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Dielectric, viscous and elastic properties of nematogenic 1-(4-*trans*-propylcyclohexyl)-2-(4-cyanophenyl)ethane

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This paper presents the results of measurements of the static and dynamic electric permittivity, the shear viscosity of a freely flowing sample, and the splay and bend elastic constants for 1-(4-*trans*-propylcyclohexyl)-2-(4-cyanophenyl)ethane ($C_3H_7{-}CyHx{-}CH_2CH_2{-}Ph{-}C{\equiv}N$) (3CCPE). The static permittivity of the isotropic phase shows pre-nematic critical behaviour which is discussed in the frame of the fluid-like model of Mukherjee. From the temperature dependence of the dielectric relaxation time (corresponding to the molecular rotation around the short axis) and the shear viscosity, the strength of the nematic potential and the effective length of the 3CCPE molecule (in the isotropic phase), were estimated. The splay and bend elastic constants were determined from the voltage dependence of the capacitance of a planar nematic cell.

1. Introduction

An anisotropy of the physical properties combined with fluidity make nematic liquid crystals unusual materials from both the basic research and technical points of view. The most important result of this combination is the possibility of controlling the molecular orientation in the whole nematic sample by an external electric or magnetic field of relatively low strength, or by an appropriate preparation of the surfaces of the cell in which the nematic sample is placed. This state of affairs allows one to study the macroscopic properties of a sample in relation to the direction of the principal axes of the nematogenic molecules [1–3].

In the case of static dielectric studies of the nematic phase, the temperature dependence of the principal permittivities, $\varepsilon_{\parallel}(T)$ and $\varepsilon_{\perp}(T)$, leads to very important molecular quantities such as the angle between the dipole moment of the mesogenic molecule and its long axis [4, 5]. In the isotropic phase of strongly polar mesogens, the static permittivity shows a critical behaviour in the vicinity of the isotropic (I) to nematic (N) phase transition. This problem is a subject of intensive studies making important contributions to verification of the theoretical model of the I–N transition [6–11].

The frequency dependence of the complex electric permittivity of nematic liquid crystals allows one to study the dynamics of mesogenic molecules. The rod-like shape of the molecules very often makes the interpretation of the dielectric relaxation spectra $\varepsilon^*_{\parallel}(\omega)$ and $\varepsilon^*_{\perp}(\omega)$ quite clear, as the molecular rotations around the three axes of symmetry (the molecular long and short axes and the director **n**), manifest themselves in the spectra as quite well separated absorption bands. Of course, the analysis of the absorption band corresponding to the molecular rotation around the short axis is the most informative since, together with the viscosity data, the strength of the nematic potential and the effective length of the rotating molecule (in the isotropic phase) can be estimated [3, 12–17].

The applications of nematic liquid crystals result from their special elastic properties. Determination of the elastic constants is based on measurements of the distortion of the director **n** caused by an external electric or magnetic field. In principle, the elastic constants corresponding to the three basic distortions of nematic liquid crystals—splay (K_{11}), twist (K_{22}) and bend (K_{33})—can be obtained from three experiments. In two of them, the electric field induces the director distortion in a planar (K_{11}) or twisted planar (K_{22}) cell and in the third experiment a magnetic field causes the distortion in a

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homeotropic cell (K_{33}). In the case of strong anchoring of the nematic molecules at the cell surfaces, the distortions have a threshold character (Fréedericksz transition). Then, the elastic constants K_{ii} ($i=1, 2, 3$) can be calculated on the basis of the threshold value of the voltage (U_{th}) or magnetic field (B_{th}) provided that the dielectric or magnetic anisotropy of the liquid crystal used is known.

Most studies on the elasticity of nematics concern the splay and bend constants only, since these constants essentially govern such switching characteristics as the threshold voltage or the response time. Many experimental methods have been elaborated for determination of the K_{11} and K_{33} elastic constants. The most widespread are based on optical or capacitance observations of the director distortion in a pre-oriented nematic cell [18–22]. In this paper the elastic constants K_{11} and K_{33} were determined using the capacitance method.

2. Experimental

1-(4-*trans*-Propylcyclohexyl)-2-(4-cyanophenyl)ethane (3CCPE) was synthesized and purified in the Institute of Chemistry, the Military University of Technology, Warsaw. The compound has the following sequence of phase transitions: crystal (Cr) 24°C–nematic (N) 44.2°C–isotropic (I), and is often used as a component of mixtures of practical significance.

The static electric permittivity was measured with a Wayne Kerr 6425 Precision Component Analyzer at a frequency of 10 kHz. The nematic sample, placed between two plane electrodes of the capacitor, was oriented with a magnetic field of about 0.6 T. The distance between the electrodes was 0.5 mm. The dielectric relaxation spectra were recorded with an HP 4194A Impedance/Gain-Phase Analyzer in the frequency range 100 kHz–100 MHz. The measuring capacitor consisted of three plane electrodes: one central ('hot') electrode and two grounded electrodes on each side. An external biasing d.c. electric field was used for ordering the nematic sample. Of course, in such circumstances only the dielectric spectrum $\varepsilon^*_{\parallel}(\omega)$ can be recorded.

The viscosity was measured with a Haake viscometer Rotovisco RV20 with the measuring system CV 100. The system consists of a rotary beaker filled with the substance being studied and a cylindrical sensor of the Mooney–Evart type (ME15), placed in the centre of the beaker. The liquid gap was 0.5 mm.

For the elastic constant measurements, the nematic 3CCPE was placed in a LINKAM cell consisting of two flat ITO-coated glass plates with a spacing of 5 μm. Due to the brushed polyimide treatment of the electrode surfaces, the nematic molecules were oriented in a planar manner with respect to the electrodes. The sinusoidal probe voltage of the HP 4284A Precision LCR-meter, up to 20 V_{rms}, at 1 kHz, was applied and the cell capacitance as a function of the applied voltage was recorded. The voltage step was 20 mV in the vicinity of the Fréedericksz transition and 200 mV for higher voltage.

3. Results and discussion

3.1. *Static permittivities*

The temperature dependences of the static permittivities measured for the nematic and isotropic phases of 3CCPE are presented in figure 1. The values of the dielectric anisotropy in the nematic phase $\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$ were exploited in the elastic constant determinations. Here, we focus on the temperature behaviour of the permittivity measured in the isotropic phase of the compound studied.

As figure 2 shows, in the vicinity of the isotropic to nematic phase transition (T_c), the static permittivity exhibits a singular behaviour which can be interpreted in terms of the critical-like approach, as suggested by Bradshaw and Raynes [23] and Thoen and Menu [24]. Such a pretransitional effect was observed in few strongly polar nematogens with a permanent dipole moment parallel (roughly) to the long axis of the molecule and some swallow-tailed compounds. The data can be described by the formula analogous to that applied to the homogeneous phase of critical solutions [25]:

$$\varepsilon(T)=\varepsilon^*+A(T-T^*)+B(T-T^*)^{1-\alpha} \quad (1)$$

where T^* denotes here the extrapolated (virtual) temperature of the hypothetical continuous phase transition, ε^* is the permittivity extrapolated to the T^*, and α is the critical exponent. The exponent α is explicitly involved

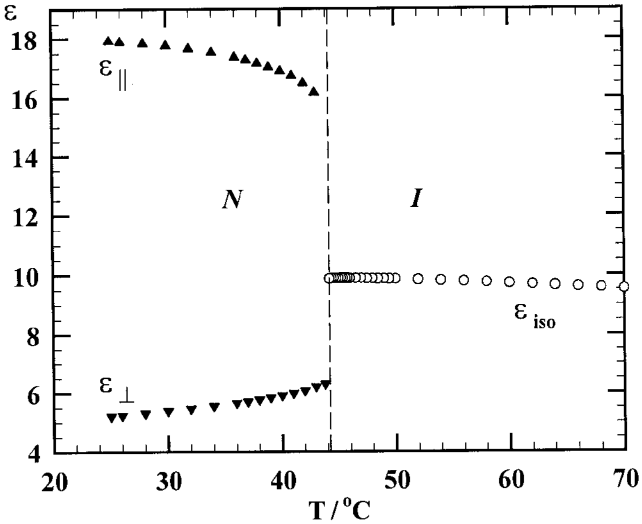

Figure 1. Static electric permittivities measured for the nematic and isotropic phases of 3CCPE.

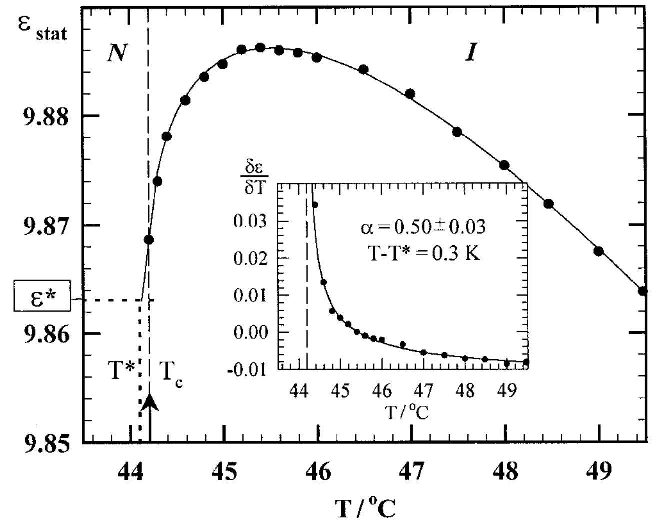

Figure 2. Temperature dependence of the static electric permittivity of 3CCPE in the vicinity of the isotropic to nematic phase transition. The inset shows the temperature derivative of the permittivity. The solid lines present the best fitting of equation (1) to the experimental data.

in the pretransitional singular temperature dependence of the specific heat $C_P(T) \propto (T - T^*)^{-\alpha}$ [26] or density $\rho(T) \propto (T - T^*)^{1-\alpha}$ [27].

The experimental results presented in figure 2 can be quite well reproduced with equation (1) for the following values of the fitting parameters: $\alpha = 0.5$ and $T^* = 43.9°\mathrm{C}$. The value of the critical exponent α agrees well with the theoretical model proposed by Mukherjee *et al.* [6, 7] and is strongly supported by the linear and non-linear dielectric results obtained by Drozd-Rzoska *et al.* [8–11]. In this 'fluid-like' model the nematic clearing point is placed on a branch of a hypothetical coexistence curve and the pre-nematic effects observed in the isotropic phase result from the vicinity of the pseudo-spinodal critical or tri-critical points [8, 28]. The latter seems to be well supported by recent experiments in which the exponent obtained for the nematic order parameter $S(T)$ is $\beta \approx 0.25$, the value also predicted by the model.

3.2. *Dielectric relaxation and viscosity*

Figure 3 presents the dielectric relaxation spectra recorded in the isotropic and nematic phases of 3CCPE. In the latter phase, the permittivity was measured for $\mathbf{E} \parallel \mathbf{n}$. The analysis of the dielectric relaxation spectra of 3CCPE can be carried out in the framework of the molecular model presented in [15]. According to the model, in an oriented nematic sample, the nematogen molecule rotates around the three axes of symmetry: two of them concern the molecule itself (the molecular long and short axes) and the third axis is the director **n**. For a typical nematogen, the electromagnetic energy absorption due to these three modes of rotation can be expected in the frequency region from several MHz to several GHz [16, 17]. In the frequency range studied, one dielectric absorption band strongly dominates both in the isotropic and nematic phases of 3CCPE. The band corresponds to the molecular rotation around the short axis and can be described with the simple Debye formula:

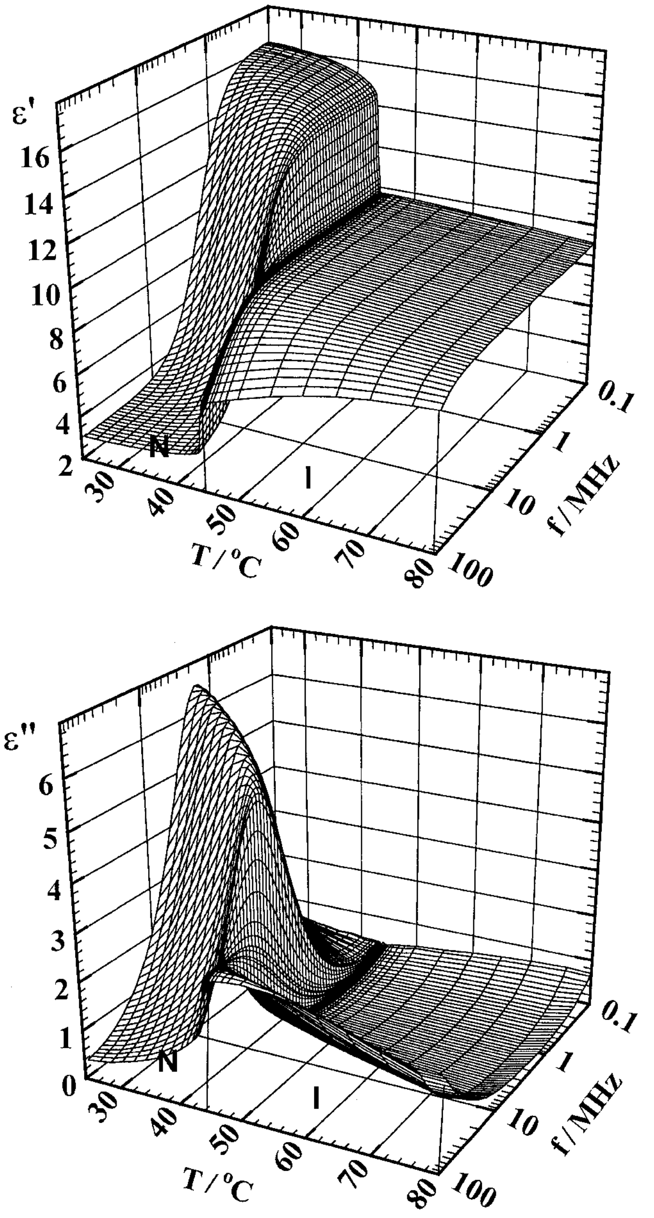

Figure 3. The real (ε') and imaginary (ε'') parts of the electric permittivity of 3CCPE in the isotropic and nematic phases as a function of frequency and temperature. In the nematic phase the permittivity $\varepsilon^*_{\parallel}(\omega, T)$ was measured.

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{A}{1 + i\omega\tau} \qquad (2)$$

where A and τ denote the dielectric strength and the relaxation time, respectively.

The temperature dependences of the relaxation time τ and the dielectric strength A of 3CCPE are presented in figure 4. At the temperature of the phase transition from the isotropic to the nematic phase one observes a strong increase in the values of A and τ. The temperature dependence of the relaxation time τ can be interpreted if the viscosity of the medium is known.

Figure 5 shows the temperature dependence of the viscosity of 3CCPE measured in the isotropic and nematic phases. At the isotropic to nematic transition temperature, a sharp decrease in the viscosity is observed. This is due to the flow alignment effect occurring in the nematic phase [1]. The effect leads to the situation where the macroscopic ordering of the flowing nematic liquid crystal becomes (roughly) parallel to the velocity **v** and perpendicular to the velocity gradient. Then, the nematic viscosity has the smallest possible value [29–31].

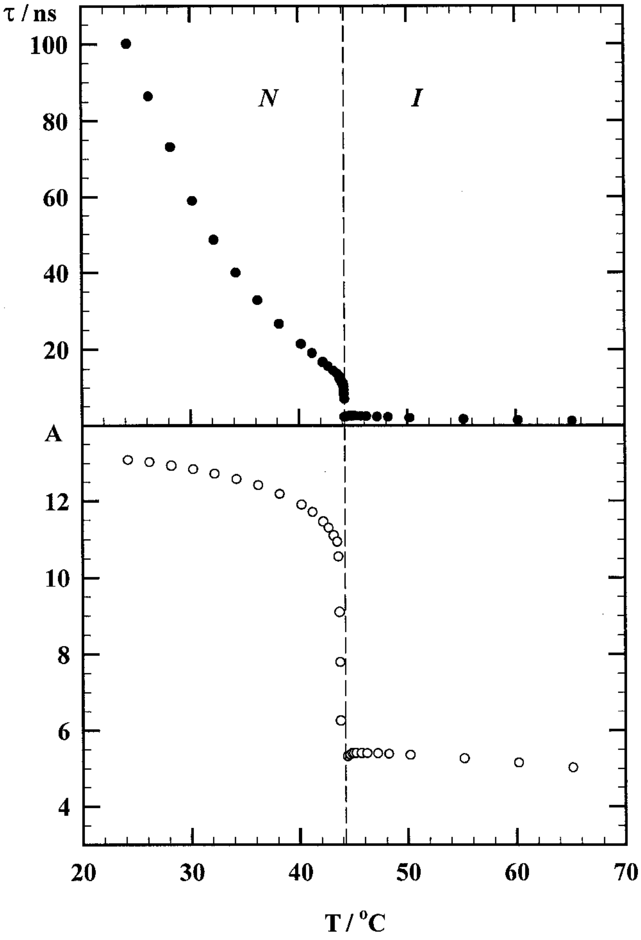

Figure 4. Temperature dependence of the relaxation time τ and the dielectric strength A corresponding to the 3CCPE molecular rotation around the short axis.

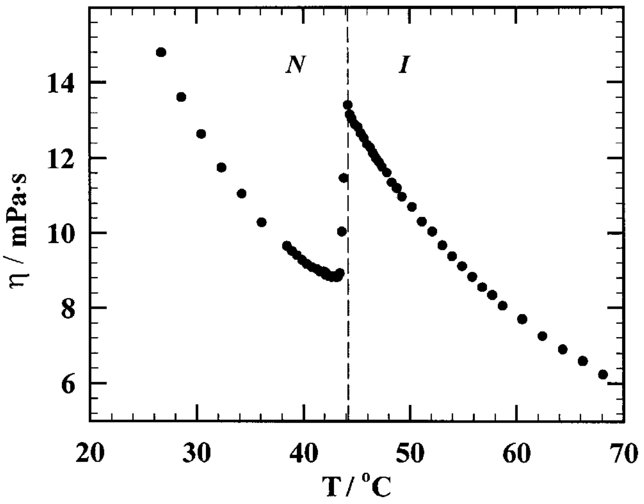

Figure 5. Temperature dependence of the shear viscosity of freely flowing 3CCPE in the isotropic and nematic phases.

Figure 6 presents the Arrhenius plots for the dielectric relaxation time and the viscosity in the isotropic and nematic phases of 3CCPE. In the isotropic phase the activation energy for the molecular rotation around the short axis and that of the viscous flow, are quite close to each other. This means that the viscosity is the main factor which determines the molecular dynamics in the isotropic phase of 3CCPE. If so, one can use the Debye model [32] for evaluation of the effective length of the 3CCPE molecule. In the model, the rotating dipolar, rigid and axially symmetric molecule is represented by a sphere of diameter l. The relation between the dielectric relaxation time corresponding to the molecular rotation

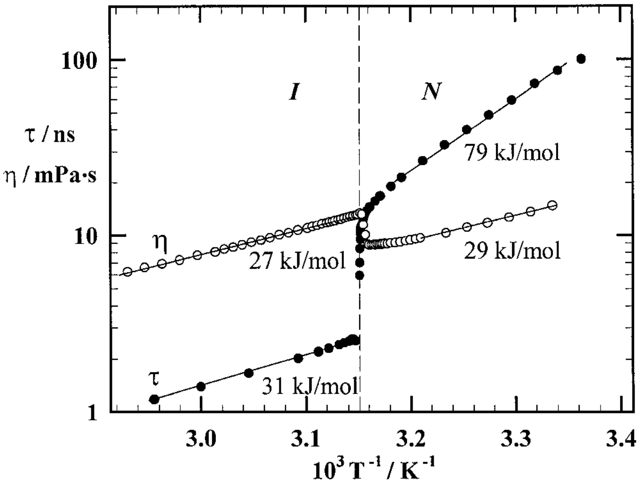

Figure 6. Arrhenius plots for the relaxation time corresponding to the molecular rotation around the short axis and for the shear viscosity of freely flowing 3CCPE. The values of the activation energy are given in the figure.

around its short axis τ, and the viscosity η of the isotropic medium in which the sphere is moving, has the following form:

$$\tau^{\mathrm{iso}} = \frac{\pi l^{3} \eta^{\mathrm{iso}}}{2kT} \tag{3}$$

where T is the absolute temperature, and k is the Boltzmann constant. The linear dependence of the relaxation time to viscosity ratio on T^{-1}, predicted by this simple model, is quite well fulfilled here (figure 7). The slope of the dependence gives the value $l \approx 11$ Å for the length of 3CCPE molecule, which is, however, somewhat different from that obtained from the quantum-chemical estimations (15 Å).

Figure 6 shows that the value of the viscosity activation energy is practically the same in the isotropic and nematic phases of 3CCPE. In the case of the dielectric relaxation time, the transition to the nematic phase manifests itself by a strong increase in the activation energy for the molecular rotation around the short axis. On the basis of these two experimental results, the strength of the nematic potential (≈ 50 kJ mol^{-1}) can be estimated as the difference between the activation energy for the molecular reorientation and that for the viscosity of the medium [12].

3.3. *Elastic constants*

The capacitance method of determination of the splay (K_{11}) and bend (K_{33}) elastic constants used in this paper consists in the analysis of the voltage dependence of the capacity of a planar aligned nematic cell. In the case of nematic liquid crystals with a positive dielectric anisotropy, ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} > 0$), the probing electric field **E** of a sufficient intensity causes a distortion of the director. With increase of the field intensity, the capacity of the cell increases from the initial value $C_{\perp}$, corresponding to $\mathbf{n} \perp \mathbf{E}$, to the final value $C_{\parallel}$, corresponding to $\mathbf{n} \parallel \mathbf{E}$. The phenomenon has a threshold, i.e. the capacity is not dependent on the voltage, before the voltage reaches the value characteristic for a given nematic liquid crystal value U_{th}. This value is the basic quantity for calculation of the splay elastic constant:

$$K_{11} = \varepsilon_0 \Delta\varepsilon U_{\mathrm{th}}^2 / \pi^2 \tag{4}$$

where $\varepsilon_0 = 8.85$ pF m^{-1}.

The K_{33} elastic constant can be determined in the same experiment from the analysis of the dependence of the cell capacitance on the voltage above the threshold value. The exact equation describing the $C(U)$ dependence was obtained first by Gruler *et al.* [33]. Next, Uchida and Takahashi [34] proposed a procedure for the determination of K_{33} which eliminates the need for a multi-parameter least square fitting of the equation of Gruler *et al.* to the experimental data. The final equation for the $C(U)$ dependence has the following form [35, 36].

$$\frac{C(U) - C_{\perp}}{C_{\perp}} = \gamma - \frac{2\gamma}{\pi}\frac{U_{\mathrm{th}}}{U}(1 + \gamma \sin^2 \varphi_{\mathrm{m}})^{1/2} \times \int_0^{\varphi_{\mathrm{m}}} \left[\frac{(1 + \chi \sin^2 \varphi)(1 - \sin^2 \varphi)}{(1 + \gamma \sin^2 \varphi)(\sin^2 \varphi_{\mathrm{m}} - \sin^2 \varphi)}\right]^{1/2} \cos \varphi \, \mathrm{d}\varphi \tag{5}$$

where $\chi = K_{33}/K_{11} - 1$, $\gamma = \varepsilon_{\parallel}/\varepsilon_{\perp} - 1$, φ is the tilt angle between the director **n** and the cell walls and φ_{m} is the tilt angle at the centre of the cell.

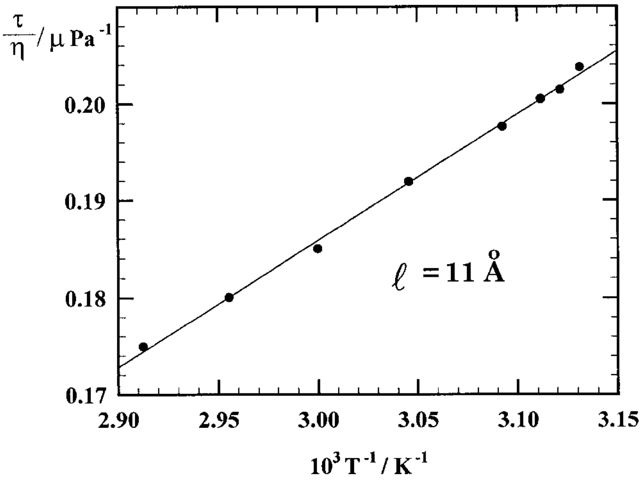

Figure 7. Debye plot, equation (3), for 3CCPE in the isotropic phase.

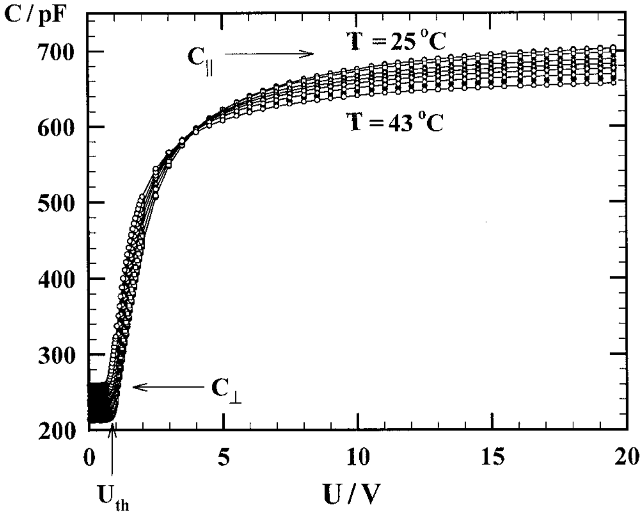

Figure 8. Capacity *vs.* voltage over the whole range of applied voltages at different temperatures (step about 2 °C).

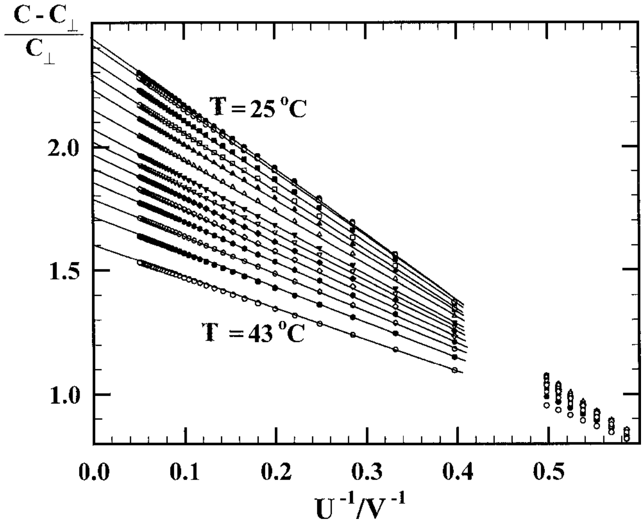

Figure 9. Dependences of $(C-C_\perp)/C_\perp$ on U^{-1} for nematic 3CCPE at different temperatures (step about 2°C).

For voltages much higher than the threshold value, the director **n** at the centre of the cell becomes perpendicular to the cell walls and $\varphi_m = \pi/2$. Then, equation (5) reduces to

$$\frac{C(U)-C_\perp}{C_\perp} = \gamma - \frac{2\gamma}{\pi}\frac{U_{th}}{U}(1+\gamma)^{1/2} \times \int_0^{\pi/2}\left(\frac{1+\chi\sin^2\varphi}{1+\gamma\sin^2\varphi}\right)^{1/2}\cos\varphi\,d\varphi\cdot \quad (6)$$

This equation predicts that for $U \gg U_{th}$ the dependence $(C-C_\perp)/C_\perp$ on U^{-1} should be linear. The extrapolation of the dependence to $U^{-1}=0$ leads directly to the value of $\gamma = \Delta\varepsilon/\varepsilon_\perp$ and the slope

$$\alpha = \frac{2\gamma}{\pi}(1+\gamma)^{1/2}U_{th}\int_0^{\pi/2}\left(\frac{1+\chi\sin^2\varphi}{1+\gamma\sin^2\varphi}\right)^{1/2}\cos\varphi\,d\varphi \quad (7)$$

contains only one unknown quantity $\chi = K_{33}/K_{11} - 1$.

The results of measurements of the $C(U)$ dependence for a planar aligned 3CCPE nematic cell over the whole range of the applied voltage are depicted in figure 8. In the range of voltage used, the capacity of the cell changes from $C_\perp$ (for $U < U_{th}$) to close to $C_\parallel$ (for $U \gg U_{th}$).

On the basis of the U_{th} value and the dielectric anisotropy $\Delta\varepsilon$ (figure 1), the splay elastic constant K_{11} can be easily calculated using equation (4). For voltages much higher than U_{th}, according to equation (6), theory predicts that the change of the cell capacity should be proportional to the reciprocal of U. The results presented in figure 9 show that this prediction is fulfilled well: for U higher than about 3 V the dependences $(C-C_\perp)/C_\perp$ on U^{-1} are linear. From the slope α of the lines one obtains the value of $\chi = K_{33}/K_{11} - 1$ and hence the K_{33} elastic constant, because the K_{11} constant is known. Figure 10 presents the temperature dependence obtained for the splay and bend elastic constants of 3CCPE.

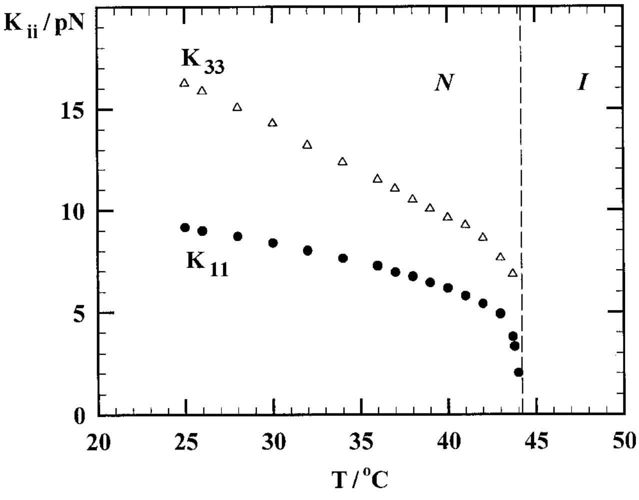

Figure 10. Temperature dependence of the splay (K_{11}) and bend (K_{33}) elastic constants of 3CCPE.

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