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High pressure studies of the static permittivity tensor components in the nematic phase of 6CB

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The dielectric permittivity tensor components, ε_{II} and $\varepsilon_{\perp}$, in the nematic phase of 6CB (4-*n*-hexyl-4′-cyanobiphenyl) were measured in the pressure range 0.1–130 MPa and the temperature range 12–58°C. The dielectric anisotropy, $\Delta\varepsilon(p, V, T)=\varepsilon_{II} - \varepsilon_{\perp}$, was analysed in isothermal, isobaric and isochoric conditions taking into account the *pVT* data and the well known Maier and Meier equation. On that basis the nematic order parameter $S(p, V, T)$ was determined. This was used to calculate the parameter γ relating the interaction potential with the volume (density). Its value $\gamma=4.1$ agrees very well with other estimates.

1. Introduction

4-*n*-Hexyl-4′-cyanobiphenyl (6CB) is one of the best known liquid crystalline substances. 6CB, as well as other members of the *n*CB homologous series, is important from the point of view of applications due to the possession of a strong dipole moment, good chemical stability and a convenient temperature range of the nematic phase. At the same time these substances are useful for testing theoretical models of the nematic state.

Dielectric properties of the *n*-alkylcyanobiphenyl homologues under high pressure (static and dynamic) have been studied in our group during the last 13 years [1–9]. In particular, the results for 6CB were reported in [3] (the low frequency relaxation process mainly), and in [6] (static permittivity tensor components, $\varepsilon_{II}-\varepsilon_{\perp}$, at two isotherms). In the meantime the equation of state was determined (*pVT* measurements [10]) for this substance which stimulated us to perform the measurement of the static permittivities over broader pressure and temperature ranges, and to analyse the data in the isothermal, isobaric and isochoric conditions. Of particular interest was the determination of the nematic order parameter $S(p, V, T)=<P_2(\cos\theta)>$ from the dielectric anisotropy $\Delta\varepsilon(p, V, T)=\varepsilon_{II}-\varepsilon_{\perp}$ data. The well known Maier-Meier equation [11] was used to achieve this. Having $S(p, V, T)$, the parameter γ relating the interaction potential with the volume (density) could be determined according to the relation derived by McColl [12].

2. Experimental

6CB was synthesized in the Institute of Chemistry, the Military University of Technology, Warsaw. Its transition temperatures at p=1 atm were: Cr–14.5°C–N–29.0°C–I. Figure 1 presents the temperature–pressure phase diagram determined in *DTA* and *pVT* studies [10] along with the points obtained in the present study. The high pressure set-up used for the dielectric measurements is described in [6, 13]. The plane capacitor was placed in a cylindrical high pressure vessel made of a non-magnetic material. For safety reasons the pressure could not exceed 130 MPa. The sample was separated

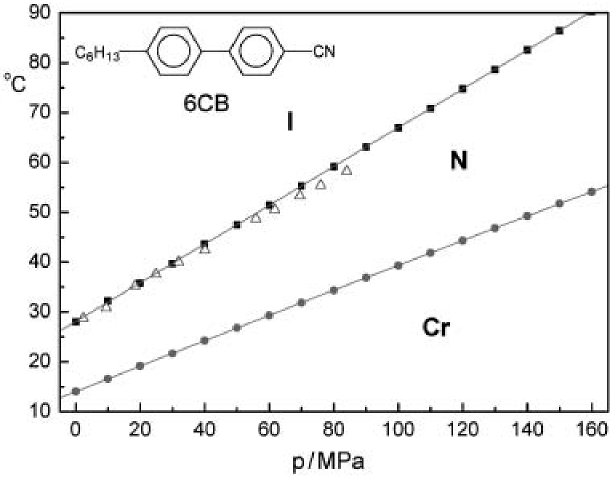

Figure 1. Pressure–temperature phase diagram for 6CB. Full symbols denote data obtained in previous DTA and *pVT* measurements [10]; open symbols represent data from the present study.

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from the pressurizing medium (silicone oil). The pressure was adjusted within ± 0.5 MPa and the temperature stabilized within ± 0.2K. The measurements were carried out at constant temperatures, with stepwise pressure change. The sample was aligned parallel to the measuring electric field by applying a d.c. electric field of $2500\,\mathrm{V\,cm^{-1}}$, while the perpendicular orientation was achieved by applying a magnetic field of 0.4 T—at a given (p, T) condition, particular fields were applied consecutively. The capacitor was calibrated using four standard liquids. The measurements at 1 atm started from the isotropic phase and the sample was cooled step by step. In this case the sample was oriented by a magnetic field of 0.8 T (the perpendicular orientation) and by a d.c. electric field of $3000\,\mathrm{V\,cm^{-1}}$ (the parallel orientation). The dielectric permittivity components, $\varepsilon_{\mathrm{II}}$ and $\varepsilon_{\perp}$, were measured by means of an HP 4194A impedance analyser in the range 10 kHz–20 MHz. The static permittivity values were taken as an average of $\varepsilon'(v)$, measured in the region of a *plateau* of the spectra (usually in the range of 10–100 kHz).

3. Results

Figure 2 presents the static dielectric permittivity, $\varepsilon_{\mathrm{II}}$ and $\varepsilon_{\perp}$, as a function of pressure at different temperatures within the nematic phase of 6CB. The dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\mathrm{II}} - \varepsilon_{\perp}$, as a function of pressure is shown in figure 3. The average permittivity, $\bar{\varepsilon} = \left(\varepsilon_{\parallel} + 2\varepsilon_{\perp}\right)/3$, is essentially independent of pressure within the nematic phase. A comparison of the permittivity components determined at T=45.4°C and at 1 atm is presented in figure 4 as a function of the reduced pressure $\Delta p = p - p_{\mathrm{NI}}$ (circles) and the reduced temperature $\Delta T = T_{\mathrm{NI}} - T$ (crosses). The scales on the lower and upper abscissa were normalized to the extent of the nematic phase at both conditions. It can be seen that the two sets of data almost match within the nematic phase, as observed similarly for 6OCB [13] and 8PCH [14].

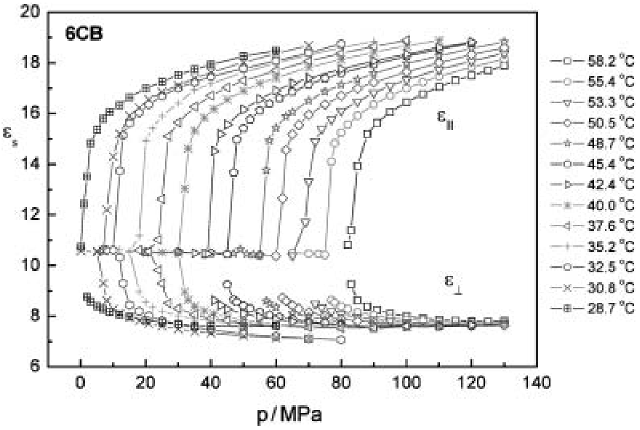

Figure 2. The principal components of the static dielectric permittivity versus pressure for several isotherms in the nematic phase of 6CB. The lines are guides for the eye.

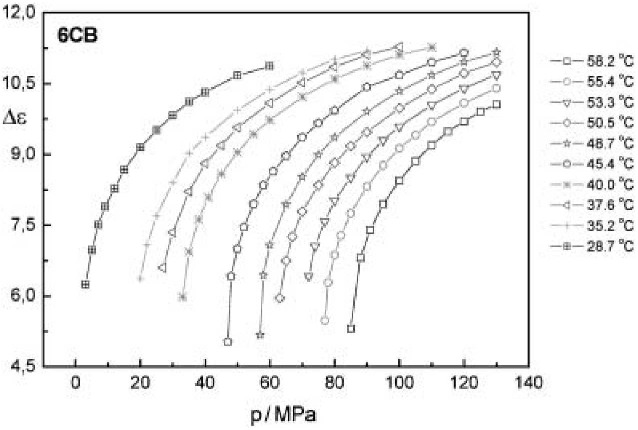

Figure 3. The dielectric anisotropy of 6CB versus pressure at different constant temperatures. The lines are guides for the eye.

4. Discussion

The static permittivity components of the nematic phase can be interpreted with the aid of the Maier–Meier

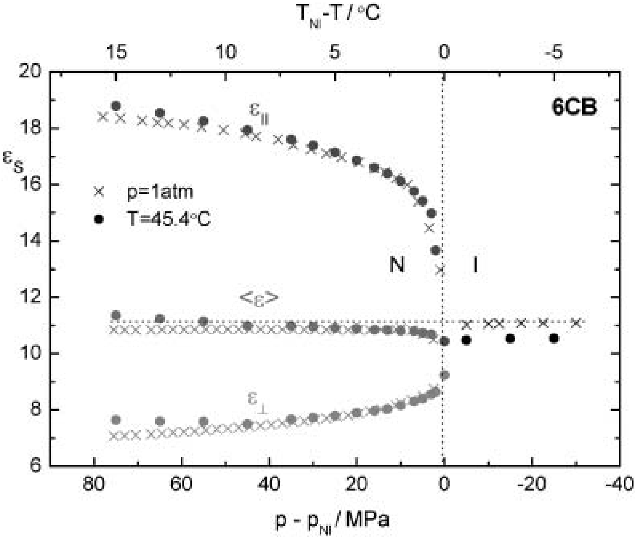

Figure 4. Comparison of the permittivity components in the nematic phase of 6CB measured at T=45.5°C as a function of the reduced pressure $\Delta p = p - p_{\mathrm{NI}}$ (circles), and at p=1 atm as a function of the reduced temperature $\Delta T = T_{\mathrm{NI}} - T$ (crosses). The scales for the lower and upper abscissa correspond to the range of the nematic phase at both conditions.

equations [11],

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

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

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

where $N=\rho N_{\mathrm{A}}/M$ (ρ=density, N_{A}=Avogadro's number, M=molar mass—(263.4 g mol^{-1} for 6CB); $\Delta\alpha=\alpha_{\mathrm{II}}$ - $\alpha_{\perp}$ and $\bar{\alpha}=\left(\alpha_{\|}+2\alpha_{\perp}\right)/3$ are the polarizability anisotropy and the mean polarizability, respectively. The Onsager field factors F and h are given by

$$F=(2\bar{\varepsilon}+1)\cdot\left(n^2+2\right)/\left[3\left(2\bar{\varepsilon}+n^2\right)\right],\quad h=3\bar{\varepsilon}/(2\bar{\varepsilon}+1) \tag{4}$$

(n is the mean refractive index). The molecular dipole moment μ was replaced by the effective dipole moment μ_{eff}, which defines the Kirkwood dipole–dipole correlation factor $g_{\mathrm{K}}=\mu^2{}_{\mathrm{eff}}/\mu^2$. β is the angle between the dipole moment μ and the molecular long axis.

In the present study the analysis of the results is focused on the equation (3). Taking into account the known molecular and material parameters (μ=4.7 D, $\beta\approx 17°$, g_{K} from [15], optical data from [16], density from [10]) we find that the local field factors as well as other parameters ($\Delta\alpha$, $\bar{\alpha}$, N) are practically pressure independent, or their variation can be neglected in comparison with the pressure dependence of the $\Delta\varepsilon$ isotherms. Moreover, because $\Delta\alpha$ is much less than the dipolar part in equation (3) it can be ignored. Thus, we can assume with good accuracy the proportionality:

$$\Delta\varepsilon(\Delta p)_{\mathrm{T}}=\mathrm{const}\cdot S(\Delta p)_{\mathrm{T}}. \tag{5}$$

Analogous analysis for the 1 atm data leads to the relation

$$\Delta\varepsilon(\Delta T)_{p=1\mathrm{atm}}\propto\frac{S(\Delta T)_{p=1\mathrm{atm}}}{T}. \tag{6}$$

Figures 5 and 6 present the order parameters derived from the data in figures (3) and (4). Of course, the proportionality constants have to be found in a more or less arbitrary way. In the temperature studies of the order parameter [17–19] it appeared that the relation proposed by Haller [20] is useful:

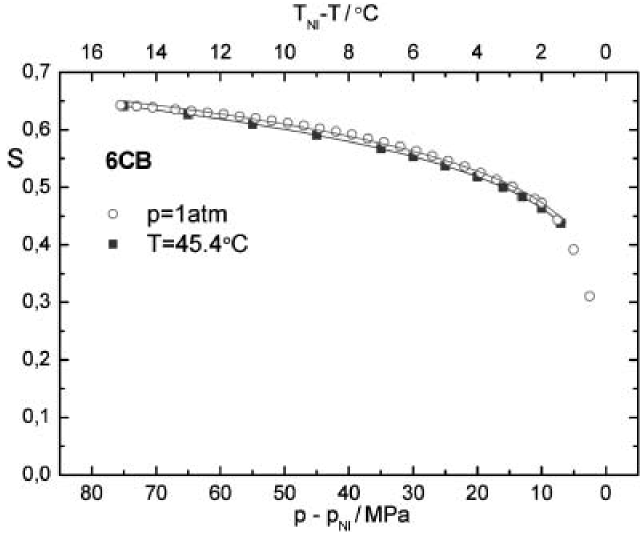

Figure 5. Dependence of the order parameter S on the reduced temperature $\Delta T=T_{\mathrm{NI}}-T$ at 1 atm (open symbols), and on the reduced pressure $\Delta p=p-p_{\mathrm{NI}}$ at constant temperature (full symbols). The lines are fits of equation (7), yielding γ=0.157 and S_{op}=0.408; and of equation (8) giving δ=0.161 and S_{oT}=0.320.

$$S(T)_p=S_{0p}(T_{\mathrm{NI}}-T)_{\mathrm{p}}^{\gamma} \tag{7}$$

with S_{0p} related to the clearing temperature: $S_{0p}=T_{\mathrm{NI}}{}^{-\gamma}$. In this way a scatter of the S-data obtained using different experimental methods could be re-scaled to practically one common line [17–19]. The obtained value of S_{0p}=0.401 is in a good agreement with the value 0.383 calculated on the basis of the Maier–Meier equation using the known molecular and material parameters (μ, β, g_{K}, $\Delta\alpha$, $\bar{\alpha}$, N).

By analogy, for the pressure dependence of the order parameter the following form of the Haller equation was applied [12, 13, 17, 21]:

$$S(p)_T=S_{0p}(p-p_{\mathrm{NI}})_{\mathrm{T}}^{\delta}. \tag{8}$$

In figure 5 the order parameters determined for 6CB at p=constant and T=constant were normalized far from the clearing point. By fitting formula (8) to the points it was found that the δ–parameter is close to the γ–parameter. In this way an excellent agreement of both order parameters within the nematic phase was obtained, which, together with the agreement between the tensor permittivity components presented in figure 4, indicates once more [12, 13] an equivalence of temperature and pressure in the formation of the nematic state.

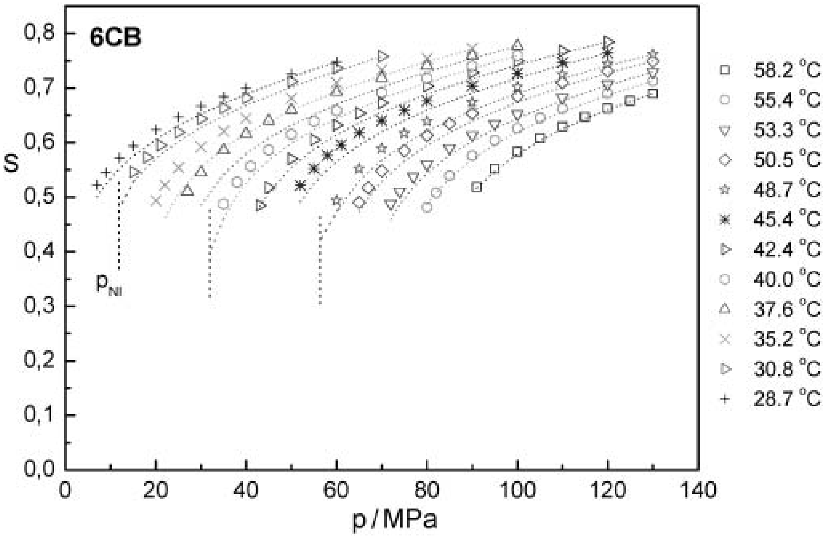

Figure 6. Nematic order parameter S determined from the data presented in figure 3 treated by the Maier–Meier equation (3). The dashed lines correspond to the order parameter derived from the NMR experiment. Both sets of data were normalized at pressures remote from the p_{NI} values. The dashed vertical lines correspond to the nematic–isotropic transition (in order to preserve picture clarity only three lines are drawn).

The procedure described was then applied to other isochors, see figure 6. These results can be compared with the order parameter obtained from the NMR experiment by Wallis and Roy [22]. Again, a normalization factor had to be adjusted. The $S^{\mathrm{NMR}}(p)_T$ isotherms were taken as true ones, and the $S(p)_T$ data were normalized to them under pressures remote from the p_{NI} values (the normalization factor was ~1.2). As can be seen in figure 6, the two sets of data give consistent dependence of the order parameter on the pressure, although some discrepancy of both sets of data is observed which may be connected with a very high sensitivity of the analytical formula given in [22] to the value of p_{NI}.

A final goal of our studies is to use the data obtained to calculate the parameter γ characterizing a steepness of the interaction potential responsible for the formation of the nematic state. In the mean-field theory by Maier and Saupe [23, 24] it was assumed that the stability of the nematic phase comes from the dipole–dipole part of the anisotropic dispersion forces. They obtained the result that the clearing temperature T_{NI} depends on r^{-6}; that is, $T_{\mathrm{NI}} \sim V^{-2}$ (r and V are the intermolecular distance and volume, respectively).

In general, one can write $T_{\mathrm{NI}} \sim V^{-\gamma}$ if the repulsive part is taken into account. Using the pVT data, Sandmann and Würflinger [10] calculated $\gamma=6.3$ for 6CB. Similar results were obtained for other nematogens [25]. Very recently Urban and Würflinger have performed the thermodynamical scaling of the low frequency relaxation time, leading to $\gamma=4.1$ for 6CB, [26].

Having the $S(p, V, T)$ data we shall apply yet another approach derived by McColl [12]

$$\Gamma = -\left(\frac{\partial \ln T}{\partial \ln V_{\mathrm{m}}}\right)_S. \qquad (9)$$

For this approach the dielectric anisotropy $\Delta\varepsilon(p, V, T)$ values were plotted as a function of the molar volume $V_m=1/\rho$, figure 7. This enables us to construct the $\ln T$ versus $\ln \rho$ plots (see figure 8) at $\Delta\varepsilon=constant$ which is equivalent to $S=constant$ according to equation (5). The

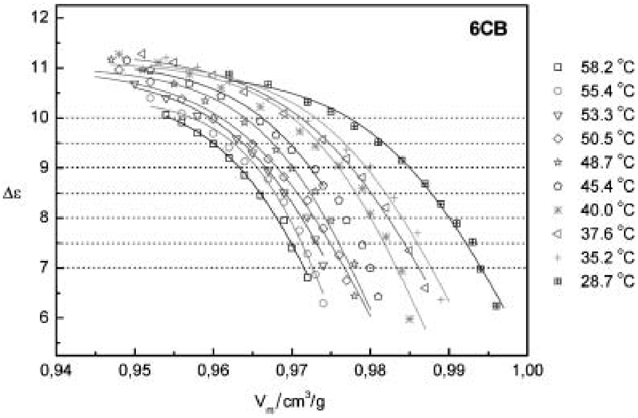

Figure 7. The dielectric anisotropy versus volume at different constant temperatures in the nematic phase of 6CB. The data on V_{m} were taken from [10]. The lines are guides for the eye.

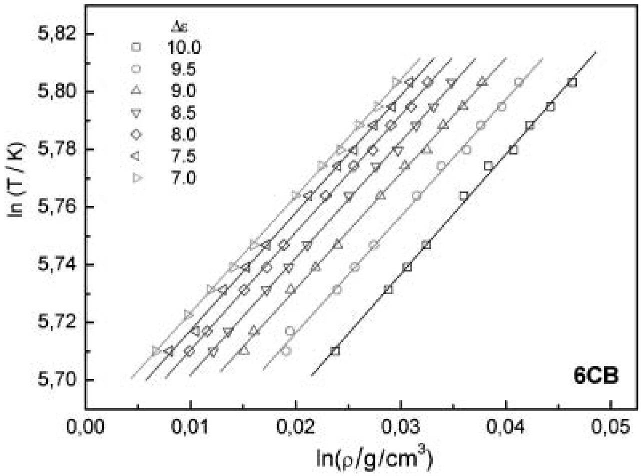

Figure 8. Plot of ln T versus ln ρ for different constant values of the dielectric anisotropy. Straight lines are fits to the points with the slopes γ=4,1 ± 0.1.

slopes of the plots are almost the same for all $\Delta\varepsilon$ values. The mean value of $\gamma=4.1\pm0.1$ is the same as that obtained from the scaling procedure [26]. Thus, the Lennard–Jones form of the distance-dependent part of the intermolecular potential, $\Phi(r)=(-A/r^6+B/r^{12})$, seems to be a little steeper for 6CB than was assumed in its original form. The fact that γ is larger than 2 indicates that the repulsive part cannot be neglected, as was assumed in the Maier and Saupe theory [23, 24].

In conclusion, one can say that high pressure measurements of the dielectric anisotropy in the nematic phase enable the determination of the order parameter as a function of pressure and density, in good agreement with data obtained from other experiments. The $S(p, V, T)$ data, combined with the experimental equation of state, lead to reasonable value of the γ -parameter describing the steepness of the intermolecular potential.

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