

DTA and Dielectric Studies of a Substance with the Nematic, Smectic A and Smectic C Polymorphism at Ambient and Elevated Pressures

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For the first time the low frequency relaxation process in two liquid-like smectic phases (smectic A and smectic C) was studied at elevated pressures with the aid of DTA and dielectric spectroscopy methods. The substance studied, 2-(4-hexyloxyphenyl)-5-octylpyrimidine (6OPB8 in short) exhibits the nematic (N) – S_A – S_C phase sequence. The p-T phase diagram was established with DTA. However, the S_A – S_C transition was not observed in the DTA, but could be detected in the dielectric relaxation measurements. The dielectric relaxation time measured as function of temperature and pressure, $\tau_{||}(p,T)$, enabled us to calculate the activation volume, $\Delta^{\#}V = RT(\partial \ln \tau / \partial p)_T$, and activation enthalpy, $\Delta^{\#}H = R(\partial \ln \tau / \partial T^{-1})_p$. It was found that $\Delta^{\#}V(S_A) > \Delta^{\#}V(S_C)$ and $\Delta^{\#}H(N) \gg \Delta^{\#}H(S_A) > \Delta^{\#}H(S_C)$ indicating that the molecular rotations around the short axes are more feasible in the tilted S_C than in the orthogonal S_A phase.

I. Introduction

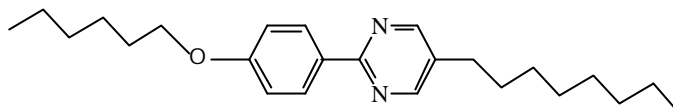
Dielectric relaxation method is a useful tool for analyzing the rotation motions of polar molecules in liquid crystalline (LC) phases. In the case of rod-like molecules two reorientation processes have to be distinguished that are related to the rotations around the short and long molecular axes. In the nematic (N) phase they are studied in two geometries when the measuring field is parallel and orthogonal to the director \mathbf{n} . The dipole components, longitudinal $\mu_{||}$ and transverse μ_{\perp} , are responsible for the low frequency (occurring in MHz frequencies) and high frequency (falling on hundreds MHz or even GHz frequencies) relaxation processes, respectively. The relaxation times $\tau_{||}$ and τ_{\perp} are characteristic quantities describing the rates of the respective processes. In this paper we shall be dealing with the low frequency process only.

Dielectric relaxation studies of liquid crystals under elevated pressure were performed for several substances with the nematic [1-3], nematic and smectic A_d [4,5], smectic A_l [6,7] and smectic (crystalline) E [8-10] phases. The low frequency relaxation time characterizing the molecular rotations around the short axes was analysed as a function of pressure at constant temperature yielding the activation volume, $\Delta^{\#}V = RT(\partial \ln \tau / \partial p)_T$, as a function of temperature at constant pressure yielding the activation enthalpy, $\Delta^{\#}H = R(\partial \ln \tau / \partial T^{-1})_p$, and as function of temperature at constant volume (density) yielding the activation energy, $\Delta^{\#}U = R(\partial \ln \tau / \partial T^{-1})_V$ (R - gas constant). The substances studied belong to two-ring homologous series with the alkyl or alkoxy tail from one side and the strongly polar CN or NCS group at the other side of molecules. The following interesting results are worthy to be pointed out.

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The values of the activation volume, which may be considered as the free volume the molecules need in order to perform the rotational jump over the potential barrier, are of the order of 60 - 70 cm³/mol for the nematic and smectic E phases, whereas for the smectic A phases they are markedly lower [4,5,8]. Analogous features concern also the behaviour of the activation enthalpy in particular phases. Independently of the phase studied (nematic, smectic A_d or the crystal-like smectic E phase) the activation energy amounts to approximately half of the activation enthalpy [7,9] which indicates that both temperature and volume effects determine the molecular rotations around the short axes in LC phases to the same extent. In the present work yet another liquid-like phase, the smectic C phase, will be studied as function of temperature and pressure. The substance chosen, 2-(4-hexyloxyphenyl)-5-octylpyrimidine (6OPB8 in short)



exhibits the following phase sequence: crystalline (Cr) - smectic C (S_C) - smectic A (S_A) - nematic (N) - isotropic (Is). However, its molecular structure differs from those previously studied because of the presence of flexible wings at both sides of the molecule. Thus, one may expect some different behaviour of quantities characterising the molecular rotations around the short axis in particular phases.

II. Experimental

The 6OPB8 sample was synthesised in the Institute of Chemistry, Military University of Technology, Warsaw. DTA measurements have been carried out with the set-ups described in [11,12]. Heating rates of 1 or 2 K/min were applied.

The measurements at 1 atm of the complex dielectric permittivity, $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$, have been carried out in the frequency range of 10 kHz - 15 MHz (Agilent 4192A impedance analyser) and temperature range covering all LC phases. A parallel-plate capacitor ($C_0 \approx 50$ pF) was calibrated with the use of standard liquids. The measurements were carried out with heating and then cooling of the sample. During the collection of the spectra the temperature was stabilised within ± 0.1 K. The high pressure experiment was performed at the Institute of Physics of the Silesian University, Katowice. For measurements at elevated pressure we used a Novo-Control GmbH dielectric spectrometer equipped with a Novo-Control Alpha dielectric analyzer. The sample was placed in specially designed capacitor, with gap $d = 0.3$ mm and $C_0 = 6.6$ pF, made from Invar. The capacitor contained 0.3 cm³ of the sample. The pressure was transmitted to the sample by deformation of 0.05 mm Teflon membrane [13-15]. The sample was always isolated from the pressurizing medium (mixture of heptane and silicon oil). The capacitor was placed in a chamber, the pressure was generated via a hydraulic press. The pressure was measured by a Nova Swiss tensometric pressure meter (resolution ± 0.1 MPa). Temperature was controlled within ± 0.1 K by liquid flow from a thermostatic bath. Data were analyzed by means of 6.1 ORIGIN software.

III. Results

P-T phase diagram. Figure 1 presents the temperature - pressure phase diagram established for 6OPB8 in the pressure range up to 170 MPa. Typical DTA traces are shown in the insert of Fig. 1. The transition between both smectic phases was not detected in DTA measurements. At ambient pressure this transition could be detected under polarizing microscope equipped with a hot stage. Also the dielectric relaxation data measured in function of temperature could detect this transition (see below). The open points in the phase diagram

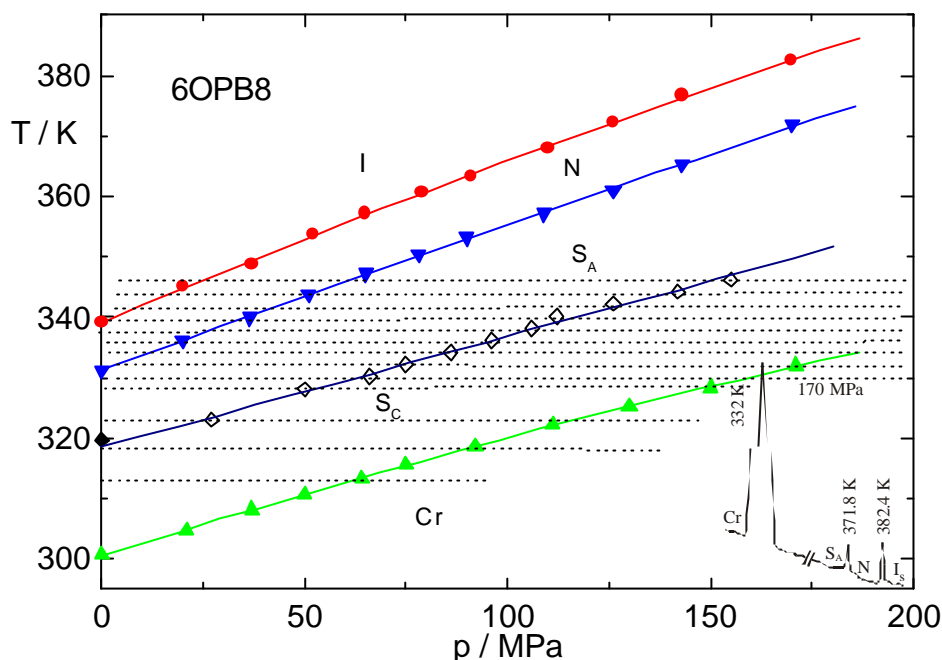


Figure 1. Pressure-temperature phase diagram for 6OPB8. Full points - DTA results, open points - derived from the dielectric measurements (compare Figure 6). Horizontal dotted lines indicate the isotherms at which the dielectric measurements were performed. The insert presents a typical DTA trace.

were established from the analysis of the dielectric results (see Figure 6). The extrapolation to 1 atm of the straight line fitted to the points well agrees with the observed transition temperature T_{A-C} . The pressure dependence of the transition temperatures can be expressed by quadratic polynomials with the parameters in Table 1.

Table 1. The parameters of the polynomial $T/K = a + b \cdot (p/\text{MPa}) + c \cdot (p/\text{MPa})^2$ fitted to the transition points shown in Figure 1.

| Transition | a | b | $c \cdot 10^4$ |
|-----------------------|-------|-------|----------------|
| N \rightarrow Is | 339.2 | 0.234 | 1.68 |
| $S_A \rightarrow$ N | 331.3 | 0.247 | 0.58 |
| $S_C \rightarrow S_A$ | 318.5 | 0.184 | – |
| Cr $\rightarrow S_C$ | 300.5 | 0.213 | 1.74 |

Dielectric studies at 1 atm. At ambient pressure the 6OPB8 sample was studied in the heating and then the cooling runs. For the former case the sample reacted on the orienting magnetic field (0.8 T) after transition to the nematic phase only. On cooling the alignment adjusted in the N phase did not survive to the S_A phase. The results of measurements of the static permittivities $\epsilon_{s\parallel}$ and $\epsilon_{s\perp}$ are shown in Figure 2. Typical absorption spectra measured in particular phases of 6OPB8 (heating rate) are presented in Figure 3a. They can be very well described by the Debye equation

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty) \omega \tau}{1 + (\omega \tau)^2} + \frac{s}{\epsilon_0 \omega}, \quad (1)$$

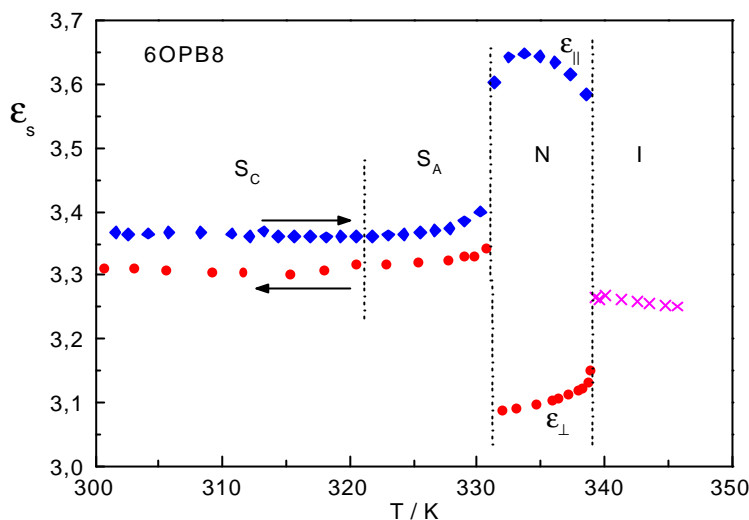


Figure 2. Static dielectric permittivities measured in different phases of 6OPB8 for the parallel orientation (heating run) and the perpendicular orientation (cooling run) of the sample.

where ϵ_s and ϵ_{∞} are the static and high frequency permittivities, respectively, $\omega = 2\pi f$, f is the frequency, ϵ_0 – free space permittivity, and τ is the dielectric relaxation time. At low frequencies (especially in the N phase) the conductivity term $\sigma/\epsilon_0\omega$ was substantial (low frequency wings in the spectra presented in Figure 3a). The determined relaxation times τ_{\parallel} are presented in Figure 4 in form of the activation plot $\ln\tau_{\parallel}$ versus T^{-1} for heating run. The data for the heating and cooling runs agree very well. The transition temperatures observed on heating correspond excellently with the points in the phase diagram, Figure 1. On cooling the transition $S_A \rightarrow S_C$ was considerably shifted down from 319 K to 313 K (see insert). The activation enthalpy, $\Delta^{\#}H_{\parallel} = R(\partial \ln\tau_{\parallel} / \partial T^{-1})$, determined from the plots in Figure 4 are: 173 ± 5 kJ/mol in the N phase, 83 ± 3 kJ/mol in the S_A phase, and 70 ± 3 kJ/mol in the S_C phase.

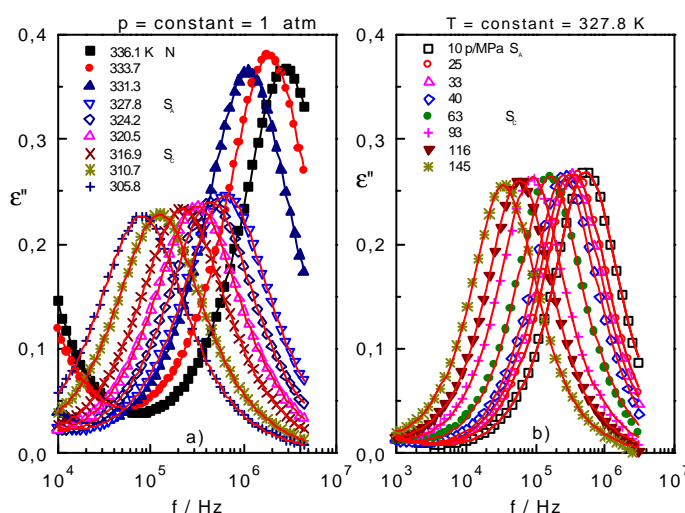


Figure 3. Typical absorption spectra measured in the S_A and S_C phases of 6OPB8 at 1 atm in function of temperature (a), and at constant temperature in function of pressure (b). The sample could not be aligned in smectic phases which resulted in different amplitudes of the dielectric losses. The lines are the fits of the Debye equation.

Relaxation studies at elevated pressures. Figure 3b presents typical absorption spectra collected at constant temperature and different pressures. In these measurements the sample was not oriented at all. The Debye formula fits the spectra excellently. The relaxation times determined from the frequency corresponding to the maximum of losses ϵ''_{\max} , $\tau = 1/(2\pi f_{\max})$, are presented in Figure 5 as $\ln\tau_{\parallel}$ versus p plots. The slopes of the lines fitted to the points yield the activation volume $\Delta^{\#}V_{\parallel} = RT(\partial\ln\tau_{\parallel}/\partial p)_T$. Looking at the activation plot in Figure 4 one could expect that in the pressure studies some differences in the behaviour of the relaxation time τ_{\parallel} in both smectic phases would be seen as well. Figure 6 shows that the transition between S_A and S_C phases is really visible as the change of the slopes of straight lines fitted to the low and high pressure parts of the data. The transition pressures taken as the crossing point of the lines were put on the phase diagram (Figure 1) and marked by the open points. As one can see they lie on a straight line which intercepts the $p = 0$ axis close to the transition point determined from the optical observation at 1 atm. This happens because the measurements were done with the increasing of pressure (that corresponds to rising of temperature).

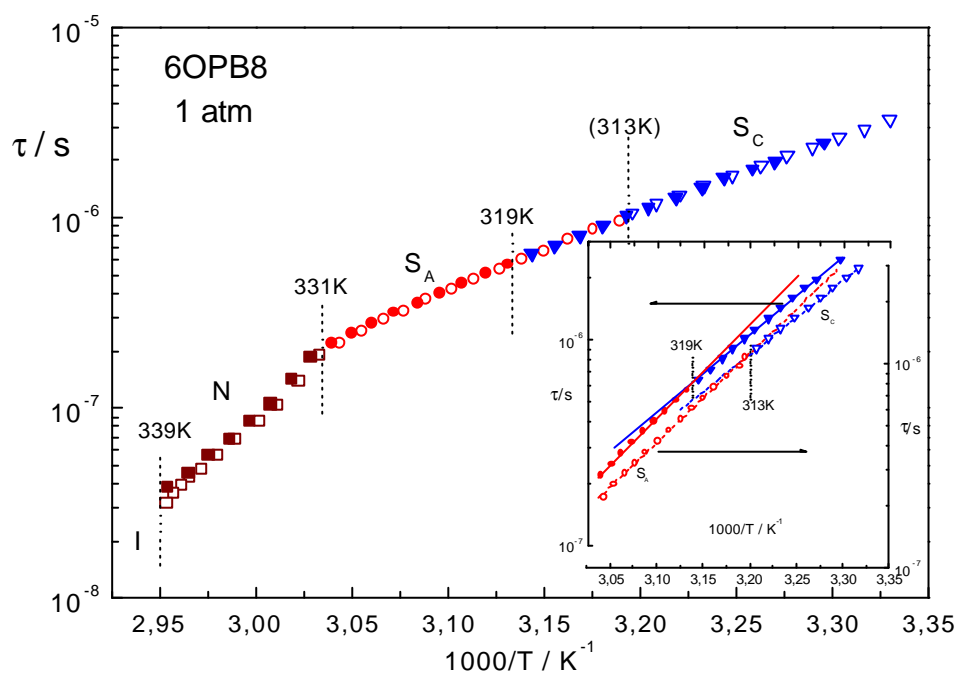


Figure 4. Activation plot for the low frequency relaxation process in LC phases of 6OPB8 at 1 atm. Full points correspond to the heating and open points to the cooling run. The insert shows in larger scale the vicinity of the $S_A - S_C$ transition for both runs.

The values of the activation volume determined for both smectic phases of 6OPB8 are presented in Figure 7a and compared with the data obtained recently for several other compounds (Figure 7b).

The establishment of the $S_A \rightarrow S_C$ transition line allows us to analyse the relaxation times in function of inverted temperature at constant pressures separately for the S_A and S_C phases. Figures 8a,b show that the points lie nicely on straight lines in a broad range of pressures. The slope of the lines yield the activation enthalpy $\Delta^{\#}H_{\parallel} = R(\partial\ln\tau_{\parallel}/\partial T^{-1})_p$ that are presented in Figure 9a and compared with the data obtained for other two-ring compounds in different phases (Figure 9b).

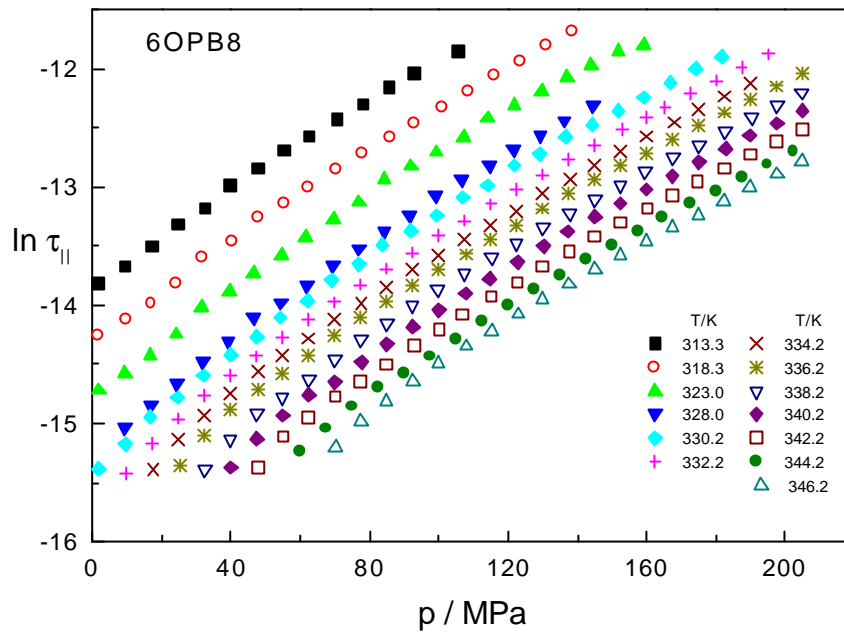


Figure 5. $\ln \tau_{||}$ versus pressure for all isotherms studied within the S_A and S_C phases of 6OPB8.

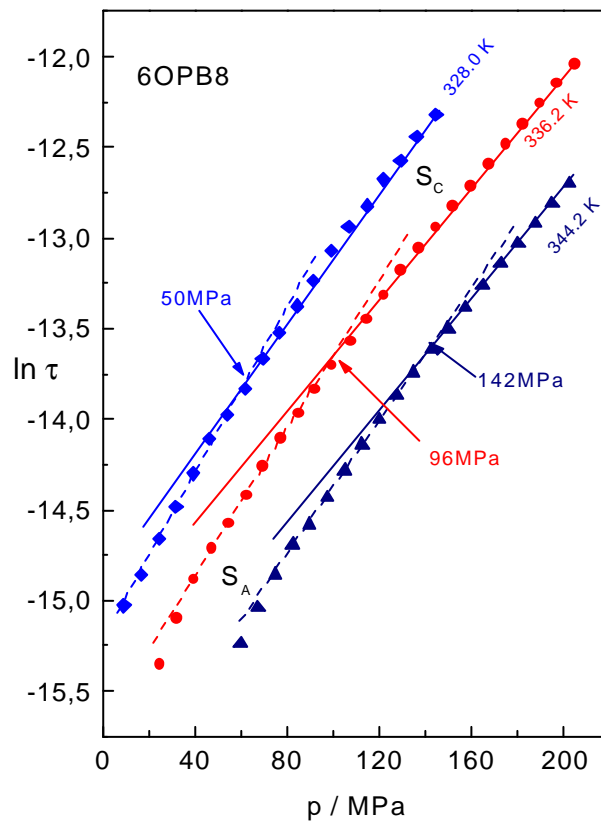


Figure 6. Three isotherms from Figure 5: the straight lines fitted to the low and high pressure parts allow for calculation of the activation volume for both smectic phases, and from intersection of the lines to determine the transition pressures indicated in Fig. 1 as open points.

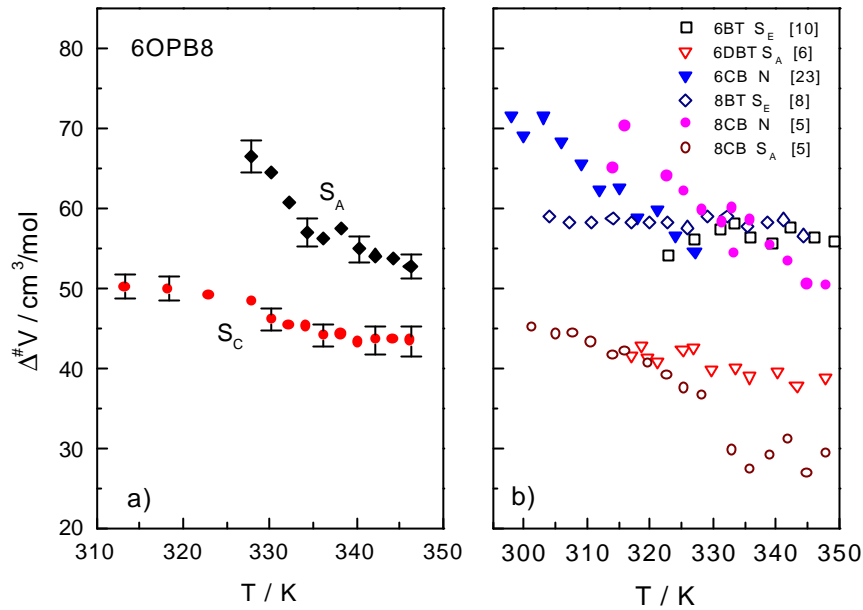


Figure 7. Activation volumes versus temperature a) determined for 6OPB8 in the S_A and S_C phases, and b) obtained for several alkyl — two-ring — CN or NCS compounds in different phases.

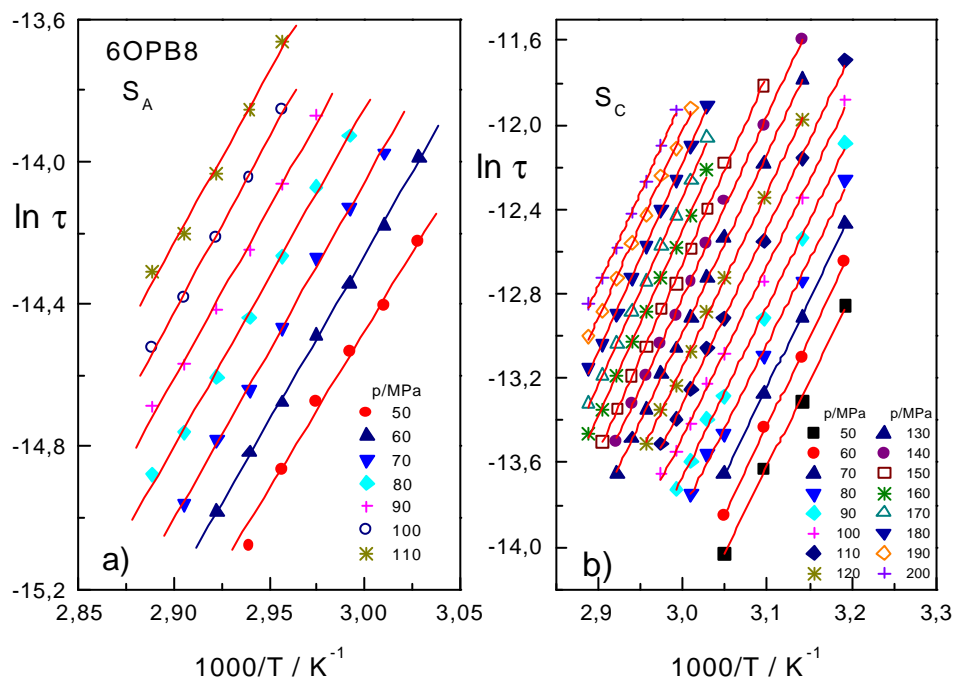


Figure 8. Activation plots for several isobars within the S_A and S_C phases of 6OPB8. The points were taken from the data in Figure 5 using interpolations shown in Figure 6.

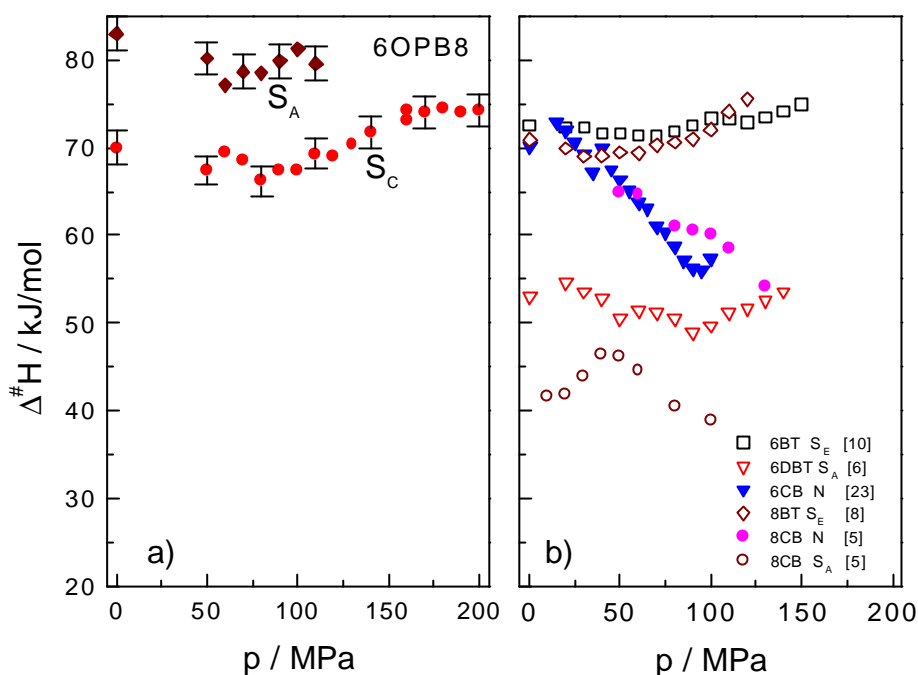


Figure 9. Activation enthalpy versus pressure determined for 6OPB8 in the S_A and S_C phases (a), and obtained for several alkyl — two-ring — CN or NCS compounds in different phases (b).

IV. Discussion

The 6OPB8 molecule consists of two dipolar groups: the pyrimidine ring and the hexyloxy tail. According to Kresse [16] the longitudinal component of the dipole moment $\mu_l = 1.5$ D, whereas the transverse component $\mu_t = 1.2$ D. The values of permittivity components in the N phase, shown in Fig. 2, reflect roughly the dipole structure of the molecule ($\epsilon_{\parallel} - \epsilon_{\infty} \sim \mu_l^2$, $\epsilon_{\perp} - \epsilon_{\infty} \sim \mu_t^2$, with $\epsilon_{\infty} \approx 2.8$). The experimental geometry ($\mathbf{E} \parallel \mathbf{B}$) and the available frequency range (up to 10 MHz) allow for the study of the low frequency relaxation process only.

Figures 4 and 5 show that the l. f. relaxation time does not change stepwise at the transitions between all liquid-like phases, in accordance with other studies done for substances with the same phase sequence [17-20]. As usually, a large decrease of the activation barrier hindering molecular rotation around the short axis when the nematic phase transforms to the smectic A phase is observed, Figure 4 and refs. [1,5,17-24]. Madhusudana et al. [23,24] have suggested that such lowering of the activation barrier is due to the anisotropic packing effects: the volume expansion mainly causes an expansion within the smectic layer whereas the layer spacing hardly varies with temperature; this favours a lowering of the activation energy in the smectic A phase. It is characteristic that the activation barrier is even smaller in the tilted than in the orthogonal smectic phase. Similar behaviour was noted for other smectogens [17-20] as well.

Figure 7a shows that the activation volume diminishes with raising temperature (and thus with increasing pressure - compare Figures 1 and 5). Similar effect was noted for several cyanobiphenyls (Figure 7b) [1,5,25] and was interpreted as a result of the breaking of the dipole-dipole associations with pressure. In the case of 6OPB8 one can rather suppose that the

increasing pressure favours less extended conformers of the hexyloxy and octyl tails which reduces the total molecular length. In the orthogonal smectic A phase the effect is stronger than in the tilted smectic C phase. The values of $\Delta^\#V$ in smectic phases of 6OPB8 (Figure 7a) are larger than those established for other smectics studied (Figure 7b) which may be connected with different lengths of molecules.

The nematic phase of 6OPB8 was not studied under pressure in this work but one can assume that the value of the activation enthalpy $\Delta^\#H \approx 170$ kJ/mol determined at ambient pressure cannot change markedly with pressure. Thus, the reduction of the barrier hindering the molecular rotation around the short axes in the smectic A phase with respect to the nematic phase is much greater in the case of 6OPB8 than for 8CB (octyl-cyanobiphenyl) (Figure 9).

V. Summary

The presented high pressure studies of the low frequency relaxation process in liquid crystalline phases for the first time concern the substance with the tilted smectic C phase. The phase sequence N - S_A - S_C observed for 6OPB8 enables us to observe how the parameters describing the rotational motion of molecules change at the phase transition between the orthogonal and tilted phase in the same substance. Additionally, some interesting observations arise from comparing the present results with those obtained recently for the cyano and isothiocyanato two-ring compounds in different phases.

The p-T phase diagram of 6OPB8 is typical for LC substances [1]. In the pressure range studied it does not exhibit any special features like a pressure induced or pressure limited phases observed for other substances [1,7-9,25]. In DTA measurements the melting and the S_A → N and N → I_s transitions are easily detected, whereas the S_C → S_A transition is not visible at all. However, it cannot be considered as the second order phase transition because of its strong supercooling observed at ambient pressure. This transition can, however, be determined by texture observation and due to the changes in the activation plots.

The low frequency relaxation time passes smoothly through the transitions between the liquid-like LC phases. However, both activation quantities determined, the activation volume and the activation enthalpy, which characterise the molecular rotations around the short axes, change in the following way: $\Delta^\#V(S_A) > \Delta^\#V(S_C)$, and $\Delta^\#H(N) \gg \Delta^\#H(S_A) > \Delta^\#H(S_C)$. At the same time they are markedly larger than those observed in the same phases for compounds with one tail and the CN or NCS groups. Both activation parameters are smaller in the tilted than in the orthogonal phase of 6OPB8. The activation volume in both smectic phases diminish with raising temperature (and pressure) which can be interpreted as an indication of shortening of the effective molecular length due to conformation motions of the tails.

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