Dielectric Studies on Liquid Crystals under High Pressure: VI. Low Frequency Relaxation Process in the Nematic and Smectic A Phase of 4-n-Octyl-4′-Cyanobiphenyl (8 CB)

S. Urban

Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland

T. Brückert and A. Würflinger

Physikalische Chemie II, Ruhr-Universität, D-44780 Bochum, Germany

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Dielectric relaxation studies of 4-n-octyl-4′-cyanobiphenyl (8 CB) were performed in the pressure range 0.1–120 MPa, the frequency range 1 kHz–13 MHz and the temperature range 295–331 K. The dielectric behaviour of 8 CB in the nematic phase is similar to that of 5 CB, 6 CB and 7 CB. In particular, the activation enthalpy decreases with increasing pressure and the activation volume decreases with increasing temperature in the nematic phase. In the smectic A phase of 8 CB both these parameters are markedly lower and show opposite pressure and temperature dependencies. We tentatively interpret these effects as a result of breaking of the dipole-dipole correlations which manifests itself differently in these liquid crystalline phases.

Key words: Dielectric relaxation; High pressure; Liquid crystals; Activation quantities.

1. Introduction

Dielectric studies can provide valuable information about characteristic properties of liquid crystals (LCs) [1–3]. Most of the dielectric measurements of liquid crystals were performed only at atmospheric pressure as a function of temperature and the frequency of the external electric field. However, our recent dielectric studies of series of LCs carried out under hydrostatic pressure have shown [4–8] that some additional information can be obtained in that way. These studies concerned mainly the relaxation process connected with the molecular reorientations around the short axes in the nematic phase of the substances having a strong dipole moment directed along the symmetry axis of the molecules. This motion is observed for the parallel orientation of a sample ($\boldsymbol{n} \parallel \boldsymbol{E}(\omega)$). Large inertia moments of the molecules and the interaction potential (the "nematic potential" [25]) opposing the rotation cause that the respective relaxation time, $\tau_{\parallel}$, is measured at MHz frequencies. Relaxations around the long axes occur at GHz frequencies.

The temperature and pressure dependencies of $\tau_{\parallel}$ yield the activation enthalpy, $\Delta^{+}H_{\parallel}$, and activation volume, $\Delta^{+}V_{\parallel}$, respectively. We have observed that both these parameters markedly decrease when we move away from the isotropic-nematic transition line, either on decreasing temperature at constant pressure or increasing pressure at constant temperature [4, 7, 8]. This led to the conclusion that relatively low pressures strongly influence the monomer-dimer equilibrium in the nematic phase, involving the breaking of well known antiparallel dipole-dipole correlations in the nCB compounds.

The substances recently studied at high pressures (h.p.) exhibit the nematic and isotropic phase. Now we report on h.p. dielectric studies of 4-n-octyl-4′-cyanobiphenyl (8 CB) which additionally has a smectic A phase (S_A). The pressure-temperature phase diagram of 8 CB has been recently obtained by DTA [9] and is presented in Figure 1. However, neither data of the pressure dependence of the order parameter S, nor p-V-T data are available for 8 CB. Therefore the discussion of the results cannot be as complete as for the other nCBs studied.

2. Experimental

The sample of 8 CB was obtained from R. Dabrowski (Military Technical Academy, Warsaw). The tran-

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Reprint requests to Prof. Dr. A. Würflinger, Physikalische Chemie II, Ruhr-Universität, D-44780 Bochum, Germany.

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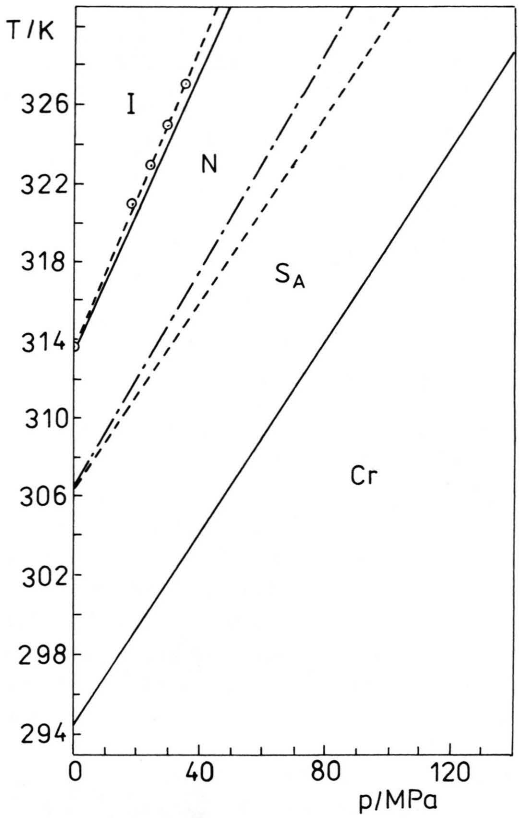

Fig. 1. Temperature-pressure phase diagram for 8 CB. −⊙−, – – – this work; —— [9]; — — — [17]. Cr, S_A, N, and I refer to the crystalline, smectic A, nematic and isotropic phase, respectively.

sition points at atmospheric pressure were: 294.8 K for the melting, 306.7 K for the smectic A-nematic and 313.8 K for the nematic-isotropic transitions, in good agreement with literature data [10–15, 17].

The experimental set-up for the dielectric measurements was the same as in previous studies and has been described in [16]. The dielectric relaxation was measured in the frequency range between 1 kHz and 13 MHz. The very low conductivity of the sample allowed us to apply a DC bias field $E \simeq 300$ V/cm which oriented the sample parallely to the measuring field ($\boldsymbol{n} \parallel \boldsymbol{E}_{\text{Bias}}$). However, it was sufficient to obtain a good orientation of the nematic phase only. The conductivity contribution to the dielectric losses was fully subtracted.

After filling the capacitor with the sample (at a temperature corresponding to the isotropic phase) we first performed the measurements at atmospheric pressure, covering the smectic, nematic and isotropic phase of 8 CB. For the smectic A phase the static permittivity reached relatively high values at atmospheric pressure when the oriented nematic phase was slowly cooled down to the smectic phase. The dielectric spectra under pressure were in general obtained by gradually decreasing the pressure at constant temperature, after pressurizing the sample to a point near the phase boundary to the solid state. Thus we also checked the phase diagram of 8 CB [9] (see Figure 1). To check the reliability of the results we repeated some runs at constant T and at about constant p. The reproducibility of the results was very good in the nematic phase (concerning the S_A phase see below).

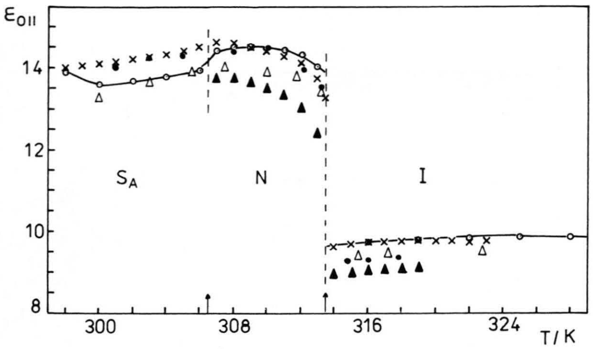

Fig. 2. Static permittivity at ambient pressure as a function of temperature. ⊙ this work; □ [14]; × [10]; ▲ [11]; △ [12].

3. Results

3.1. Measurements at Atmospheric Pressure

Figure 2 shows the static permittivity, $\varepsilon_{0\parallel}$, measured at atmospheric pressure in comparison to the results obtained by other authors [10–12, 14]. In the nematic and isotropic phase our results agree well with the results obtained by Thoen and Menu [10]. Reasons for the disagreement with other data were discussed previously [8]. For the S_A phase the static permittivity, $\varepsilon_{0\parallel}$, reached a relatively high value when the oriented nematic was slowly cooled down to the smectic phase (compare Figure 2). Small deviations from the results by Thoen and Menu may be partly caused by insufficient orientation of the smectic phase by the electric field.

In Fig. 3 a we present the variation of the dielectric permittivity ε' and the dielectric loss factor ε'' as a function of the frequency of the measuring field at different temperatures in the smectic A, nematic and

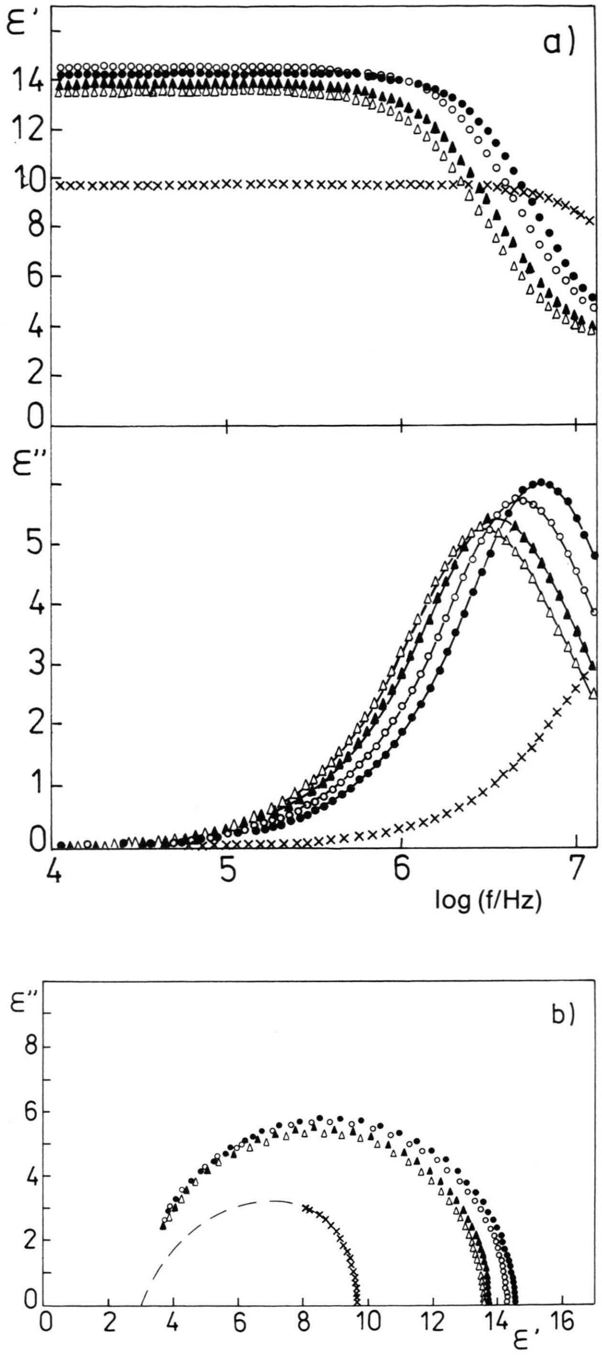

Fig. 3. (a) Dispersion and absorption spectra obtained at ambient pressure for the smectic A (△ 300 K, ▲ 304 K), nematic (○ 308 K, ● 312 K) and isotropic (× 316 K) phase of 8CB. (b) Cole-Cole plots for these spectra.

Table 1. Results of studies at atmospheric pressure.

T/K	Phase	$\varepsilon_{0\parallel}$	ε_∞	$\tau_\parallel \cdot 10^{-8}$/s	$\Delta^+ H_\parallel$/ kJ mol^{-1}	Ref.
300	S_A	13.69	3.28	5.29	44.3	pres.
302		13.78	3.33	4.77	44.0	[12]
304		13.92	3.36	4.24	44.3	[15]
306		14.08	3.44	3.75		
308	N	14.61	3.67	3.14	64.3	pres.
311		14.46	3.98	2.55	64.5	[12]
313		14.07	4.21	2.10	67.1	[15]
316	I	9.72	2.8	0.67	41.4	pres.
319		9.78	2.8	0.60	40.5	[18]
322		9.83	2.8	0.51	42.0	[15]
328		9.88	2.8	0.38		

isotropic phase of 8CB. The maximum of the loss curves is shifted to higher frequencies with increasing temperature. The curves for the smectic and nematic phase are clearly discernible. The loss curves have been fitted to the Jonscher, Havriliak-Negami, Cole-Cole, and Cole-Davidson equation. The Jonscher equation was preferred to calculate the dielectric relaxation time $\tau_\parallel$ from the frequency of maximum loss. The Cole-Cole plots (Fig. 3b) demonstrate that in the liquid crystalline phases one deals with a single relaxation domain of the Debye-type. Table 1 contains the values of the relaxation times together with the dielectric constants and the activation enthalpies $\Delta^+ H_\parallel$ calculated with use of the Arrhenius equation: $\Delta^+ H_\parallel = R\left(\partial \ln \tau_\parallel / \partial \frac{1}{T}\right)_p$. Thus our results corroborate previous findings [12, 15] that the activation barrier hindering molecular reorientations around the short axes is lower in the smectic A phase than in the nematic phase of 8CB.

In the isotropic phase the low and high frequency processes merge to give one broad relaxation spectrum. Due to the frequency limit of our bridge (≤ 13 MHz) we could only measure part of the loss curve in the isotropic phase. Therefore we used the Cole-Davidson equation with a fixed value for ε_∞ in order to fit the incomplete loss curves. The value for ε_∞ was taken from a dielectric study of the nCB substances in the isotropic phase carried out over a much broader frequency range [18]. The results are given in Table 1.

3.2. Measurements at Elevated Pressures

We tried to obtain an oriented smectic A phase by slowly changing the temperature at constant p close to

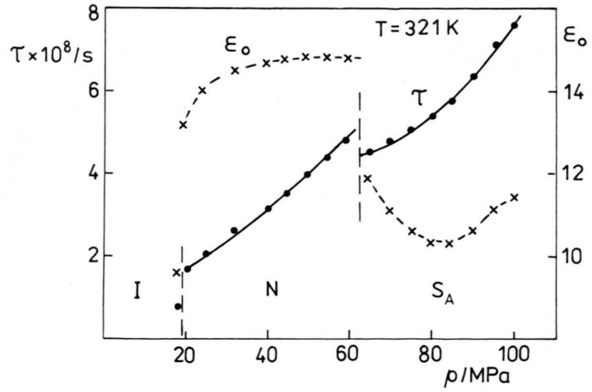

Fig. 4. Example of the pressure dependence of the static permittivity and relaxation time showing step-wise changes at the phase transitions. $T = 321$ K.

the N–S$_A$ transition line. However, the permittivity always dropped to relatively small values (see Fig. 4) in some distance from the transition. Therefore we started with measurements from points near the freezing line and reduced the pressure at constant temperature. The S$_A$–N transition was always observed by step-wise change of both the permittivity and the relaxation time (Figure 4). The transition line obtained in this way is shown in Fig. 1 (with an error ± 0.2 MPa at each T); it differs substantially from the line reported in [17]. In spite of the non-reproducibility of the values of permittivity ε' and losses ε'', the positions of the maxima of losses on the frequency scale were well reproducible within the S$_A$ phase. That allows us to calculate the relaxation times $\tau_{\|}$ as function of p and T in the S$_A$ phase, too.

In Fig. 5a we present some examples of the frequency dependence of the real and imaginary parts of the complex permittivity measured at different pressures in the smectic A, nematic and isotropic phase of 8CB. The maximum of the loss curves is shifted to higher frequencies with decreasing pressure. In the LC phases the dielectric spectra obey a single Debye relaxation very well (see Fig. 5b), whereas in the isotropic phase the Cole-Davidson skew arc is more appropriate. The relaxation times $\tau_{\|}$ calculated with the use of the Jonscher equation for different pressures in N and S$_A$ phase are presented in semi-logarithmic scale in Figure 6. In both phases the relaxation times are not a strictly exponential function of the pressure, the $\ln \tau_{\|}$ vs. p curves are bent towards opposite sides. Neglecting this small effect, we have calculated the slopes of the curves by means of linear regres-

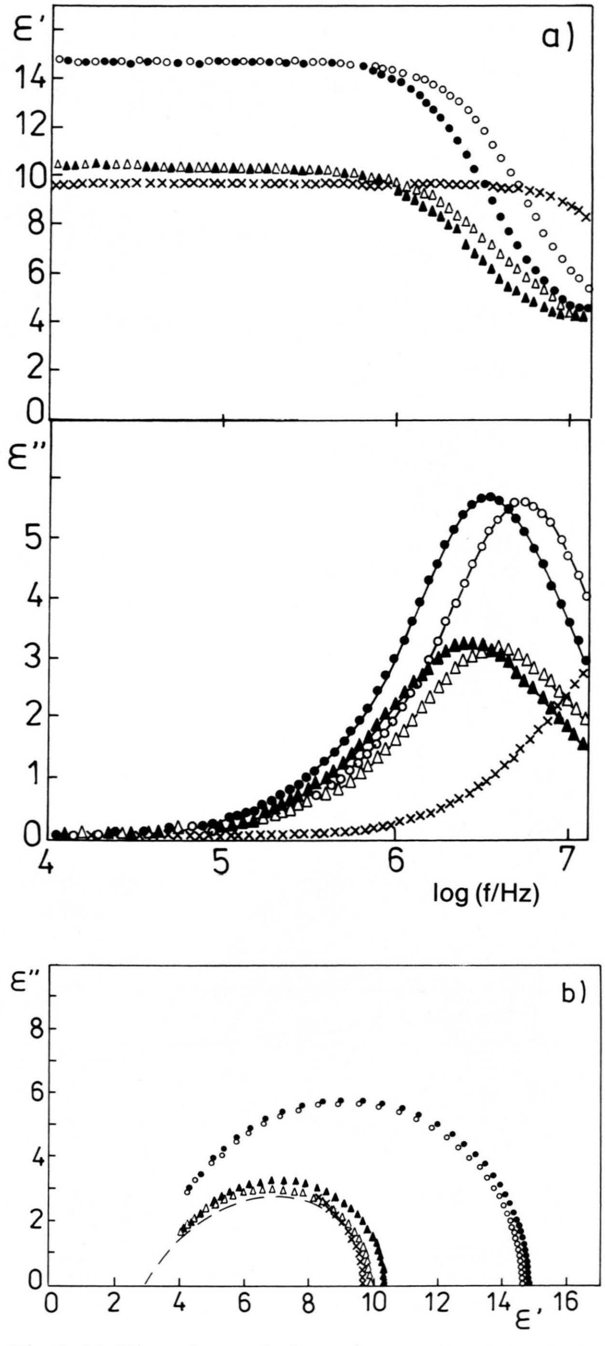

Fig. 5. (a) Dispersion and absorption spectra at constant temperature (319 K) and different pressures: ▲ 80.5 MPa, △ 60.0 MPa (smectic A phase); ● 50.0 MPa, ○ 30.0 MPa (nematic phase); × 15.0 MPa (isotropic phase). (b) Cole-Cole plots for these spectra.

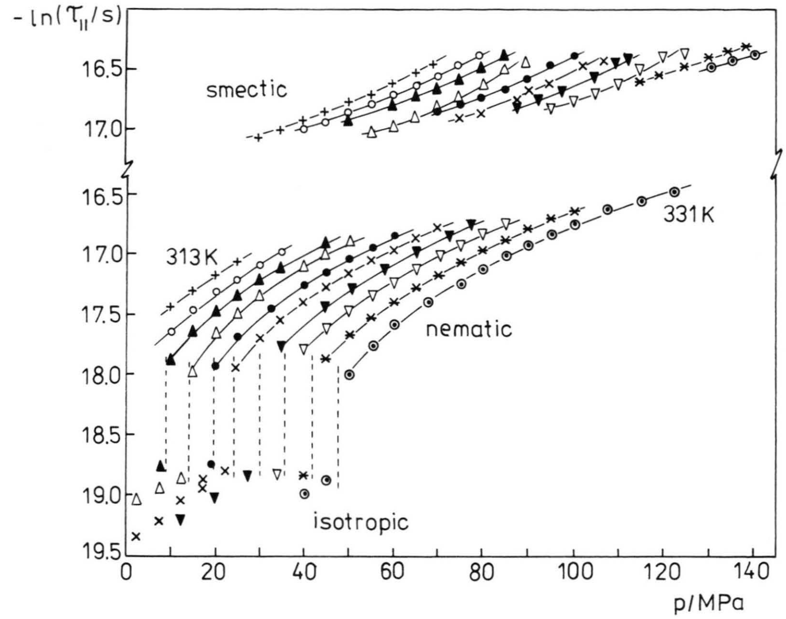

Fig. 6. ln $\tau_{\|}$ versus p plots for the smectic, nematic and isotropic phase of 8CB at different temperatures; the temperatures for different isotherms varies in steps of 2 K.

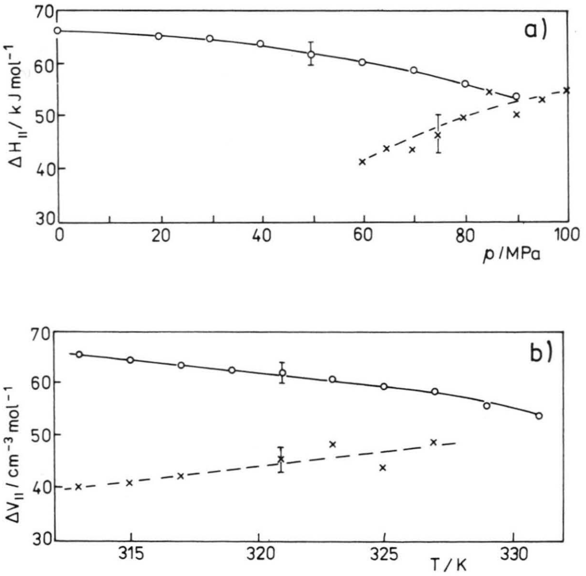

Fig. 7. Activation enthalpy, $\Delta^{+}H_{\|}$, as a function of pressure, and activation volume, $\Delta^{+}V_{\|}$, as a function of temperature for the nematic (o) and smectic A (×) phase of 8CB.

sions which yield the activation volume: $\Delta^{+}V_{\|} = RT(\partial \ln \tau_{\|}/\partial p)_T$. In Fig. 7a and 7b we present the activation volume as a function of temperature and the activation enthalpy as a function of pressure for the nematic and smectic A phase of 8CB.

4. Discussion

The nematic and smectic A phase are two of the more common intermediate phases between the crystal and the isotropic liquid. The nematic phase has a high degree of long-range orientational order of the molecules, but no long-range translational order. The smectic A phase has a layered structure with layer planes perpendicular to the preferred direction of molecular long axes; within the layers the centres of mass of the molecules are randomly distributed. In both phases the degree of long-range orientational order is similar [19] and there is an equivalency of "up" and "down" directions of the symmetry axes of the molecules. In spite of some similarities of molecular arrangements in both phases the activation enthalpy, $\Delta^{+}H_{\|}$, characterizing the molecular reorientations around the short axes, is markedly lower in the smectic A than in the nematic phase. This has been shown in dielectric studies of different types of LC substances (8CB – [12] and the present paper, "swallow tail" compounds [20], isothiocyanato compounds [21]). It seems therefore that the smectic A structure always facilitates a "flip-flop" molecular motion.

The X-ray diffraction [22] as well as the scanning tunneling microscope [23] studies have shown that the smectic layers of 8CB are formed by antiparallel molecular aggregates with interdigitated neighbouring cyano groups. Such a molecular arrangement re-

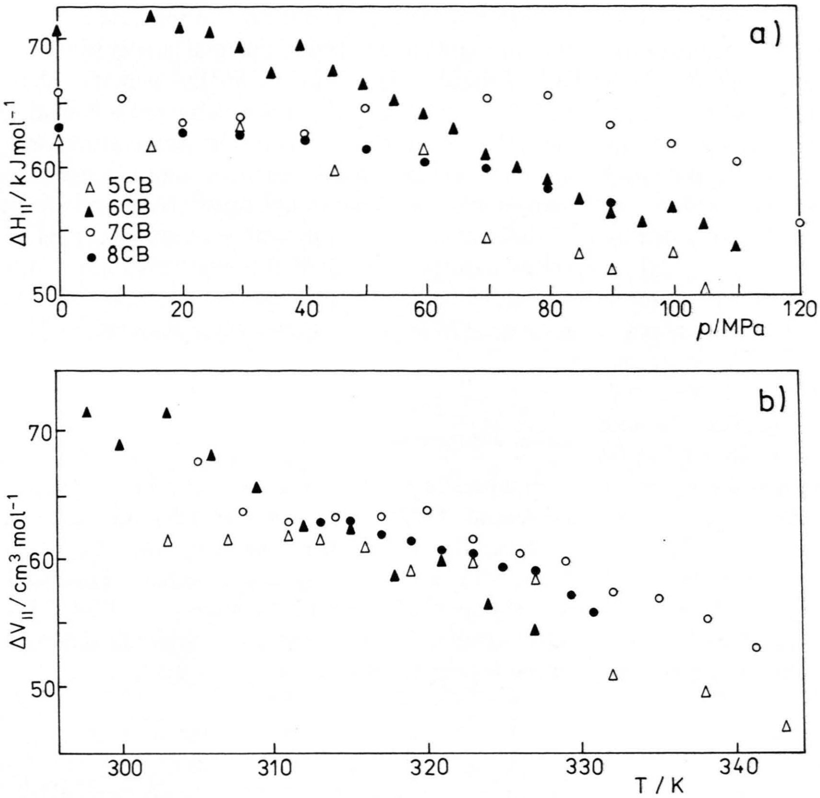

Fig. 8. Comparison of the pressure dependence of the activation enthalpy (a) and temperature dependence of the activation volume (b) of the nCB substances in the nematic phase. △ 5CB, ▲ 6CB, ○ 7CB, ● 8CB.

duces the electrostatic repulsions between the dipoles of the cyano groups and, in consequence, distinctly depresses the static permittivity $\varepsilon_{0\|}$ (the Kirkwood *g* factor is ca. 0.4 [12, 24]). Similar antiparallel correlations of molecules characterize also the nematic phase of cyanobiphenyls [24].

Our recent high pressure dielectric studies of nCB substances [4, 7, 8] have shown that both activation parameters, enthalpy and volume, systematically decrease when we move away from the isotropic-nematic transition line. That led us to the conclusion that relatively low pressures strongly influence the monomer-dimer equilibrium involving the breaking of molecular associations. Thus, the question arises: does pressure influence the molecular associations in the smectic A phase of 8CB in the same way as in the nematic phase?

The results of dielectric relaxation studies presented in Fig. 7a indicate that the activation enthalpy increases with pressure in the smectic A phase, whereas it is a decreasing function of pressure in the nematic phase, similarly to other nCB substances [4, 7, 8] (although in the 8CB case the decrease is not so pronounced – see Figure 8a). A similar behaviour is observed for the activation volume (see Fig. 7b and Figure 8b). Paradoxically, these effects mean that the pressure destroys the molecular associations in the smectic phase of 8CB, too. The existence of antiparallel molecular aggregates causes that the layer thickness, *d*, is distinctly larger than the length of the molecules, *l* ($d/l \simeq 1.4$ [22, 23]). Therefore some excluded volume [25] is supposed to facilitate the molecular reorientations. If the pressure destroys the molecular associations, the excluded volume becomes smaller and the molecules become more closely packed in the layers. Thus the activation parameters increase with increasing pressure in the smectic A phase. If this hypothesis is valid one should observe a decrease of the layer thickness with pressure. The X-ray experiment under pressure would be decisive in that respect. Such decreasing of the layer thickness with pressure was observed in the S_A phase of octyloxycyanobiphenyl (8OCB) in the pressure range used in our experiment [26].

The nCB substances can be considered as model systems when the dielectric properties are treated in terms of the mean field theory of the nematic state by Maier and Saupe [27]. On that basis Meier and Saupe [28] derived the so called retardation factor $g_{\parallel}$, which is a measure of the slowing down of the relaxation time characterizing the molecular reorientations around the short axes due to the nematic potential q: $g_{\parallel} = \tau_{\parallel}/\tau_0 = (RT/q)[\exp(q/RT) - 1]$, where τ_0 corresponds to the case $q = 0$ that can be estimated by extrapolation from the isotropic phase [1, 2, 28]. It should be noted, however, that such extrapolation is only justified when the dipole moment is directed along the symmetry axis of the molecule as for the discussed nCB series. Taking the data of Table 1 into consideration, we find values for q between ~4 and ~5 kJ/mol in the range of the nematic phase of 8CB. Rough estimations using the data shown in Fig. 6 gave similar values of the nematic potential at higher pressures, too. For details of calculations see [4–8].

The following important information could be derived from our dielectric studies [5–8]: (i) The nematic potential, q, varies between ca. 3 kJ/mol near to T_{NI} and ca. 6 kJ/mol near to the melting temperature (or nematic/smectic transition – in the case of 8CB). (ii) q amounts to ca. 10% of the total barrier hindering the molecular reorientation in the nematic phase ($\Delta^+ H_{\parallel} \sim 60$ kJ/mol). (iii) q is roughly proportional to the order parameter S at constant temperature, pressure and volume [6–8]; corroborating the main assumption of the Maier-Saupe theory. (iv) The decrease of the activation enthalpy with pressure, observed for the nematic phase of all nCB compounds studied [4, 7, 8] (Fig. 8), can be understood if one assumes that the pressure destroys the dipole-dipole associations [7].

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