High Pressure Dielectric Studies of 8CB in the Isotropic, Nematic, and Smectic A Phases

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The static and complex permittivity of 4-*n*-octyl-4'-cyanobiphenyl (8CB) has been measured for the isotropic, nematic and smectic A phases as functions of temperature and pressure. The ranges of 297 - 361 K, 0.1 - 220 MPa, and 0.1 - 13 MHz, were covered. Only the parallel component of the complex permittivity, $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$, was measured. The relaxation times $\tau_{\|}(p,T)$ as well as $\tau_{\text{is}}(p,T)$ were analysed at constant temperature, pressure and volume, yielding the activation volume, $\Delta^{\neq}V(T)$, activation enthalpy $\Delta^{\neq}H(p)$, and activation energy $\Delta^{\neq}U(V)$, respectively. All activation parameters calculated for the smectic A phase of 8CB are smaller than those obtained for the nematic phase. The activation energy constitutes approximately half of the activation enthalpy value in all three phases studied. The pressure study allowed to calculate the pressure dependence of the retardation factor $g_{\|}(p,T)$, from which the nematic potential $q(p,T)$ can be derived. Using the relationships between $g_{\|}$ and q/RT proposed by Kalmykov and Coffey, the order parameter $\langle P_2(p,T)\rangle$ was calculated as a function of pressure.

Key words: Liquid Crystals; 8CB; High Pressure; Dielectric; Thermodynamics; Order Parameter.

1. Introduction

In the last years various homologous series of liquid crystals have been investigated dielectrically under high pressure in our group [1]. In particular we studied the dielectric relaxation in the nematic phase for *n*-alkyl-cyanobiphenyls, (*n*CB) [2], *n*-alkyl-cyclohexyl-benzonitriles (*n*PCH) [3, 4], *n*-alkyloxy-cyanobiphenyls (*n*OCB) [5], and *n*-alkyl-bicyclo-hexyl-carbonitriles (*n*CCH) [6]. Due to the presence of the CN group these molecules possess a large longitudinal dipole moment allowing dielectric relaxation studies probing rotational motion about the short-molecular axes (the low-frequency relaxation process characterised by the relaxation time $\tau_{\|}$). From the pressure and temperature dependence of $\tau_{\|}$ we derive the activation enthalpy and the activation volume, respectively. With the help of pVT data we are able to calculate also the activation energy, i. e. we can distinguish between isochoric and isobaric temperature variation. In this work we extend previous dielectric measurements for octyl-cyanobiphenyl (8CB) [2] to higher temperatures and pressures. In particular the isotropic and smectic A phase is investigated in a larger pressure and temperature range (Figure 1).

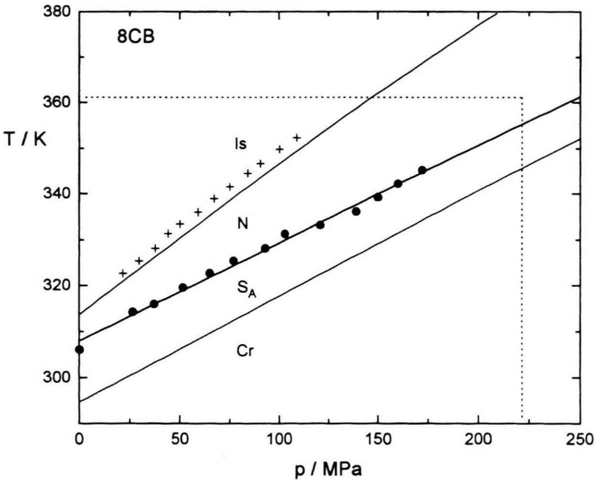

Fig. 1. Phase diagram of 8CB after [7] (solid lines) with transition points detected in the present study, dotted lines mark the limits of the pressure and temperature range accessible in this study.

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Moreover recently established pVT data for 8CB [7] enable us to analyse the volume properties of the activation parameters and retardation factors in more detail.

2. Experimental

For the dielectric measurements a high-pressure autoclave is employed that is described in [4]. The pressure is transmitted by compressed oil. The frequency dependence of the complex permittivity was measured with a computer-assisted impedance bridge Hewlett Packard 4192 A up to 13 MHz. In the nematic state the sample is oriented parallel to the probing electric field by superimposing a constant field of $E \sim$ 300 V/cm. In this way only the parallel component of the permittivity is recorded. The apparatus provides temperature and pressure readings with an accuracy of ± 0.2 K and ± 0.2 MPa, respectively.

3. Results

3.1. Complex Permittivity

In general the measurements were performed on decreasing the pressure at constant temperature. Figure 2 shows the real and imaginary part of the permittivity as functions of frequency for various pressures at 333 K. This isotherm exhibits the isotropic, nematic, and smectic A phases (for details of the phase diagram see [7]). We note that the static permittivity ε_s (low frequency value of the real part) is greatest for the nematic phase and smallest for the isotropic phase. Despite the presence of a permanent electric field to achieve molecular ordering a small but distinct step in ε_s is observed at the smectic A - nematic transition, in agreement with previous experiments [2]. The frequency of maximum loss ν_m gives us the dielectric relaxation time $\tau = 1/(2\pi\nu_m)$, from which the activation parameters are derived. In the isotropic phase we can only measure the low frequency part of the loss curves, since the frequency range of our impedance bridge is limited to $\nu < 13$ MHz. However, due to recent TDS measurements at atmospheric pressure [8], τ_{iso} has been fitted to $\tau = 3.48 \cdot 10^{-15} \exp(4502.7/T)$ that is used to adjust the pressure dependence of the relaxation time τ_{iso}.

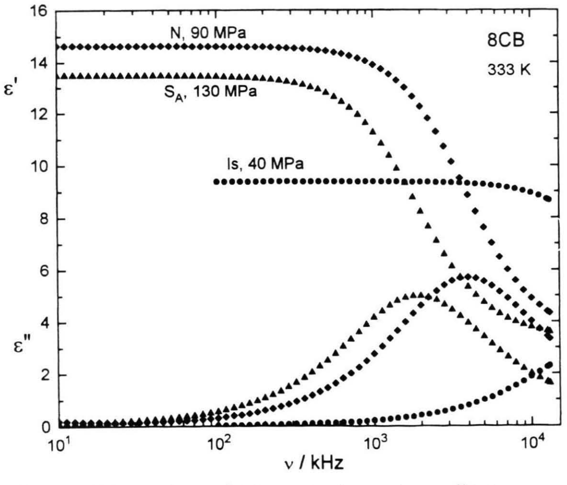

Fig. 2. Dispersion $\varepsilon'(\nu)$ and absorption $\varepsilon''(\nu)$ spectra recorded at one isotherm in the isotropic, nematic, and smectic A phases of 8CB.

3.2. Activation Parameters

The dielectric relaxation time is presented in Fig. 3 as a function of pressure for various temperatures in the isotropic, nematic, and smectic A phases. There is a distinct step at the clearing temperature, showing the slowing down of the rotational motion in the nematic phase. At the nematic-smectic transition τ changes almost continously, so the N-S$_A$ phase transition is better detected by the break in the static permittivity (compare Figure 2).

The slope of the curves in Fig. 3 defines the activation volume: $\Delta^{\neq}V_{\|} = RT(\partial \ln \tau_{\|}\partial p)_T$, which is plotted vs. temperature in Figure 4. $\Delta^{\neq}V_{\|}$ decreases with increasing temperature in all phases studied. The same temperature dependence of $\Delta^{\neq}V_{\|}$ in the smectic phase has also been found for 8OCB [5]. Surprisingly the activation volume is larger in the isotropic than in the smectic phase.

The activation enthalpy, $\Delta^{\neq}H_{\|} = R(\partial \ln \tau_{\|}/\partial T^{-1})_p$ and energy, $\Delta^{\neq}U_{\|} = R(\partial \ln \tau_{\|}/\partial T^{-1})_V$ can be derived from plots of $\ln\tau_{\|}$ against $1/T$ at isobaric and isochoric conditions, respectively. An example for the nematic phase is shown in Fig. 5, where specific volumes from Sandmann et al. [7] have been used. The results for $\Delta^{\neq}H_{\|}$ and $\Delta^{\neq}U_{\|}$ are displayed in Figure 6. $\Delta^{\neq}H_{\|}$ decreases with increasing pressure from 65 to 55 kJ mol^{-1} in the nematic phase, and from 45 to 30 kJ mol^{-1} in the smectic phase. For the isotropic phase $\Delta^{\neq}H_{\|}$ ($\sim$ 35 - 40 kJ mol^{-1}) increases negligibly, but this result should not be overestimated due to the limited measurements in the isotropic phase. From the TDS measurements [8] a value of $\Delta^{\neq}H_{iso} =$

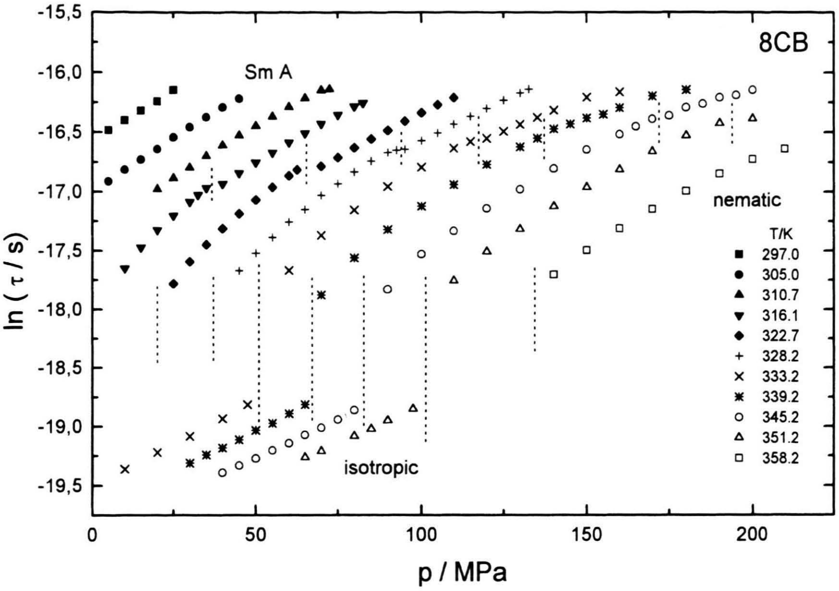

Fig. 3. Pressure dependence of the relaxation times at selected isotherms in the isotropic, nematic and smectic A phases of 8CB; the dotted lines mark the phase transitions detected in the measurements.

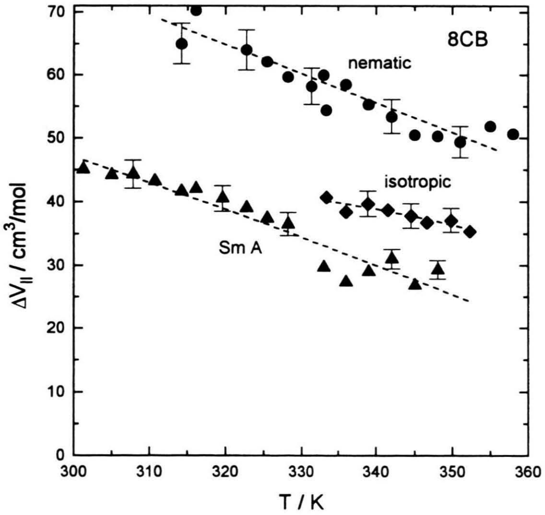

Fig. 4. Activation volume $\Delta^{\neq}V_{\|}$ as a function of temperature in the isotropic (◆), nematic (●), and smectic A (▲) phases of 8CB.

37.4 kJ mol^{-1} is derived, in good agreement with the high pressure study. The above values of the activation enthalpies correspond well with those obtained at ambient pressure [9].

The temperature and pressure dependences of the activation parameters correspond well to previous results on other similar liquid crystals [3 - 6]; in particular we note that 8CB and 8OCB [5] reveal the same pressure dependence of $\Delta^{\neq}H_{\|}$. Again we find that $\Delta^{\neq}U_{\|}$ ($\sim$ 32 kJ mol^{-1} for the nematic phase, $\sim$ 24 kJ mol^{-1} for the smectic phase, $\sim$ 20 kJ mol^{-1} for the isotropic phase) amounts to approximately half the value of $\Delta^{\neq}H_{\|}$, showing that half of the relaxation process is governed by steric effects. The same ratio was found for the volume part of the NI transition entropy [7].

The activation parameters characterising the molecular reorientation process in different phases of 8CB reveal an unexpected feature – the values for the S_mA phase are much closer to those for the isotropic than for the nematic phase. This means that the layer ordering of molecules facilitates their flip-flop motion. It should be added that such a reduction of the $\Delta^{\neq}H_{\|}$ values has also been observed at ambient pressure for other substances with the nematic - smectic A phase sequence [10, 11], but not for the nematic - smectic C phase transition [11]. In case of the other orthogonal smectic phase, S_mB, such an effect was also observed which was accompanied, however, by a considerable slowing down of the relaxation process [6, 12].

3.3. Retardation Factor and Nematic Potential

The large shift of τ at the nematic-isotropic phase transition is caused by the steric hindrances due to

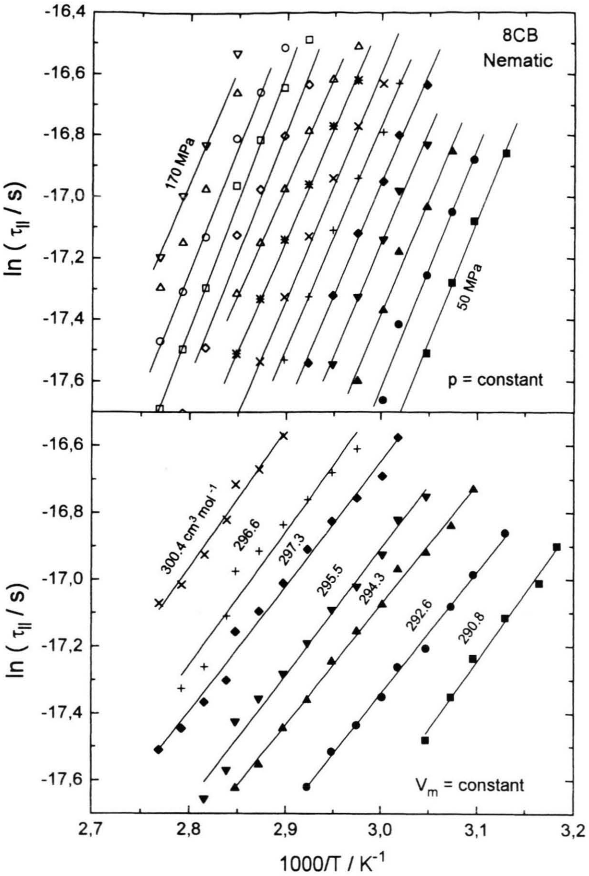

Fig. 5. Activation plots for the nematic phase of 8CB at constant pressure (in steps of 10 MPa) yielding the activation enthalpy $\Delta^{\neq}H_{\|}$, and at constant molar volume yielding the activation energy $\Delta^{\neq}U_{|}$.

the nematic order. This can be expressed as a retardation factor, $g_{\|} = \tau_{\|}/\tau_{\mathrm{o}}$, where τ_{o} is obtained by an extrapolation from the isotropic phase [1, 13]. The $g_{\|}$-factors increase from *ca.* 2.5 to *ca.* 5.4 with rising pressure and allow us to calculate the nematic potential q, as described in [13]. We have found [13] that the Kalmykov and Coffey (KC) theory [14] better relates the retardation factor $g_{\|}$ with the nematic potential barrier parameter $\sigma = q/(RT)$ and, subsequently, the order parameter S, than the well-known Meier and Saupe theory (MS [15]). Therefore we use here the KC equations

$$g_{\mathrm{II}} = \frac{e^{\sigma}-1}{\sigma}\left(\frac{2}{1+1/\sigma}\sqrt{\sigma/\pi}+2^{-\sigma}\right)^{-1}, \quad (1)$$

$$S = \frac{3S(5-\pi S)}{2(1-S^2)}. \quad (2)$$

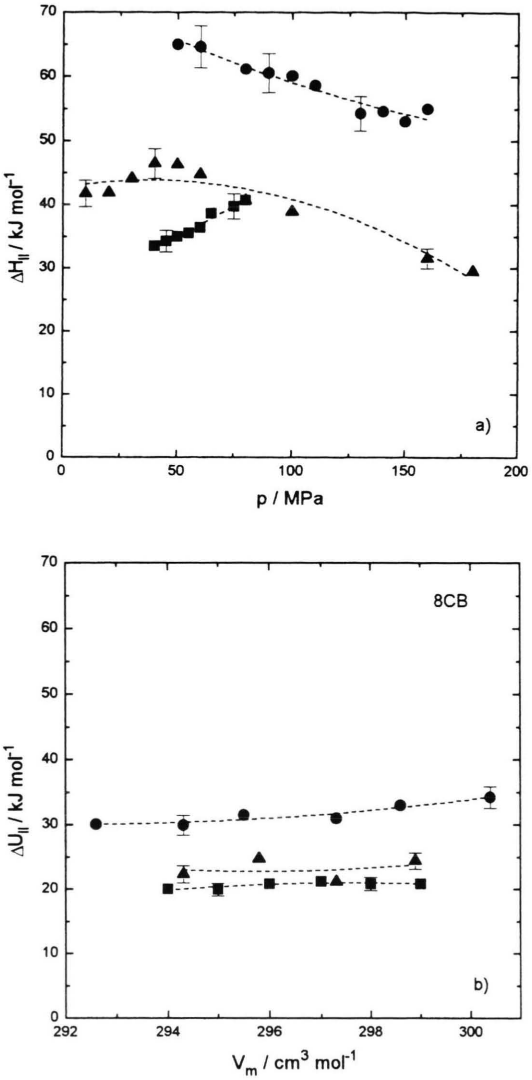

Fig. 6. Activation enthalpy as a function of pressure, and activation energy as a function of volume, obtained for the isotropic (■), nematic (●), and smectic A (▲) phases of 8CB.

The pressure dependence of the nematic potential q and the order parameter S for selected isotherms in the nematic phase of 8CB is shown in Figure 7. The calculated q values increase with increasing pressure and are considerably smaller than found for *n*PCHs [3, 4] and *n*CCHs [6]. Similar trends are observed for the activation quantities [1] and the bulk density [16]. Assuming that the order parameter can be described by the Haller-type formula $S = S_{\mathrm{o}}\cdot(p-p_{\mathrm{NI}})^{\alpha}$ [13, 17] the results presented in Fig. 7

(bottom) can be approximated well by $\alpha = 0.10$ with slightly pressure dependent S_o.

3.4. Summary

Results of the present h. p. studies of 8CB have shed more light on the dynamic properties of LC molecules in different phases. For the first time we find that the relation $\Delta^{\neq}U_{\|} \approx \frac{1}{2}\Delta^{\neq}H_{\|}$ is obeyed not only for the LC phases but also for the isotropic phase. This can be understood if we take into account the fact that the nematic potential resulting from the anisotropy of intermolecular interactions consists of only 15% of the total energy barrier hindering the flip-flop motion in the nematic phase (compare Figs. 6, 7). The rest must be related to the steric hindrances which, whilst strongly dependent on the intermolecular distance, seem to be weakly dependent on the actual phase.

Considerable decrease of all activation parameters at the N-$\mathrm{S_m}$A transition is an astonishing effect, especially if one takes into account the well-known antiparallel dipole-dipole associations observed in the diffraction [18] as well as in tunneling microscopy [19] observations. It seems that such associations are stronger in the smectic phase leading to a partial overlapping of the molecules (smectic $\mathrm{A_d}$ phase).

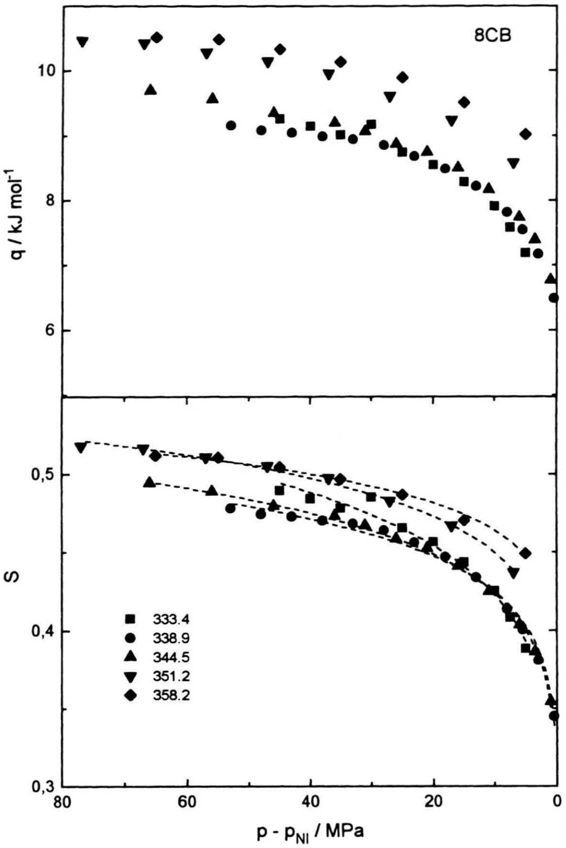

Fig. 7. Nematic potential q and the order parameter S as a function of pressure for selected isotherms in the nematic phase of 8CB; the dotted lines are fits of the Haller equation with $a = 0.10$.

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