Dielectric Studies of 4-*n*-Hexyloxy-4′-Cyanobiphenyl (6OCB) at Elevated Pressure*

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The principal dielectric permittivity components in the nematic phase of 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) were measured as functions of temperature at ambient pressure and as functions of pressure up to 100 MPa at several constant temperatures. The dielectric anisotropy is analized in the frame of the Maier-Meier equations. The pressure dependence of the order parameter is deduced. Preliminary results for the activation volume and activation enthalpy from the pressure and temperature dependences of the longitudinal relaxation times are obtained.

Key words: Nematic Liquid Crystal; 6OCB; Dielectric Anisotropy; Order Parameter; High Pressure.

Introduction

4-*n*-Hexyloxy-4′-cyanobiphenyl (6OCB) is one of the best known liquid crystalline (LC) substances. It exhibits the nematic (N) phase between 57.0 and 75.7 °C. Its dielectric properties were studied in the past by several experimental groups (e.g. [1–4]). No report dealing with the dielectric properties of 6OCB as functions of pressure is known. The temperature-pressure phase diagram of this substance has been obtained by Krombacher and Schneider [5], using the DTA method (Figure 1).

6OCB has a strong longitudinal dipole moment μ_l, caused by the terminal –CN group, and a weak transvers component μ_t, connected with the alkoxy group and a small inclination of the *para*-axis of the benzene ring from the major inertia axis [1, 6]. This leads to a large positive dielectric anisotropy in the nematic phase, $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp > 10$, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ correspond respectively, to the $\boldsymbol{E} \parallel \boldsymbol{n}$ and $\boldsymbol{E} \perp \boldsymbol{n}$ geometry ($\boldsymbol{E}$ is the external electric field and $\boldsymbol{n}$ is the nematic director). The dielectric relaxation process in the N phase is dominated by molecular rotations around the short axis. The faster rotations around the long axis are also visible in the dielectric studies [1, 6].

In the present paper the results of dielectric studies of 6OCB at elevated pressure are presented. The dielectric anisotropy $\Delta\varepsilon(p)$ is compared with the ambient pressure data and with the high pressure results obtained for similar substances, pentyl and hexyl cyanobiphenyls (5CB and 6CB) [7]. The relaxation times $\tau_\parallel (p, T)$ yield the activation volume $\Delta^{\#}V_\parallel$ and the activation enthalpy $\Delta^{\#}H_\parallel$. They can be compared with the results obtained for many LC substances by Würflinger et al. [6, 8–11].

Experimental

The high pressure vessel built with non-magnetic materials and the parallel-plate capacitor used allowed us to apply an electric and/or magnetic field for orienting a nematic sample. The high pressure vessel, shown in Fig. 2,

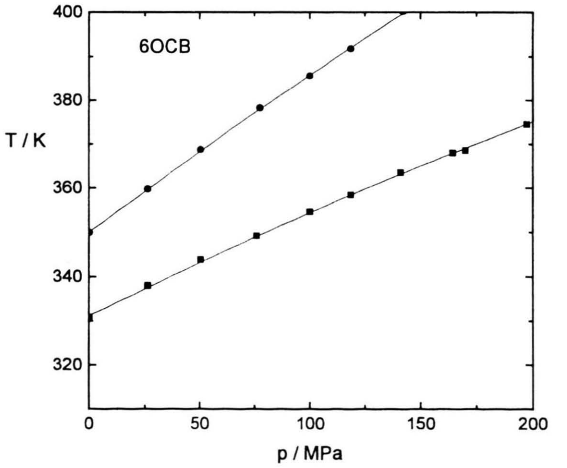

Fig. 1. Temperature–pressure phase diagram of 6OCB according to [5].

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* Dedicated to Professor Albert Würflinger, Ruhr University of Bochum, on the occasion of his 60th birthday.

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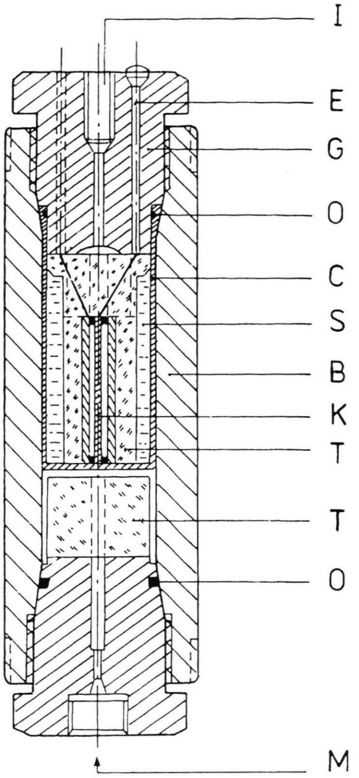

Fig. 2. The modified vessel [7] for high pressure dielectric studies of liquid crystals oriented by a magnetic field. Main parts are: B – corps of beryllium bronze, G – plug of beryllium bronze, I – sample inlet, E – electrical feed-through, C – cylindrical capsule of plastic material, S – sample, K – parallel-plate capacitor, T – teflon parts, O – o-rings, M – pressurizing oil inlet.

is a modified version of that used in [7]. In cooperation with the High Pressure Centre UNIPRESS, Warsaw, two important changes were made. The moving piston was replaced by a cylindrical capsule closed at the bottom, made of a thin plastic material. Inside the capsule the capacitor immersed in a sample is placed. A little thicker capsule's collar is pressed by a screw plug which seals the sample holder. As pressurising medium silicon oil instead of gas was used. It is pumped by a NOVA SWISS hand pump. The pressure was measured with a manganin gauge placed far from the vessel, so a heating of the sample does not influence the pressure reading. The pressure was measured with an accuracy of ±0.5 MPa. The temperature was stabilised within ±0.2 K. The dielectric spectra were measured with an HP 4192A impedance analyser in the range of 10 kHz–13 MHz. The parallel orientation was achieved by a bias electric field of ca. 300 V/cm, whereas the perpendicular orientation was established by a magnetic field of ca. 0.6 T. For safety-reasons the measurements could not be extended beyond 100 MPa and 350 K.

Results

Static Permittivity

Figure 3 (left) presents the static dielectric permittivities, $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and $\bar{\varepsilon} = (\varepsilon_{\parallel}+2\,\varepsilon_{\perp})/3$ of the nematic phase of 6OCB versus the pressure at five temperatures. Only at the highest temperature the N-I transition was crossed (at 1 atm $T_{\rm NI} = 348.9$ K). In spite of that, the mean values $\bar{\varepsilon}$ are practically independent of temperature and are close to the isotropic value. The same was observed for 5CB and 6CB [7]. Figure 3 (right) shows the variation of the dielectric anisotropy $\Delta\varepsilon$ with pressure.

Dielectric Relaxation

Typical relaxation spectra of the nematic phase of 6OCB are shown in Fig. 4 in the form of the dispersion (ε') and absorption (ε'') curves. As usually the spectra could well be described by the Debye equation. However, in case of the dielectric losses the conductivity contribution in the form σ_0/ω had to be subtracted:

$$\varepsilon'' = \frac{(\varepsilon_{\rm s} - \varepsilon_{\infty})\,\omega\,\tau}{1+(\omega\,\tau)^2} + \frac{\sigma_0}{\omega} \qquad (1)$$

The relaxation time $\tau_{\parallel}$ was calculated from the frequency corresponding to the maximum of losses: $\tau_{\parallel} = 1/(2\pi \cdot \nu_{\rm max})$. Unfortunately, the limited frequency range (up to 13 MHz) caused that ε'' reached a maximum at low temperatures or high pressures only. Figure 5 presents the relaxation times versus pressure available in the experiment.

Discussion

It seems interesting to compare the permittivities measured at 1 atm as a function of temperature with those measured at T = constant as a function of pressure (experimental conditions were the same). This is done in Fig. 6 where the clearing points coincide whereas the p and T scales were roughly normalised to the ranges of the N phase observed in both conditions. (It should be added that the N phase was considerably supercooled; if

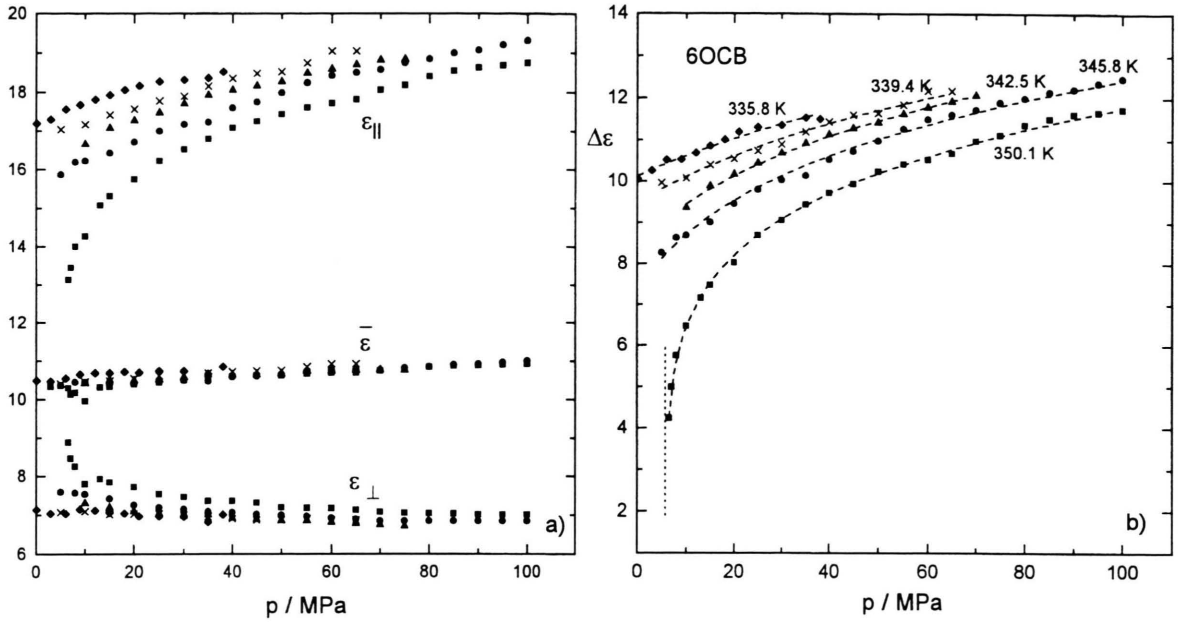

Fig. 3. The principal permittivity components and the dielectric anisotropy at five temperatures of the nematic phase of 6OCB as functions of pressure. The dashed lines are the fits as explained in the text.

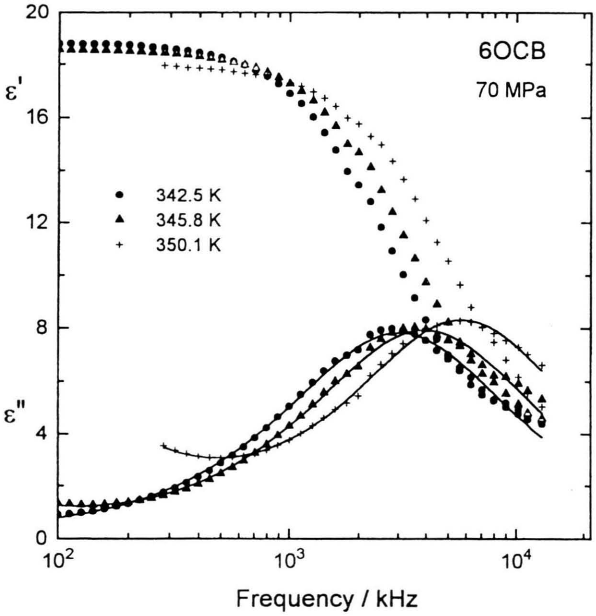

Fig. 4. Dispersion (ε') and absorption (ε'') spectra of 6OCB measured at 70 MPa and three temperatures. Solid lines are fits of the Debye equation with the conductivity contribution

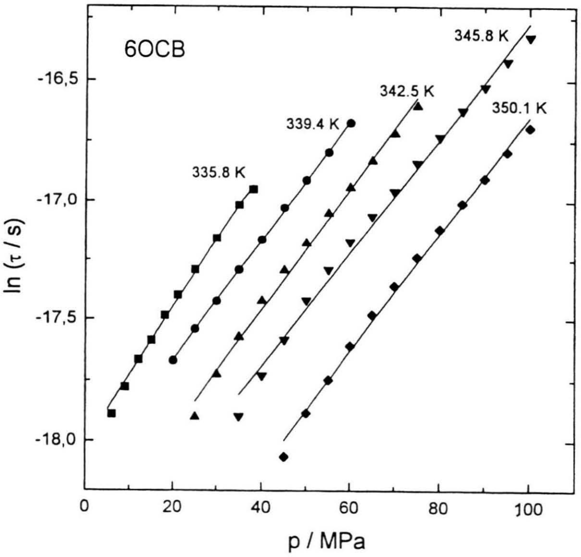

Fig. 5. Logarithm of the dielectric relaxation times as a function of pressure at five temperatures in the nematic phase of 6OCB.

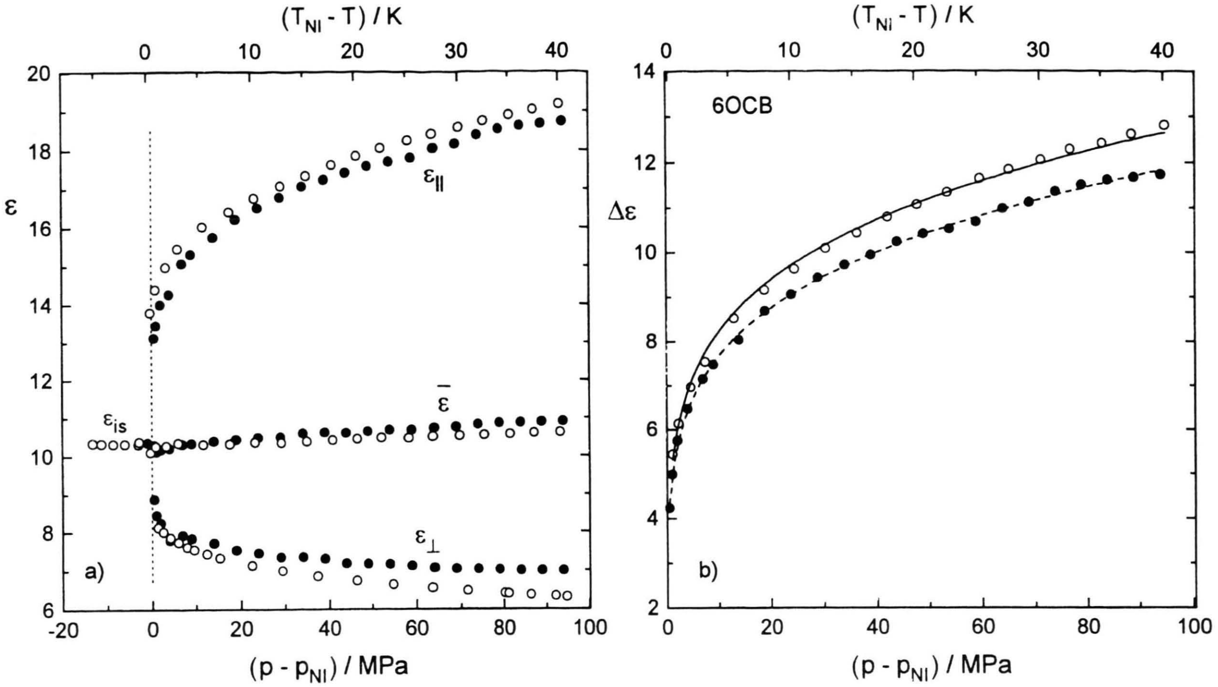

Fig. 6. Principal permittivity components and the dielectric anisotropy versus reduced temperature ($p = 1$ atm, top scale and open points) and versus reduced pressure ($T = 350.1$ K, bottom scale and full points) in the nematic and isotropic phases of 6OCB. The scales at abscissa axes are roughly normalised to the extent of the N phase observed at a given condition. The lines are the fits as explained in the text.

the temperature scale is limited to 28 K both sets of points in Fig. 6b overlap).

In order to discuss the observed differences let us consider the Maier and Meier equations [12] for the principal permittivity components and the dielectric anisotropy of the nematic phase

$$(\varepsilon_{\|} - 1) = \varepsilon_0^{-1} N \cdot F \cdot h \cdot \left\{ \bar{\alpha} + \frac{2}{3} \Delta\alpha\, S + F \frac{\mu^2}{3kT} \left[1 - (1 - 3\cos^2\beta) S \right] \right\} \quad (2)$$

$$(\varepsilon_{\perp} - 1) = \varepsilon_0^{-1} N \cdot F \cdot h \cdot \left\{ \bar{\alpha} - \frac{1}{3} \Delta\alpha\, S + F \frac{\mu^2}{3kT} \left[1 + \frac{1}{2} (1 - 3\cos^2\beta) S \right] \right\} \quad (3)$$

$$\Delta\varepsilon = (\varepsilon_{\|} - \varepsilon_{\perp}) = \varepsilon_0^{-1} N \cdot F \cdot h \cdot \left[\Delta\alpha - F \frac{\mu^2}{2kT} (1 - 3\cos^2\beta) \right] S , \quad (4)$$

where N is the number density, β is the angle between the dipole moment μ and the major inertia axis and ε_0 is the permittivity of free space, $\Delta\alpha$ and α are the polarizability anisotropy and the mean polarizability, respectively. The local field parameters F and h are expressed by the mean polarizability $\bar{\alpha}$ and mean permittivity $\bar{\varepsilon}$. $S = \langle 3\cos^2\theta - 1 \rangle / 2$ is the order parameter.

The parameters N, F, and h in the Maier-Meier equations vary little with the temperature and pressure [7]. In case of 6OCB the contributions from the polarizability might be neglected in comparison with a large dipolar contribution, so

$$\Delta\varepsilon \propto \frac{\mu^2}{2kT} S .$$

Therefore the anisotropy $\Delta\varepsilon$ varies with T like $S(T)/T$. Especially interesting seems to be the case T = constant because the dependence of $\Delta\varepsilon$ on the pressure is contained in the order parameter S only: $\Delta\varepsilon(p)_T \propto S(p)_T$. However, it was well established (e.g. [2, 3, 7, 9]) that the cyano-compounds exhibit strong dipole-dipole associations in the nematic as well as in the isotropic phase. Therefore, the dipole moment in equations (2)–(5) has to be replaced by $\mu_{\text{eff}}^2 = g\,\mu^2$, where g is the Kirkwood-

Fröhlich correlation factor. Obviously, the *g*-factor is temperature and pressure dependent.

At ambient pressure the order parameter $S(T)$ for 6OCB is known from NMR measurements [13] and can be approximated by the Haller equation: $S^{\mathrm{NMR}}(T) = S_0(T_{\mathrm{NI}}-T)^{\gamma}$ with $S_0 = 0.355$ and $\gamma = 0.192$ [11]. In Fig. 6 the solid line is the fit of eq. (4) to the experimental points with the above order parameter and with $g(T)$ varying linearly between 0.71 at T_{NI} to 0.58 at $T_{\mathrm{NI}}-T = 40$ K (for details of the calculations see [14]). Similar $g(T)$-values were obtained by Jadżyn et al. [2].

Let us assume that accordingly for $g(p)_T$-factor is given by $g(p)_T = 0.71-C(p-p_{\mathrm{NI}})$ in the range of the nematic phase at $T = 350.1$ K and that $S(p)_T$ can also be approximated by the Haller-type formula: $S(p)_T = S_p(p-p_{\mathrm{NI}})^{\gamma}$ [11]. The dashed line in Fig. 6 is the fit of $g(p)_T \cdot S(p)_T$ to the experimental points with $\gamma = 0.189$ and $C = 8 \cdot 10^{-5}$ MPa^{-1}. This means that the $g(p)_T$-factor is practically independent of the pressure which is opposite to the conclusions derived from the high pressure studies of the low frequency relaxation process in other cyanobiphenyls [9, 10].

The obtained γ-value seems to be reasonable in the light of pressure studies of other similar substances (0.17 for 5CB and 0.144 for 8PCH, see [11]). Taking the above γ-value we fitted the formula $\Delta\varepsilon = A(p-B)^{\gamma}$ (A and B being the adjustable parameters) to all measured isotherms. As can be seen in Fig. 3 the fits are quite satisfactory.

The relaxation times $\tau_{\|}(p, T)$ presented in Fig. 5 can yield the activation volume $\Delta^{\#}V_{\|} = RT(\partial \ln \tau_{\|}/\partial p)_T$ and the activation enthalpy $\Delta^{\#}H_{\|} = R(\partial \ln \tau_{\|}/\partial T^{-1})_p$. The mean value of $\Delta^{\#}V_{\|}$ is 73 ± 3 cm^3/mol and is close to that measured for 6CB [10] and similar substances [9]. The estimated activation enthalpy $\Delta^{\#}H_{\|} = 80\pm10$ kJ/mol is rather too high if one compares the ambient pressure value (68 kJ/mol [1]). The large error bar is caused by the limited temperature range available.

Summarizing one can say that a common analysis of the dielectric anisotropy of 6OCB measured at a constant (ambient) pressure and at a constant temperature enable a more extended discussion of the basic formulae describing the dielectric properties of the nematic phase. An especially interesting information concern the pressure dependence of the order parameter. The relaxation data presented in the paper can be treated as preliminary because of the inconvenient experimental conditions for this type of dielectric measurements.

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