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Dielectric anisotropy in the nematic phase of 8PCH as a function of temperature and pressure

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The dielectric permittivity components, $\varepsilon_\parallel$ and $\varepsilon_\perp$, in the nematic phase of 8PCH (*trans*-4-*n*-octyl-(4-cyanophenyl)cyclohexane) were measured at 1 atm as a function of temperature (T), and at two temperatures as a function of pressure (p). A close similarity of the temperature and pressure behaviours of the dielectric anisotropy, $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, was established. It is argued that p and T are equivalent quantities in the formation of the nematic state. The well known Maier and Meier equations describe the dielectric parameters under both p = constant and T = constant conditions fairly well.

1. Introduction

Temperature (T) and pressure (p) are equivalent thermodynamic quantities. However, due to experimental difficulties, measurements with pressure as a variable are rather scarce. This concerns especially studies of liquids and liquid crystals (LCs) where separation of the samples from the pressurizing medium is the most important problem [1]. Therefore the number of liquid crystals studied under pressure is rather limited—for reviews see [1–4]. The title substance, *trans*-4-*n*-octyl-(4-cyanophenyl)-cyclohexane (8PCH), was recently studied by us [3–6] with the aim of obtaining information about the (p, T) phase diagram (figure 1), the molar volume $V_m(p, T)$ and the dielectric relaxation time $\tau_\parallel(p, T)$ characterizing the molecular reorientations around the short axis in the nematic and isotropic phases. These data enabled us to calculate the activation parameters (volume, enthalpy and energy) as well as the order parameter $S \equiv \langle P_2(\cos\theta)\rangle$, under isobaric, isothermal and isochoric conditions [5, 6]. In the relaxation studies, the sample was oriented by a d.c. electric field which limited the measurements to the parallel component of the dielectric tensor. In the present report we present the results obtained for both permittivity components, $\varepsilon_\parallel$ and $\varepsilon_\perp$, measured at atmospheric pressure as a function of temperature, and at two temperatures as a function of pressure. This allows us to compare the changes of the dielectric anisotropy, $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, with p and T within the nematic phase of 8PCH. Additionally, we can check the applicability of the well known Maier and Meier equations [7] to describe the dielectric permittivities at p = constant and at T = constant.

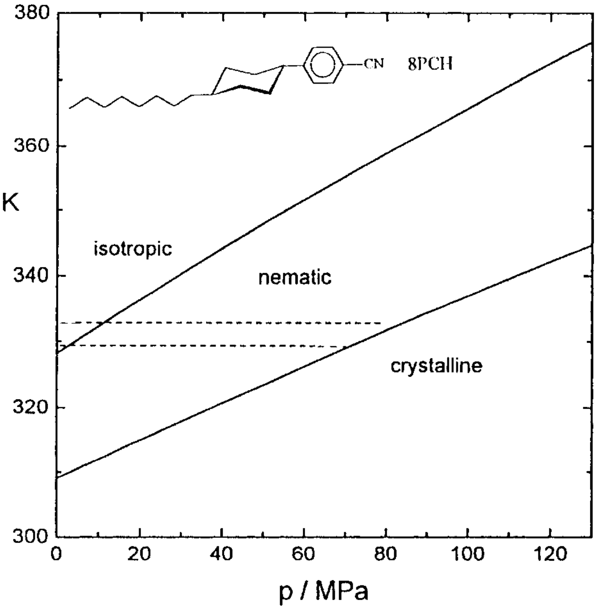

Figure 1. Pressure–temperature phase diagram for 8PCH [4, 5]. Dashed lines mark isotherms for which the dielectric measurements were made.

2. Experimental

The sample was obtained from R. Dąbrowski, Military Technical University, Warsaw. Its transition temperatures at 1 atm were: Cr–30°C–N–54.2°C–I. The high

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pressure set-up has been described elsewhere [8, 9]. The measurements always started from the isotropic liquid and the sample was cooled (at 1 atm) or pressurized step by step (at $T = 328.5$ K in the range 0.1–60 MPa, and at 332.8 K in the range 0.1–80 MPa). Under given conditions (p, T), the sample was aligned parallel to the measuring electric field by applying a d.c. field of *c.* 3000 V cm^{-1}, and then the perpendicular alignment was achieved by applying a magnetic field of 0.6 T. The dielectric permittivity components, $\varepsilon_\|$ and $\varepsilon_\perp$, were measured with the aid of an HP 4192A impedance analyser in the range 10 kHz–10 MHz. The static permittivity values were taken to be the average of the values of $\varepsilon'(\nu)$ measured in the region of the plateau of the spectra (usually in the range 10–150 kHz). The temperature was stabilized within ± 0.2 K.

3. Results and Discussion

In figure 2 the permittivity components measured as functions of temperature are compared with those obtained by other authors (in the latter case both components were measured with **B**-field) [10]. The $\varepsilon_\|$ component measured by Jadzyn is significantly smaller; similar disagreement was also observed in previous studies [5]. A feature characteristic for strongly polar LC substances is observed: the mean permittivity, $\bar{\varepsilon} = (\varepsilon_\| + 2\varepsilon_\perp)/3$, is smaller than the $\varepsilon_{\rm is}$ extrapolated to the nematic phase.

In figure 3 all data obtained are presented as functions of the reduced temperature $\Delta T = T_{\rm NI} - T$ (crosses and top scale) and the reduced pressure $\Delta p = p - p_{\rm NI}$ (full points and bottom scale). The scales for the upper and lower abscissa axes were chosen in such a way that the clearing points coincide, whereas the left hand parts were roughly normalized to the range of the nematic phase under the given conditions. As can be seen from the figure all permittivity components almost coincide within the nematic phase in spite of the different parameters used as variables. Similar behaviour was observed in the studies of 6OCB [9].

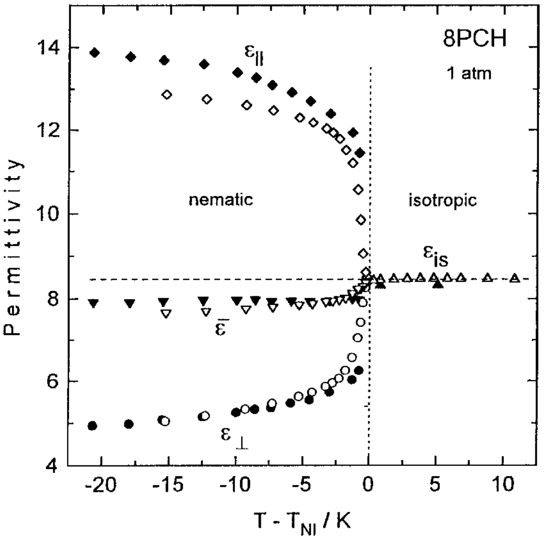

Figure 2. Permittivity components of 8PCH: $\varepsilon_\|$, $\varepsilon_\perp$, $\bar{\varepsilon} = (\varepsilon_\| + 2\varepsilon_\perp)/3$ and $\varepsilon_{\rm is}$, versus temperature at 1 atm. Full points: present study; open points: taken from [10].

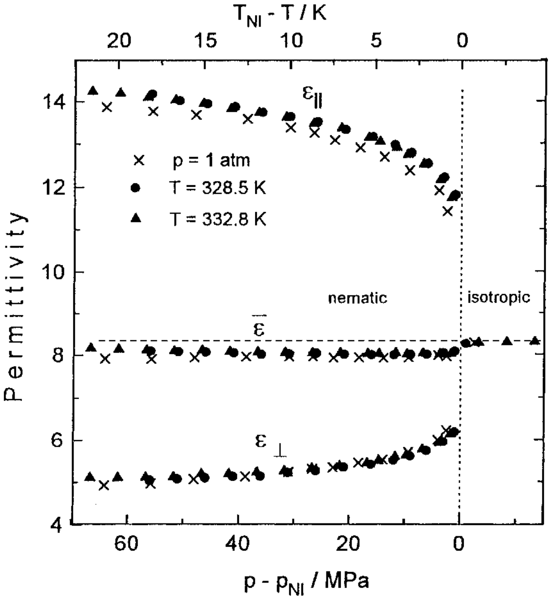

Figure 3. Comparison of the permittivity components in the nematic phase of 8PCH measured at 1 atm as a function of the shifted temperature $\Delta T = T_{\rm NI} - T$ (crosses and the top scale), and at two temperatures (full points and the bottom scale) as a function of the shifted pressure $\Delta p = p - p_{\rm NI}$. The scales for the upper and lower axes correspond roughly to the range of the nematic phase under particular conditions.

It seems valuable to discuss the results obtained taking into consideration the Maier and Meier equations [7] for the principal permittivity components:

$$(\varepsilon_\| - 1) = \varepsilon_0^{-1} NFh \left\{ \bar{\alpha} + \frac{2}{3}\Delta\alpha S + F\frac{\mu_{\rm eff}^2}{3kT}[1 - (1 - 3\cos^2\beta)S] \right\} \qquad (1)$$

$$(\varepsilon_\perp - 1) = \varepsilon_0^{-1} NFh \left\{ \bar{\alpha} - \frac{1}{3}\Delta\alpha S + F\frac{\mu_{\rm eff}^2}{3kT}\left[1 + \frac{1}{2}(1 - 3\cos^2\beta)S\right] \right\} \qquad (2)$$

$$\Delta\varepsilon = (\varepsilon_\| - \varepsilon_\perp) = \varepsilon_0^{-1} NFh \left[\Delta\alpha - F\frac{\mu_{\rm eff}^2}{2kT}(1 - 3\cos^2\beta)\right] S \qquad (3)$$

where $N=\rho N_A/M$ (ρ = density, N_A = Avogadro's number, M = molar mass), $\Delta\alpha=\alpha_\parallel-\alpha_\perp$ and $\bar{\alpha}=(\alpha_l+2\alpha_t)/3$ are the polarizability components and the mean polarizability, respectively. The local field parameters F and h are expressed by the mean polarizability $\bar{\alpha}$ and the mean permittivity $\bar{\varepsilon}$: $F=1/(1-f\bar{\alpha})$ with $f=(N/3\varepsilon_0)[(2\bar{\varepsilon}-2)/(2\bar{\varepsilon}_s+1)]$, and $h=3\varepsilon_s/(2\varepsilon_s+1)$. The molecular dipole moment μ was replaced by the effective dipole moment in order to account for the dipole–dipole correlations described by the Kirkwood g_K factor: $\mu^2_{\mathrm{eff}}=g_K\mu^2$. Obviously, g_K is temperature and pressure dependent.

Similarly as in [11], we have fitted the following form of equation (3) to the experimental points:

$$\Delta\varepsilon^{\mathrm{MM}}(X)=\varepsilon_0^{-1}N(X)h(X)F(X)$$
$$\times[\Delta\alpha-F(X)A(g_0+g_tX)B]S(X) \qquad (4)$$

where $X=T_{\mathrm{NI}}-T$ or $X=p-p_{\mathrm{NI}}$, $A=\mu^2/2k_BT$, and $B=1-3\cos^2\beta$. The fitting parameters were g_0, g_t (assuming a linear change of g_K with X), and B. Other parameters were taken from experiments (ρ from [4, 12], polarizability values from [13], permittivity values from the present experiments). The order parameter S was accepted in the Haller-type forms: $S=S_0\Delta T^\gamma$ or $S=S_0\Delta p^\gamma$ (p/MPa) with S_0 and γ taken from [6]. Figure 4 (top) shows that the fits were quite good with the parameters shown in the table. Then, using the established quantities, the permittivity components $\varepsilon_\parallel$ and $\varepsilon_\perp$ were calculated according to formulae (1) and (2) (open points in figure 4, bottom) which are compared with the measured values (full points). The β-value obtained (26.5° ± 1°) is in reasonable agreement with that estimated for the isotropic phase (32°) from the analysis of the dielectric relaxation spectra [14] and that obtained from molecular mechanics calculations (24°) [10]. The Kirkwood g_K factor indicates the existence of antiparallel dipole–dipole correlations and its value is typical for other cyano compounds [10, 11, 15] (we do not discuss this in detail because the μ value assumed was not determined experimentally [10, 16]).

According to Maier and Saupe [17] theory, the nematic state is established by the orientational ordering of the rod-like molecules; the ability of the molecules to orientate is described by the order parameter S. It was

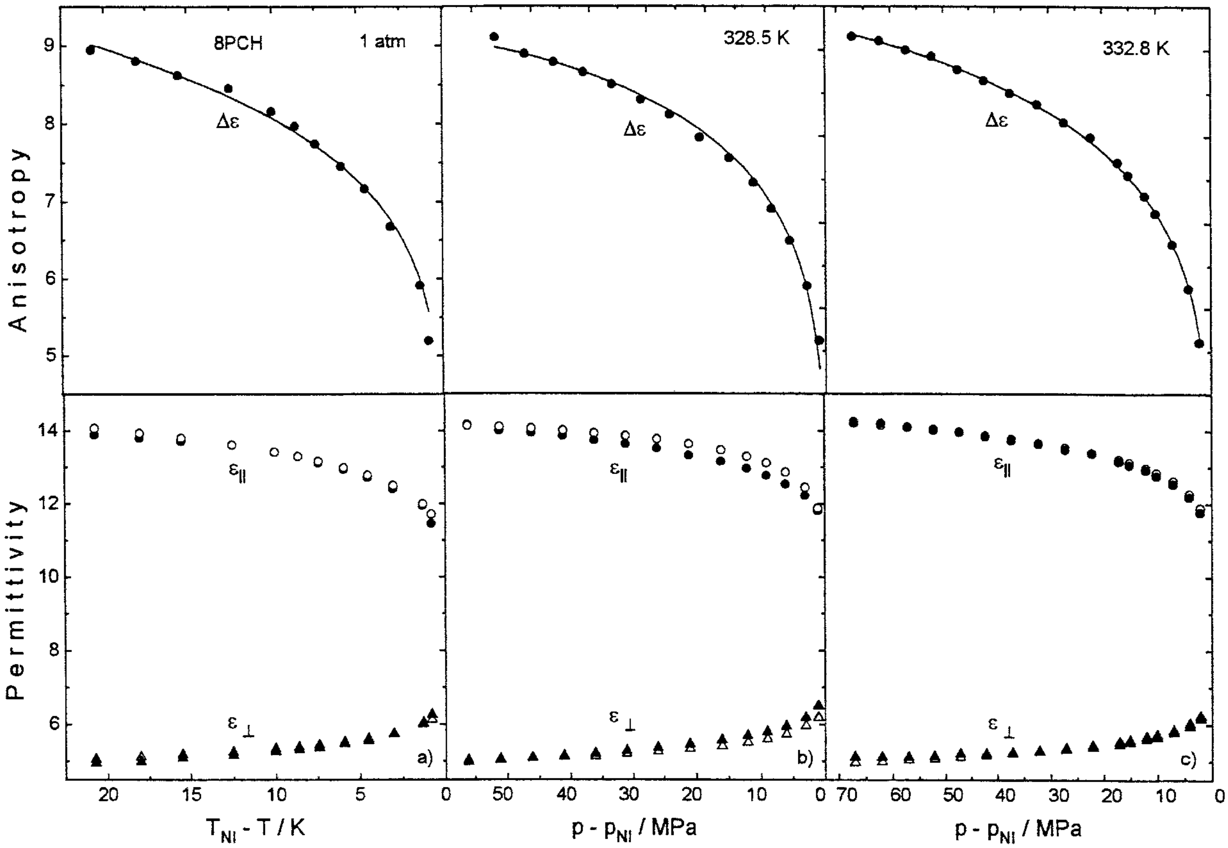

Figure 4. Top: dielectric anisotropy in the nematic phase of 8PCH versus shifted temperature (*a*) and versus shifted pressure (*b*, *c*); the lines are the fits of equation (4) to the experimental points with the parameters gathered in the table. Bottom: comparison of the permittivity components, experimental (full points) and calculated using equations (1) and (2) (open points).

Table. The physical parameters for 8PCH which were used in the analyses of the Maier–Meier equations and the parameters obtained from the fits of equation (4) to the experimental data.

		Fitting parameters		
Physical parameters	Variables	$\beta/°$	g_0	g_t
$T_{NI} = 327.7$ K, $M = 297.5$ g mol^{-1} $\mu = 15.0 \times 10^{-30}$ C m (4.5 D)	$p = 1$ atm (329–307 K)	27.5	0.680	-0.0024
$\bar{\alpha} = 42.2$, $\Delta\alpha = 11.96$ [$\times 10^{40}$ J^{-1} C^2 m^2] $S = 0.434\Delta T^{0.145}$, $S = 0.367\Delta p^{0.144}$	$T = 328.5$ K, $p_{NI} = 4$ MPa (0.1–60 MPa)	25.7	0.713	-0.0011
	$T = 332.8$ K, $p_{NI} = 13$ MPa (0.1–80 MPa)	26.3	0.700	-0.0006

proved (present study and [9, 11, 15]) that the dielectric anisotropy of nematics formed by strongly polar molecules is proportional to the $S(T)/T$ or $S(p)$ factors (the changes with p and T of the other parameters in equations (1)–(3) can be neglected). Considering the range of the nematic phase at $p = 1$ atm and at $T =$ constant as a proper normalization condition, we observe (figure 3) a coinciding of the anisotropy data measured at the same relative distance from the clearing point. This seems to indicate the equivalency of temperature and pressure in the formation of the nematic state. Excellent agreement of the experimental permittivity data with the calculated values (figure 4), seem to indicate that the Maier–Meier equations give not only a qualitative, but also a good quantitative description of the dielectric permittivity tensor in the nematic phase.

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