, \pm q)} \pm \frac{(p^2 \mp 4q + 4q^2)(e^p - e^{-p})}{16q^{5/2}I(p, \pm q)}, \\
 L_4(p, \pm q) &= \frac{p^4 + 12q(q \mp p^2)}{16q^4} \pm \frac{(p^2 \mp 6q + 4q^2)(e^p + e^{-p})}{16q^{5/2}I(p, \pm q)} - \\
 &\quad - \frac{p(p^2 + 4q^2 \mp 10q)(e^p - e^{-p})}{32q^{7/2}I(p, \pm q)}.
 \end{aligned} \tag{33}$$

#### 4. APPLICATIONS TO PARTICULAR CASES

When the macromolecules in solution have dimensions comparable to the dimensions of the molecules of the solvent, the field  $F$  really acting on the macromolecules is in general different from the mean macroscopic field  $E$  in the medium; in an approximation, the field  $F$  can be assumed in the form (21). By (19), we now have:

$$\left( \frac{\partial P_{E_m}}{\partial E_m} \right)_{E_m=0} = \rho \left( \alpha + \frac{\mu_3^2}{3kT} \right) \left( \frac{\varepsilon_0 + 2}{3} \right),$$

whence, by eq. (17),

$$4\pi \frac{\partial}{\partial \varepsilon} \left( \frac{\partial P_E}{\partial E_m} \right)_{E_m=0} = \frac{4\pi}{3} \rho \left( \alpha + \frac{\mu_3^2}{3kT} \right) = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2},$$

which, when inserted into eq. (23), leads to the following value of the macroscopic parameter:

$$Q(\varepsilon) = \left( \frac{\varepsilon_0 + 2}{3} \right)^2. \tag{34}$$

When the dimensions of the macromolecules in solution exceed those of the solvent molecules, the field really acting on a macromolecule does not practically differ from the mean macroscopic field i.e. we have  $F=E$ , and the parameter (23) reduces to unity:

$$Q(\varepsilon) = 1. \tag{35}$$

##### 4.1. WEAKLY DIPOLAR MACROMOLECULES

In the case when the macromolecules in solution do not possess permanent electric dipoles, or when their permanent dipoles are small, but when these macromolecules are anisotropically polarisable, it is convenient to write the expression (24) as follows:

$$\delta \varepsilon(E) = \pm \frac{8\pi}{3} \rho Q(\varepsilon) |\alpha_3 - \alpha_1| S_\alpha(p, \pm q). \tag{36}$$

Eq. (36) contains the function of reorientation saturation of induced dipoles

$$S_\alpha(p, \pm q) = R_\alpha(p, \pm q) \mp \left( \frac{p^2}{4q} \right) R_\mu(p, \pm q) \tag{37}$$

affected by the presence of weak permanent electric dipoles, as implied by the parameter  $p$ .



In particular, when the macromolecules have no permanent dipoles ( $p=0$ ), we have  $S_\alpha(\pm q) = R_\alpha(\pm q)$  and eq. (36) becomes [9]:

$$\delta\epsilon(E) = \pm \frac{8\pi}{3} \rho Q(\epsilon) |\alpha_3 - \alpha_1| S_\alpha(\pm q), \quad (38)$$

where the reorientation saturation function for non-dipolar macromolecules is (on putting  $p=0$  in eq. (28)):

$$S_\alpha(\pm q) = \Phi(\pm q) \pm 3q \{L_4(\pm q) - L_2^2(\pm q)\}, \quad (39)$$

the Kerr saturation function being:

$$\Phi(\pm q) = \frac{1}{2} \{3L_2(\pm q) - 1\}. \quad (40)$$

Graphs of the functions (39) and (40) vs. the parameter  $q$  are plotted in Fig. 2.

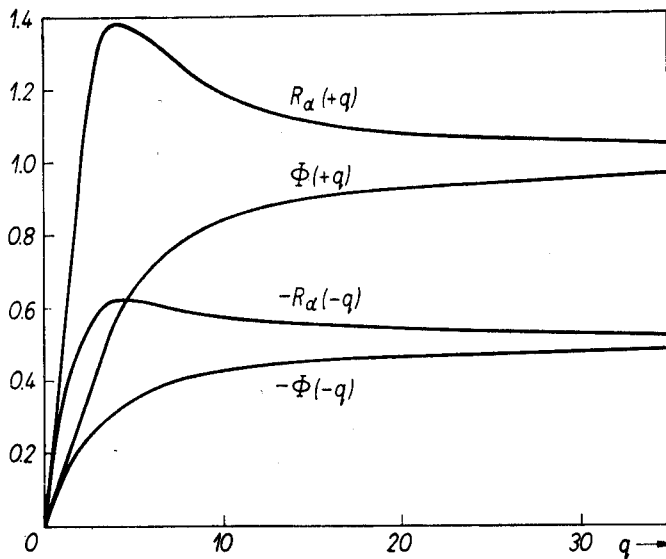


Fig. 2. Graphs of the electric reorientation saturation function  $R_\alpha(\pm q)$  for non-dipolar liquids, and of the function  $\Phi(\pm q)$  describing electric saturation of Kerr's effect

The Langevin functions of even order now appearing in eqs. (39) and (40) (they result from eqs. (32) and (33) for  $p=0$ ) are of the form [22]:

$$L_2(\pm q) = \mp \frac{1}{2q} \pm \frac{1}{2q^{1/2} I(\pm q)}, \quad (41)$$

$$L_4(\pm q) = \frac{3}{4q^2} \pm \frac{2q \mp 3}{4q^{3/2} I(\pm q)},$$

where

$$I(\pm q) = \exp(\mp q) \int_0^{\sqrt{q}} \exp(\pm t^2) dt. \quad (42)$$

a) In the case of weak reorientation, when  $q < 1$  (corresponding to a weak field or low polarizability anisotropy or high temperature), the Langevin functions (41) can be expanded in a series in powers of  $q$  yielding with good accuracy [6, 20]:

$$L_2(\pm q) = \frac{1}{3} \pm \frac{4q}{45} + \frac{8q^2}{945} \mp \frac{16q^3}{14175} + \dots,$$

$$L_4(\pm q) = \frac{1}{5} \pm \frac{8q}{105} + \frac{16q^2}{1575} \mp \frac{32q^3}{51975} + \dots \quad (43)$$

Consequently, the reorientation functions (39) and (40) now become:

$$S_\alpha(\pm q) = \pm \frac{2q}{5} + \frac{4q^2}{63} \mp \frac{8q^3}{675} + \dots \quad (44)$$

$$\Phi(\pm q) = \pm \frac{2q}{15} + \frac{4q^2}{315} \mp \frac{8q^3}{4725} + \dots \quad (45)$$

b) In the case of very strong reorientation, at  $q \geq 10$  (corresponding to an intense field or considerable anisotropy of polarizability or low temperature), the Langevin functions can be replaced by the following expressions [23]:

for positive anisotropy

$$L_2(+q) = 1 - \frac{1}{q} + 0\left(\frac{1}{q^2}\right), \quad (46)$$

$$L_4(+q) = 1 - \frac{2}{q} + 0\left(\frac{1}{q^2}\right),$$

for negative anisotropy

$$L_2(-q) = \frac{1}{2q} + 0\left(\frac{1}{q^2}\right), \quad (47)$$

$$L_4(-q) = \frac{3}{4q^2} + 0\left(\frac{1}{q^2}\right).$$

In the case of complete electric saturation, with all the macromolecules aligned along the electric field vector, i.e. when  $q \rightarrow \infty$ , the Langevin functions (46) for prolate microsystems tend to unity and so do the reorientation functions (39) and (40):

$$S_\alpha(+q \rightarrow \infty) = \Phi(+q \rightarrow \infty) = 1, \quad (48)$$

and eq. (38) now yields:

$$\delta\varepsilon(+\infty) = \frac{8\pi}{3} \rho Q(\varepsilon) |\alpha_3 - \alpha_1|. \quad (49)$$

In the case of complete saturation (alignment) of oblate macromolecules, the Langevin functions (47) vanish at  $q \rightarrow \infty$ , and one has:

$$S_\alpha(-q \rightarrow \infty) = \Phi(-q \rightarrow \infty) = -\frac{1}{2}; \quad (50)$$

accordingly, dielectric saturation is now given as:

$$\delta\varepsilon(-\infty) = \frac{4\pi}{3} \rho Q(\varepsilon) |\alpha_3 - \alpha_1|. \quad (51)$$

Thus, in the case of non-dipolar microsystems, complete saturation of electric permittivity is always positive, and we have the relation:

$$\delta\varepsilon(+\infty) = 2\delta\varepsilon(-\infty), \quad (52)$$

i.e. complete dielectric saturation of prolate microsystems is double that of oblate ones with negative anisotropy of polarizability.

For the case of anisotropically polarizable microsystems presenting moreover a permanent electric dipole moment, reorientation is quite generally given by the function (37), graphs of which are plotted vs.  $q$ , for various values of the parameter  $p$ , in Fig. 3.

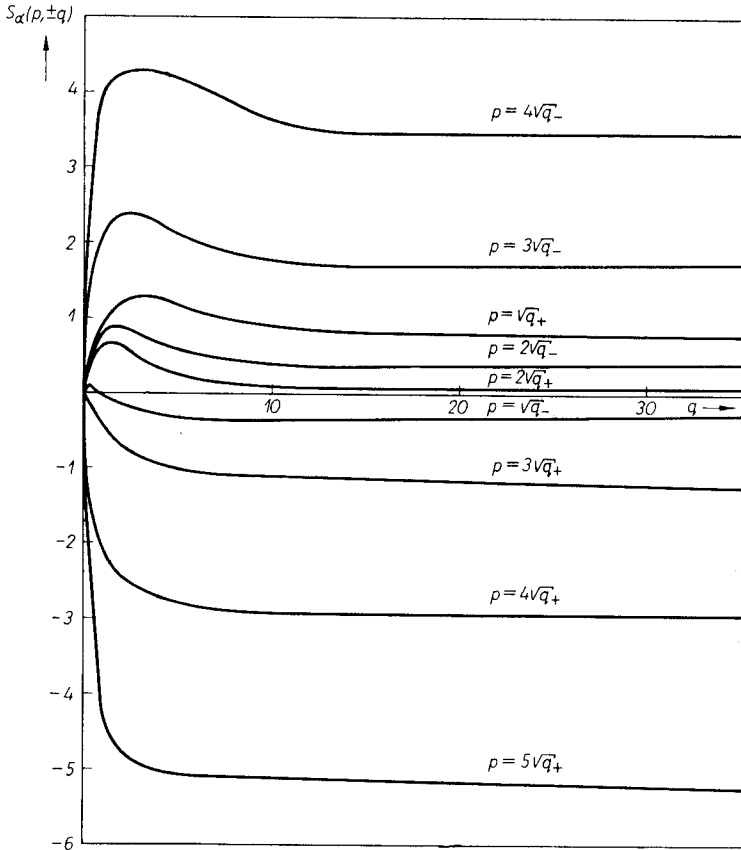


Fig. 3. Graphs visualizing the changes in shape of the function  $S_\alpha(p, \pm q)$  due to superposition of permanent dipole reorientation (parameter  $p$ ) on the reorientation of positively anisotropic induced dipoles ( $p, +q$ ) and negatively anisotropic induced dipoles ( $p, -q$ )

## 4.2. STRONGLY DIPOLAR MACROMOLECULES

For strongly dipolar anisotropically polarizable macromolecules, we have by eq. (24):

$$\delta\varepsilon(E) = -\frac{4\pi\mu_3^2}{3kT_1}\rho Q(\varepsilon)S_\mu(p, \pm q), \quad (53)$$

where the reorientation saturation function for dipolar macromolecules is:

$$S_\mu(p, \pm q) = R_\mu(p, \pm q) \mp 4\frac{q^1}{p^2}R_x(p, \pm q). \quad (54)$$

If, in particular, the macromolecules are strongly dipolar whereas their polarizability anisotropy is quite negligible or vanishing ( $q \ll p^2$ ), one can write eq. (53) in the form:

$$\delta\varepsilon(E) = -\frac{4\pi\mu_3^2}{3kT_1}\rho Q(\varepsilon)S_\mu(p) \quad (55)$$

the reorientation function (54) reducing to:

$$S_\mu(p) \equiv R_\mu(p) = 3L_1^2(p) - 2\Phi(p), \quad (56)$$

with:

$$\Phi(p) = \frac{1}{2}\{3L_2(p) - 1\}. \quad (57)$$

The Langevin functions occurring here are of the form [6, 14]

$$L_1(p) \equiv L(p) = \coth p - \frac{1}{p}, \quad L_2(p) = 1 - 2\frac{L(p)}{p}. \quad (58)$$

For weak dipolar reorientation ( $p < 1$ ), we have the expansions:

$$L_1(p) = \frac{p}{3} - \frac{p^3}{45} + \frac{2p^5}{945} - \frac{p^7}{4725} \dots \quad (59)$$

$$L_2(p) = \frac{1}{3} + \frac{2p^2}{45} - \frac{4p^4}{945} + \frac{2p^6}{4725} \dots$$

with regard to (59) the reorientation functions (56) become:

$$S_\mu(p) = \frac{p^2}{5} - \frac{2p^4}{63} + \frac{p^6}{225} - \dots \quad (60)$$

For strong reorientation ( $p \geq 10$ ), we have the following expressions for the functions (58):

$$L_1(p) = 1 - \frac{1}{p}, \quad L_2 = 1 - \frac{2}{p} + \frac{2}{p^2} \quad (61)$$

and the function (56) reduces simply to:

$$S_\mu(p) = 1 - \frac{3}{p^2}. \quad (62)$$

Electric saturation of dipolar reorientation ( $p \rightarrow \infty$ ) is described by the function:

$$S_\mu(p \rightarrow \infty) = 1, \quad (62a)$$

and, with regard to (55), one can express electric saturation of the change in electric permittivity of strongly dipolar liquids in the form:

$$\delta\varepsilon(\infty) = -\frac{4\pi\mu_3^2}{3kT} \rho Q(\varepsilon) \quad (63)$$

which, as one sees, is negative and independent of the DC electric field strength.

For the case of dipolar, anisotropically polarizable macromolecules which exhibit weak reorientation in a DC electric field, the Langevin functions (14) take the form [24]:

$$\begin{aligned} L_1(p, \pm q) &= \frac{p}{3} - \frac{p^3}{45} \pm \frac{4pq}{45} \\ L_2(p, \pm q) &= \frac{1}{3} + \frac{2p^2}{45} \pm \frac{4q}{45} \\ L_3(p, \pm q) &= \frac{p}{5} - \frac{p^3}{105} \pm \frac{8pq}{105} \\ L_4(p, \pm q) &= \frac{1}{5} + \frac{4p^2}{105} \pm \frac{8q}{105} \end{aligned} \quad (64)$$

so that now the functions (28) and (29) become:

$$R_\alpha(p, \pm q) = \frac{p^2}{5} \pm \frac{2q}{5} \quad (65)$$

$$R_\mu(p, \pm q) = \frac{p^2}{5} \mp \frac{4q}{5}. \quad (66)$$

On inserting (65) and (66) into eq. (54), one obtains for moderate reorientation:

$$S_\mu(p, \pm q) = \frac{\left( p^2 \mp 8q - \frac{8q^2}{p^2} \right)}{5}. \quad (67)$$

On taking into consideration the explicit form of the reorientation parameters of permanent and induced electric dipoles (10) and (11), one obtains with regard to (53) and (67) the following expression for the quadratic change in electric permittivity:

$$\delta\varepsilon(E) = \frac{4\pi\rho}{15kT} Q(\varepsilon) \left\{ 2|\alpha_3 - \alpha_1|^2 \pm \frac{4|\alpha_3 - \alpha_1|\mu_3^2}{kT} - \frac{\mu_3^4}{k^2T^2} \right\} F^2, \quad (68)$$

which, on the assumption of the Lorentz model (21), goes over with regard to (34) into the well-known Langevin [4] – Debye [5] – Herweg [25] formula:

$$\delta\varepsilon(E) = \frac{4\pi\rho}{15kT} \left\{ 2|\alpha_3 - \alpha_1|^2 \pm 4|\alpha_3 - \alpha_1| \frac{\mu_3^2}{kT} - \frac{\mu_3^4}{k^2T^2} \right\} \left( \frac{\varepsilon_0 + 2}{3} \right)^4 E^2. \quad (69)$$

Reorientation of strongly dipolar anisotropically polarizable macromolecules is quite generally described by the saturation function (54), graphs of which are shown in Fig. 4.

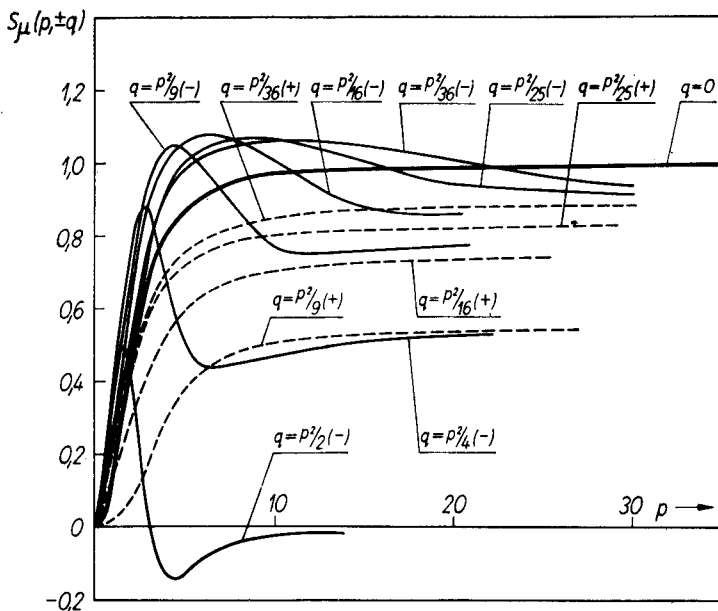


Fig. 4a. Graphs of the electric reorientation saturation function  $S_{\mu}(p, \pm q)$  for dipolar liquids

The bold-face type curve ( $q=0$ ) describes the electric saturation due only to reorientation of permanent electric dipoles. The dashed type curves describe superposition of the reorientations of permanent and induced dipoles for the case of prolate (cigar-like) macro-molecules (positive electric anisotropy); the continuous thin type curves describe this superposition for the case of oblate (disc-shaped) macro-molecules (negative electric anisotropy)

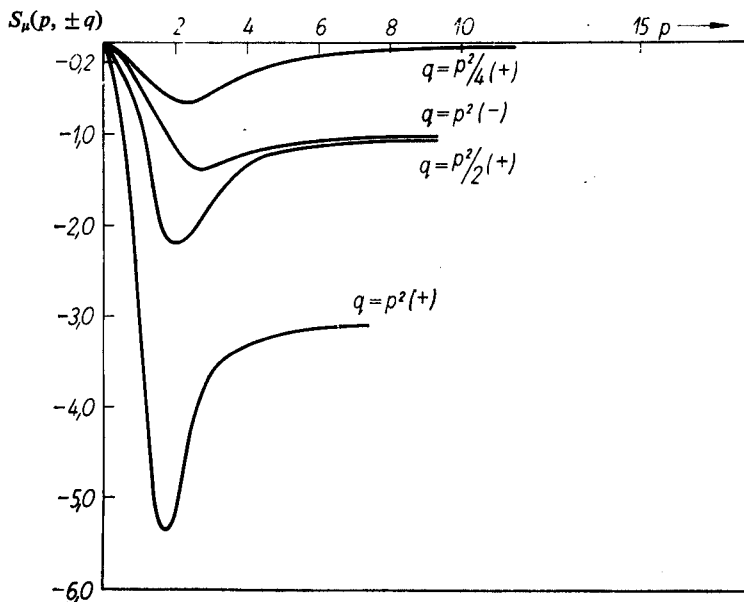


Fig. 4b. Graph of the function  $S_{\mu}(p, \pm q)$  exhibiting an anomalously steep increase in dielectric saturation

## 5. DISCUSSION AND CONCLUSIONS

Fig. 2 shows graphs of the function  $S_\alpha(\pm q)$  describing electric saturation of the change in electric permittivity of solutions of non-dipolar macromolecules as compared with the function  $\Phi(\pm q)$  of electric saturation of Kerr's effect. Whereas in the region of moderate reorientation (for values of  $q$  between 1 and 10) the two functions lie wide apart, they become identical in shape and value for very small values of  $q$  (i.e.  $q \ll 1$ ) and resemble one another in the region of very strong reorientation  $q \approx 10$ . Now, why do  $S_\alpha$  and  $\Phi$  differ in shape in function of  $q$ ? In Kerr's effect, the quantity subject to measurement by means of the light beam is, in fact, the change in refractive index due to reorientation in the strong DC electric field alone, but not due to reorientation in the oscillating electric field of the measuring light wave, whose intensity is very weak. (One can, of course, measure optical reorientation in the so-called „optical Kerr effect” induced by an intense laser beam [26, 27]). On the other hand, when measuring the changes in electric permittivity, what we measure is the reorientation of macromolecules in both the strong polarizing DC electric field and the weak measuring field, provided the time-variations of the latter are sufficiently slow to allow the macromolecules to align themselves (the oscillation frequency of the measuring field has to lie below the value of Debye dipole dispersion [5]). In our measurements, the liquid condenser  $C_c$  was in the resonance circuit of a measuring generator able to produce oscillations between 2 and 8 MHz, according to the total capacitance in the resonance circuit [8].

Let us still draw attention to the following: Suppose we had calculated, instead of the differential change in electric permittivity defined by eq. (18), a difference-variation [28, 29] defined as:

$$\Delta\varepsilon(E) = \frac{D}{E} - \left( \frac{D}{E} \right)_{E=0} = \varepsilon(E) - \varepsilon(0) \quad (70)$$

i.e. defined as the difference between the dielectric constant in a strong DC field  $\varepsilon(E)$  and in the absence of a field (at  $E=0$ ). The definition (70) corresponds to the case of a single strong field  $E$ ; we would have obtained, in place of eqs. (36) and (53):

$$\Delta\varepsilon(E) = \pm \frac{8\pi}{3} \rho \left( \frac{\varepsilon_0 + 2}{3} \right)^2 |\alpha_3 - \alpha_1| G_\alpha(p, \pm q), \quad (71)$$

$$\Delta\varepsilon(E) = - \frac{4\pi\mu_3^2}{3kT} \rho \left( \frac{\varepsilon_0 + 2}{3} \right)^2 G_\mu(p, \pm q) \quad (72)$$

where the reorientation saturation functions are now of the form:

$$G_\alpha(p, \pm q) = \Phi(p, \pm q) \pm \frac{p}{4q} \{3L_1(p, \pm q) - p\}, \quad (73)$$

$$G_\mu(p, \pm q) = 1 - \frac{3}{p} L_1(p, \pm q) \mp 4 \frac{q}{p^2} \Phi(p, \pm q), \quad (74)$$

and are consequently seen to differ from the previous functions (37) and (54). Graphs of the functions (73) and (74) are plotted in Figs 5 and 6.

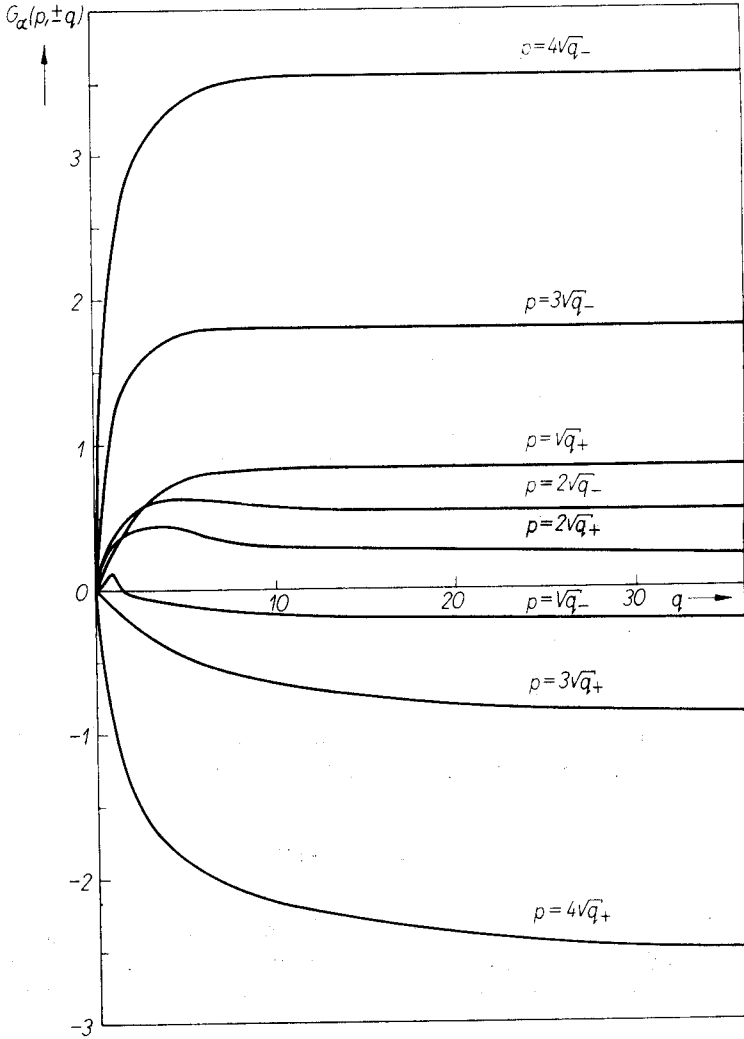


Fig. 5. Graphs of the function  $G_\alpha(p, \pm q)$  versus  $q$ , for some fixed values of the parameter

Restricting ourselves in the case of weak reorientation to a first approximation defining quadratic variations, we obtain the following relations:

$$S_\alpha(p, \pm q) = 3G_\alpha(p, \pm q) = \frac{\left( \pm 2q + 2p^2 - \frac{p^4}{4q} \right)}{5}, \quad (75)$$

$$S_\mu(p, \pm q) = 3G_\mu(p, \pm q) = \frac{\left( p^2 \mp 8q - \frac{8q^2}{p^2} \right)}{5}. \quad (76)$$

Thus, in a first approximation, the quadratic changes in permittivity  $\delta\epsilon(E)$  are 3 times larger than the changes  $\Delta\epsilon(E)$ ; that is to say, we have the relation:

$$\delta\epsilon(E) = 3\Delta\epsilon(E). \quad (77)$$



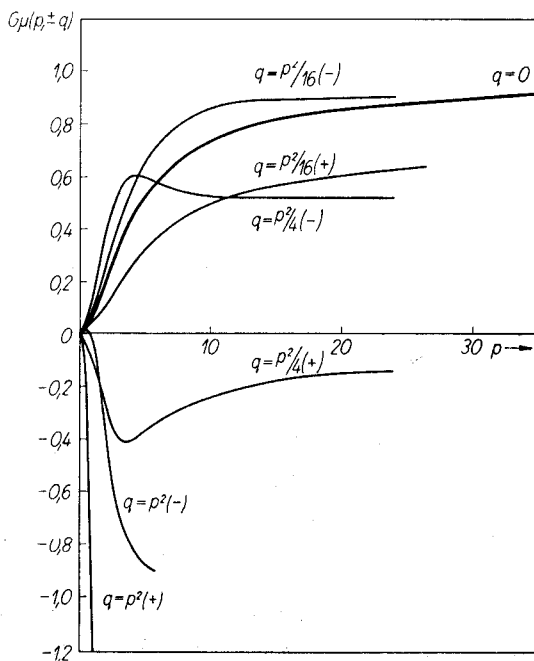


Fig. 6. Graphs of the function  $G_{\mu}(p, \pm q)$  versus  $p$ , for some fixed values of the parameter  $q$ , for prolate and oblate macromolecules

From the graphs of Figs. (2) - (6), one notes that the variations  $\delta\epsilon(E)$  differ considerably from the variations  $\Delta\epsilon(E)$  at moderate values of the DC field strength (i.e. when, in measurements of  $\delta\epsilon$ , reorientation in the measuring field superimposes itself perceptibly on the reorientation due to the strong DC field); however, as the DC fields become stronger and stronger, the discrepancies between  $\delta\epsilon(E)$  and  $\Delta\epsilon(E)$  tend to become smaller and vanish altogether at complete saturation, when  $\delta\epsilon(\infty) = \Delta\epsilon(\infty)$ . In experiment, obviously, one measures the variation  $\delta\epsilon(E)$  defined by eqs. (18) and (24), whereas the quantity  $\Delta\epsilon(E)$  is of purely theoretical significance [29].

From the graphs of Figs. 4 and 6 one sees that in strongly dipolar liquids, where only reorientation of permanent dipoles is apparent (but reorientation of induced dipoles is not), the variations in electric permittivity are negative in the entire range of values of the electric field, including saturation. On the other hand, in liquids the molecules of which are anisotropically polarizable, the variations in electric permittivity can exhibit a change in sign to positive, with a steep numerical increase in  $\delta\epsilon$ , according to the shape of the molecules and the strength of the applied electric field. E.g. the curve  $q=p^2/2$  of Fig. 4a shows that for disc-like molecules  $\delta\epsilon$  is at first negative, then grows, attains a maximal value, falls to zero (at  $p=3$ ), becomes positive, exhibits an extremum (at  $p=4.5$ ), falls to zero, to become negative again at saturation (not all of the curve is plotted here). In Fig. 4b we have curves showing the possibility of initially positive variations  $\delta\epsilon$  (for prolate as well as oblate macromolecules) which can increase more than five-fold in the prolate case (cf. the curve  $q=p^2$ ) and fall to zero at higher field strengths.

Thus, the theoretical curves (Figs 2 - 6) lead to predict new varieties of dielectric saturation (purely negative, purely positive, or involving changes in sign from negative to positive and vice versa) according to the electric and geometrical structure of the microsystems and the applied DC electric field strength. Hitherto, two shapes of complete dielectric saturation have been detected in polymer solutions: Parry Jones, Gregson and Davies [7] performed the first observations of complete negative saturation in solutions of poly- $\gamma$ -benzyl-L-glutamate in dioxane in the entire range of variation of the electric field strength. Since in this case we have [20]  $p=0.1 E$  and  $q=10^{-5} E^2$ , yielding  $q/p^2=10^{-3}$ , the phenomenon is dominated by reorientation of permanent dipoles decisively and electric saturation is described by values of the function  $S_\mu$  contained (Fig. 4a) between  $q=0$  and  $q \leq p^2/36$ .

Przeniczny [8, 9] carried out measurements in other solutions of non-dipolar and weakly dipolar macromolecules finding in all cases positive electric saturation, as shown in Fig. 7. For cases of non-dipolar macromolecules, the shapes of the saturation process are given by the curves  $R_\alpha(\pm q)$  of Fig. 2, whereas for strongly anisotropic macromolecules possessing a permanent dipole moment the saturation is rendered by the curves of Fig. 3.

The full quantitative comparison of the present theory and the experimental results will require the subtraction from  $\delta\epsilon$  of the measured electrostrictive contribution  $\delta\epsilon_{es}$  and electrocaloric contribution  $\delta\epsilon_{ec}$ . The total measured variation is in fact [18]:

$$\delta\epsilon_{mes} = \delta\epsilon + \delta\epsilon_{es} + \delta\epsilon_{ec}. \quad (78)$$

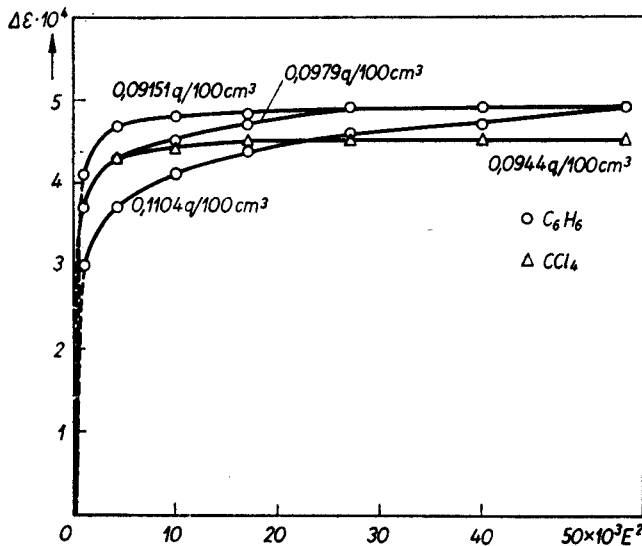


Fig. 7. Changes  $\delta\epsilon$  in electric permittivity measured versus  $E^2$  [e.s.u.], for solutions of isotactic polystyrene in  $C_6H_6$  and in  $CCl_4$ . The respective numerical data for the solutions are given in Table 1

Table 1

Concentrations, densities, electric permittivities and refractive indices of the solutions\*

Solution	Concentration g/100 cm <sup>3</sup>	Density	$\epsilon$	$n_D$	Makers
Polystyrene (isotactic) in C <sub>6</sub> H <sub>6</sub>	0.09151	0.8780	2.25 <sub>0</sub>	1.5004 <sub>6</sub>	Polystyrene (isotactic) Dr. T. Schu- chardt GMBH, Germany  C <sub>6</sub> H <sub>6</sub> ZK „Haj- duki”, Po- land  CCl <sub>4</sub> BDH En- gland
Polystyrene (isotactic) in C <sub>6</sub> H <sub>6</sub>	0.0979	0.8789	2.25 <sub>7</sub>	1.5008 <sub>5</sub>	
Polystyrene (isotactic) in C <sub>6</sub> H <sub>6</sub>	0.1104	0.8783	2.24 <sub>8</sub>	1.5010 <sub>2</sub>	
Polystyrene (isotactic) in CCl <sub>4</sub>	0.0944	1.51180	2.21 <sub>7</sub>	1.4601 <sub>6</sub>	

\* All measurements were performed at temperature (20 ± 0,5)°C.

In general, calculations [30] for molecular liquids show  $\delta\epsilon_{es}$  to be positive and  $\delta\epsilon_{ec}$  negative. In certain cases, the two effects are equal in absolute value and cancel out, but one can come upon cases where they are of the same sign and consequently affect  $\delta\epsilon$  strongly. A quantitative analysis including these effects, together with calculations of the reorientation parameters  $p$  and  $q$ , will be given in a subsequent paper.

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PROF. DR. HAB. STANISŁAW KIELICH  
BOLESŁAWA KASPROWICZ M. SCI.  
ZYGMUNT PRZENICZNY M. SCI.

Institute of Physics  
A. Mickiewicz University, Poznań