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Dielectric studies of *trans*-4-*n*-octyl-(4-cyanophenyl)cyclohexane (8PCH) at ambient and high pressure

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Dielectric relaxation studies have been performed on *trans*-4-*n*-octyl-(4-cyanophenyl)-cyclohexane (8PCH) at ambient and high pressure (0·1–175 MPa). Two experimental set-ups were applied: a time domain spectrometer (TDS) covering the frequency range 10 MHz–5 GHz, was used to study the relaxation processes in the isotropic phase (at ambient pressure); an impedance analyser (1 kHz–13 MHz) was used for high pressure measurements on both the nematic (N) and isotropic (I) phases. The low frequency (l.f.) relaxation process connected with molecular rotations about the short axis is hindered by the activation enthalpy of 70 kJ mol^{-1} and 32·6 kJ mol^{-1} in the N and I phases, respectively, whereas the high frequency process (rotations about the long axis) has an activation enthalpy of 22·6 kJ mol^{-1} (isotropic phase). From the pressure and temperature dependencies of the l.f. relaxation time $\tau_{\|}$, the activation volume, enthalpy and energy were calculated. It was found that the energy barrier hindering the molecular rotations around the short axis in the nematic phase is influenced to about one half by the volume effects. The nematic potential q was estimated at various pressures and comprises 10 ÷ 20% of the total energy barrier. The pressure dependence of q enabled the calculation of the order parameter $S(p)$ with the aid of old (Maier and Saupe) as well as recent (Coffey *et al.*) theoretical formulae.

1. Introduction

Dielectric spectroscopy is a powerful tool for the study of polar substances. Measurements at static field give information about the electric structure of molecules and, in some cases, about the dipole–dipole correlation between molecules. Measurements of the complex dielectric permittivity, $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$, enable one to determine the dielectric relaxation time τ, which is an important dynamical quantity of molecules. Its temperature and pressure dependences yield the activation enthalpy and activation volume, respectively. In the case of nematic liquid crystals (LCs), the reorientation of molecules about the molecular short and long axes must be distinguished. They can be easily detected when a proper alignment of the nematic director **n** with respect to the measuring electric field **E** is achieved ($\mathbf{E}\|\mathbf{n}$ and $\mathbf{E}\perp\mathbf{n}$, respectively). The longitudinal relaxation time $\tau_{\|}$ is an especially important quantity as it reflects the strength of the nematic potential q that opposes the molecular rotations around the short axes.

Recently we have carried out a systematic dielectric study of samples under hydrostatic pressure [1]. The materials were two-ring LC compounds having a strong longitudinal dipole moment connected with the CN group and belonging to the following homologous series: alkyl-cyanobiphenyls (*n*CB, $n = 5 \div 8$) [1–7], an alkoxy-cyanobiphenyl (*n*OCB, $n = 8$) [1, 8], alkylcyclohexylbenzonitriles (*n*PCH, $n = 5, 7$) [1, 9, 10] and an alkylbicyclohexylcarbonitrile (*n*CCH, $n = 5$) [11]. This allowed us to check the influence of different molecular cores on the dielectric properties. The main results are now summarized. The activation parameters, especially the activation volume $\Delta^{\#}V_{\|}$, decrease when we move away from the isotropic–nematic transition line; this behaviour was interpreted as the effect of changing the monomer–dimer equilibrium by pressure [1]. For a

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given n, the activation parameters increase if one or two benzene rings are replaced by the cyclohexyl rings. In the case of the thoroughly studied nCB series, no special dependence of the activation parameters on the length of the alkyl chain was observed. The values of the nematic potential seem to depend upon the structures of the molecular cores.

The title substance, 8PCH, does not exhibit smectic polymorphism, unlike 8CB and 8OCB, which both display the nematic and smectic A phase. In this paper we present the results of dielectric measurements for 8PCH in the isotropic and nematic phases. The isotropic phase was studied at atmospheric pressure by the time domain spectroscopy (TDS) method over a broad range of frequency (10 MHz–5 GHz). Two relaxation bands were observed in the TDS spectra. This allowed us to determine the relaxation time and the activation enthalpies for both processes, and to estimate the angle between the main molecular axis (long axis) and the direction of the dipole moment. For the nematic phase the low frequency relaxation process was studied at ambient as well as at elevated pressures. Different quantities characterizing the rotational motions of 8PCH molecules around the short axes (relaxation time $\tau_{\|}(p, T)$, activation volume, enthalpy and energy) could be obtained. They will be compared with those obtained for substances belonging to the same homologous series (except 6PCH which has a narrow nematic phase), as well as with other substances having the same length of the terminal groups. Additionally, from the retardation factor $g_{\|}$ characterizing the slowing down of the l.f. relaxation time at the I–N phase transition, the nematic potential q and then the order parameter S versus pressure were calculated.

The $p(T)$ phase diagram obtained for 8PCH with the aid of DTA and volumetric studies [12] is presented in figure 1, where points from the present dielectric measurements have also been included. The figure shows that the various experimental methods give good agreement.

2. Experimental

The measurements of the relaxation processes taking place in the isotropic phase of 8PCH were performed with the use of a time domain spectrometer (TDS) at Uppsala University. The details of the TDS set-up can be found elsewhere [13]. The spectra were measured with two time windows (10 and 50 ns) and then spliced as was described in [14]. This allowed us to cover the frequency range from 10 MHz to *c.* 5 GHz.

For the dielectric high pressure measurements a recently developed pressure vessel was employed that is described elsewhere [11]. The frequency dependence of the permittivity was measured with a Hewlett Packard 4192A impedance bridge up to 13 MHz. In the nematic state the sample was oriented parallel to the probing electric field by superimposing a constant field of $\mathbf{E} \sim 300\ \mathrm{V\,cm^{-1}}$. For details see preceding papers [1–11] and [22].

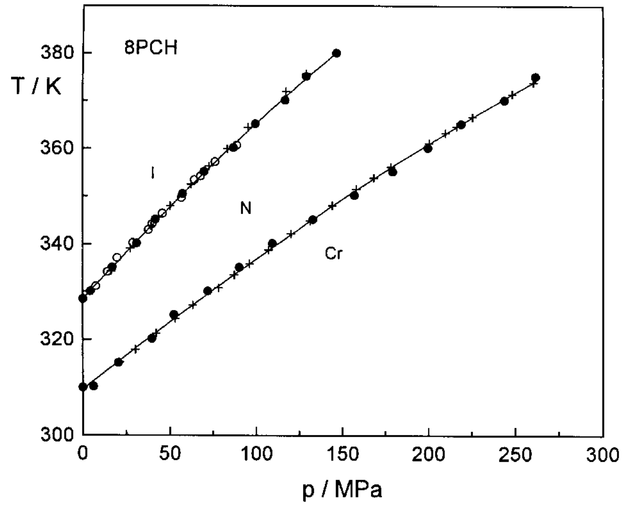

Figure 1. Temperature versus pressure phase diagram for 8PCH: ○ = present studies; ● = pVT; × = DTA.

The 8PCH sample, *trans*-4-*n*-octyl-(4-cyanophenyl)-cyclohexane $M = 297{\cdot}5\ \mathrm{g\,mol^{-1}}$, was synthesized and purified by R. Dąbrowski (Institute of Chemistry, Military Academy of Technology, Warsaw, Poland).

3. Results

3.1. *Measurements at atmospheric pressure*

The static permittivity, $\varepsilon_s(T)$, is compared with literature data [15] in figure 2. Figure 3 (*a*) shows the Cole–Cole plots characteristic for the nematic and isotropic phases (measured using the HP analyser), whereas in figure 3 (*b*) a typical result obtained for the isotropic phase by the TDS method is presented. In the spectra of the isotropic phase, two relaxation processes can be distinguished: the low frequency (l.f.) process is connected with the molecular rotations around the short axis; the high frequency (h.f.) process corresponds to the rotations around the long axis. The relaxation times obtained for both phases are presented in figure 4 in the form of Arrhenius plots. The activation enthalpies are: $\Delta^{\#}H_{\|} = (69{\cdot}9 \pm 2)\ \mathrm{kJ\,mol^{-1}}$, $\Delta^{\#}H_{\mathrm{is}}(\mathrm{l.f.}) = (32{\cdot}6 \pm 2)\ \mathrm{kJ\,mol^{-1}}$, and $\Delta^{\#}H_{\mathrm{is}}(\mathrm{h.f.}) = (22{\cdot}8 \pm 3)\ \mathrm{kJ\,mol^{-1}}$.

3.2. *Measurements at elevated pressures*

In figure 5 we present the plots of the static permittivity versus pressure for selected isotherms in the nematic and isotropic phases of 8PCH. As can be seen, the permittivity decreases strongly when the clearing temperature is approached. The dielectric dispersion $\varepsilon'(\nu)$ and

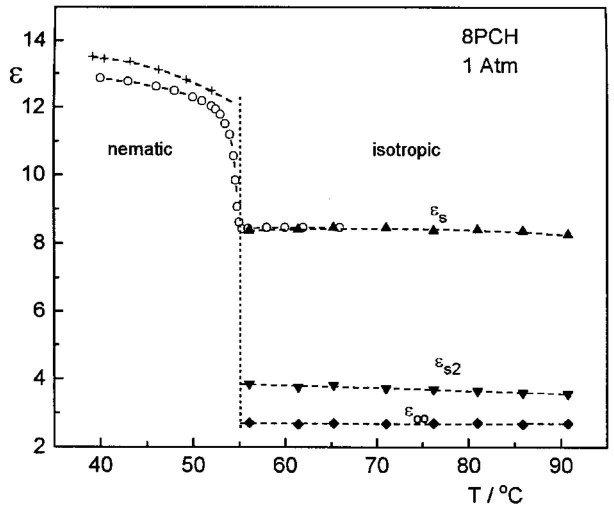

Figure 2. Static permittivity as a function of temperature in the nematic and isotropic phases of 8PCH. The data for the nematic phase were obtained for samples aligned by an electric field (+ = present study) or by a magnetic field (○ = [15]). For the isotropic phase the values obtained from the extrapolation of the TDS spectra are shown (full symbols).

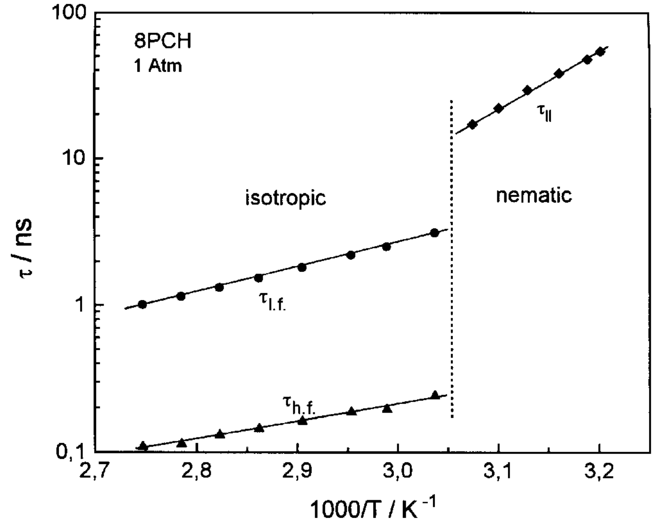

Figure 4. Arrhenius plots for the nematic and isotropic phases of 8PCH at atmospheric pressure.

absorption $\varepsilon''(\nu)$ for a few isotherms are presented in figure 6. The dielectric relaxation times $\tau_\parallel$ were calculated from the frequencies corresponding to the maximum losses: $\tau_\parallel = 1/(2\pi\nu_{\max})$. They are presented in figure 7 in the form of ln $\tau_\parallel$ versus p plots. Due to the limited range of frequency (up to 13 MHz), the spectra for the isotropic phase could not give the proper values of the relaxation times τ_{is} [compare figure 3 (*a*)], but they were sufficient to obtain the pressure dependencies of τ_{ap} at a particular constant temperature. Taking the slopes $[\partial(\ln\, \tau_{\text{ap}})/\partial p]_T$ and the known values of τ_{is} at 1 atm from the TDS

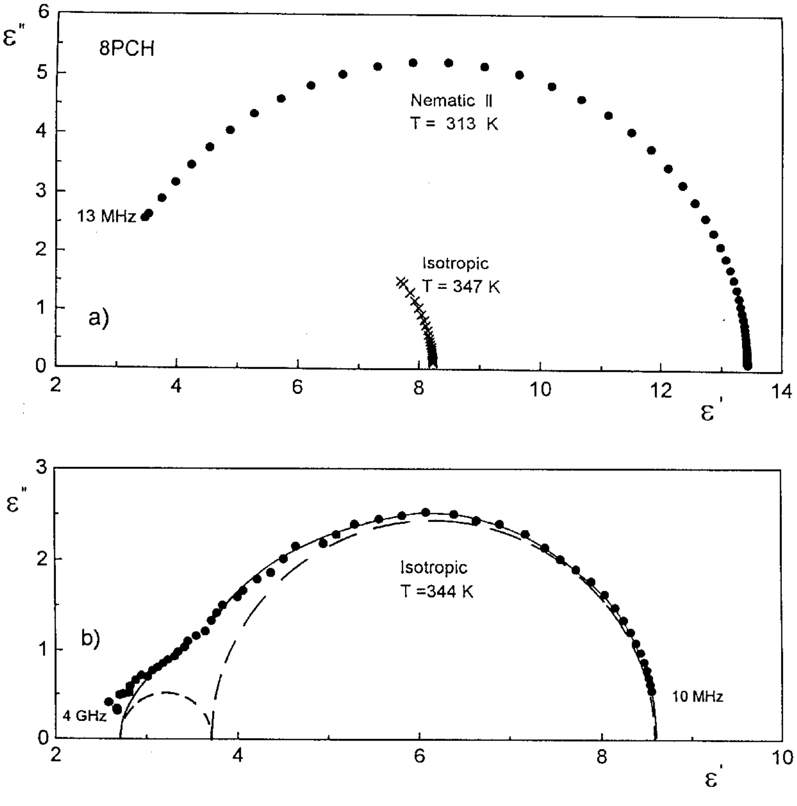

Figure 3. (*a*) Typical Cole–Cole plots for the nematic and isotropic phases of 8PCH obtained from the HP analyser. (*b*) The Cole–Cole plot for the isotropic phase of 8PCH obtained by the TDS method. The dashed lines correspond to two Debye-type processes.

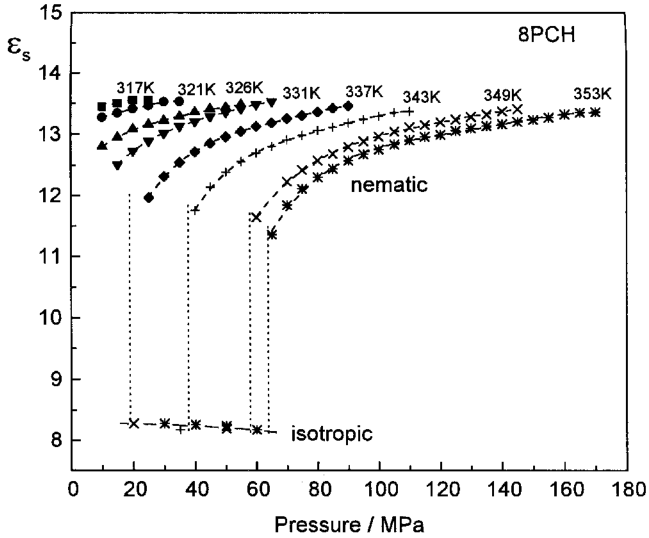

Figure 5. Dependence of the static permittivity on pressure in the nematic and isotropic phases of 8PCH for selected isotherms.

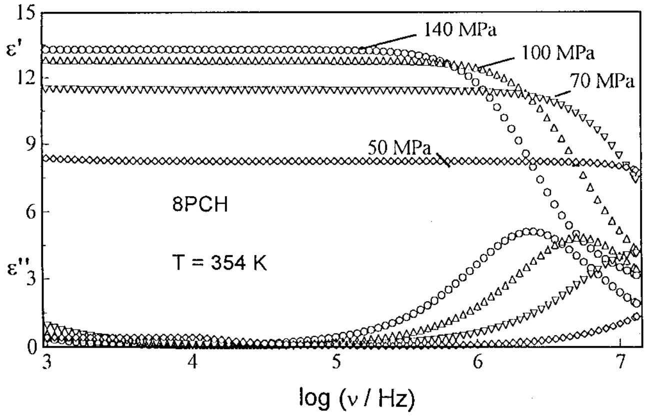

Figure 6. Examples of the dispersion, $\varepsilon'(\nu)$, and absorption, $\varepsilon''(\nu)$, spectra measured for the nematic and isotropic phases of 8PCH at several isobars.

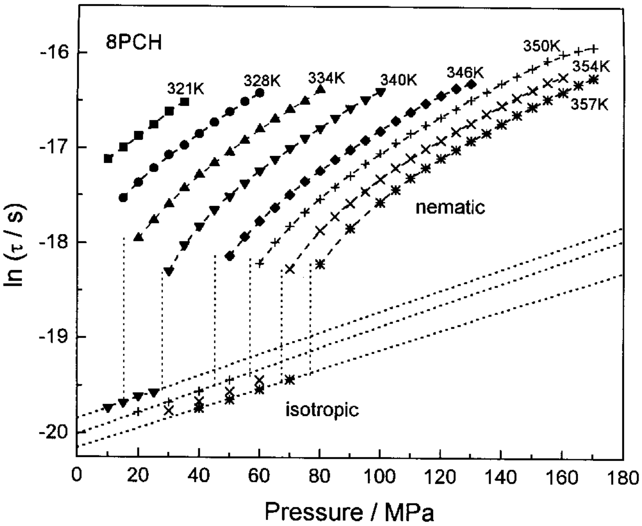

Figure 7. Logarithm of the relaxation times as a function of pressure for selected isotherms in the nematic and isotropic phases of 8PCH. The dotted lines show the extrapolation of $\tau_{is}(p)$ to the nematic phase. Vertical lines correspond to the N–I transition.

measurements, we were able to extrapolate relaxation time to a broad range of pressures as is shown in figure 7.

As is seen in figure 7 the relaxation times $\tau_{\parallel}$ are not a strictly exponential function of the pressure, the ln $\tau_{\parallel}$ versus p curves are bent in the neighbourhood of the N–I transition line. The origin of this bend will be discussed in a forthcoming paper [16]. Here we neglect a few points close to p_{NI} and calculate the slopes by means of linear regressions which yield the activation volume $\Delta^{\#}V_{\parallel} = RT(\partial \ln \tau_{\parallel}/\partial p)_T$. In figure 8 (*a*) we present the activation volume as a function of temperature for all isotherms measured. Using the Arrhenius equation we calculated the activation enthalpy for several isobars: $\Delta^{\#}H_{\parallel} = R(\partial \ln \tau_{\parallel}/\partial T^{-1})_p$ (for details see [17]). The results are presented in figure 8 (*b*) as a function of pressure. Additionally, knowing the equation of state from PVT measurements [12] we calculated the activation energy $\Delta^{\#}U_{\parallel} = R(\partial \ln \tau_{\parallel}/\partial T^{-1})_V$. The results are presented in figure 8 (*c*) as a function of molar volume.

4. Discussion

As is seen in figure 2, both sets of static permittivity data are fully consistent for the isotropic phase, whereas they differ markedly for the N phase. In many other measurements the alignment of the nematic sample by an electric field leads to higher permittivity values $\varepsilon_{s\parallel}$ compared with samples oriented by a magnetic field [4–10]. This relates especially to substances built up with non-benzene rings for which the anisotropy of the magnetic susceptibility is small. On approaching the N–I transition the permittivity decreases due to the decrease of the order parameter [18, 19].

The dielectric spectra of the isotropic phase of 8PCH reveal the existence of two relaxation processes with a large difference in the amplitudes (increments). It is obvious to connect them with molecular rotations around the long axis (h.f. band) and about the short axis (l.f. band). This would mean that the 8PCH molecule possesses a transverse component of the dipole moment (μ_t), besides the strong longitudinal dipole (μ_l). Taking into consideration the Onsager equation

$$\mu^2 = \frac{9kT\varepsilon_0(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{N\varepsilon_s(\varepsilon_\infty + 2)^2} \qquad (1)$$

and the values of the permittivities presented in figures 2 and 3 (*b*), we can estimate the ratio of the components $\mu_t/\mu_l = tg\beta$. At 344 K we have: $\varepsilon_s = 8{\cdot}45$, $\varepsilon_s - \varepsilon_{s2} = 4{\cdot}72$

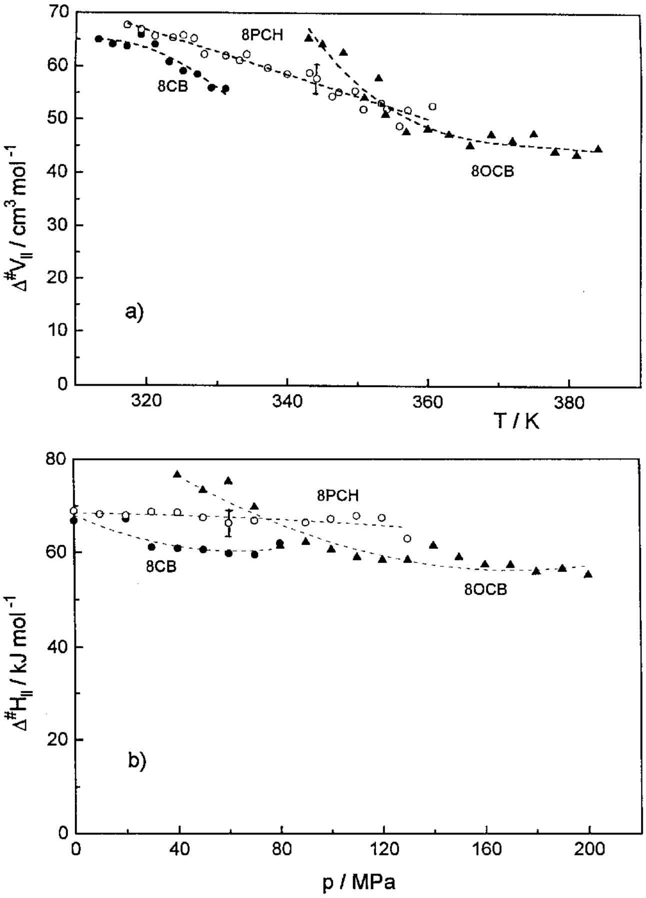

Figure 8. Activation volume as a function of temperature (*a*) and activation enthalpy as a function of pressure (*b*) in the nematic phase of three substances having the same lengths of the terminal groups.

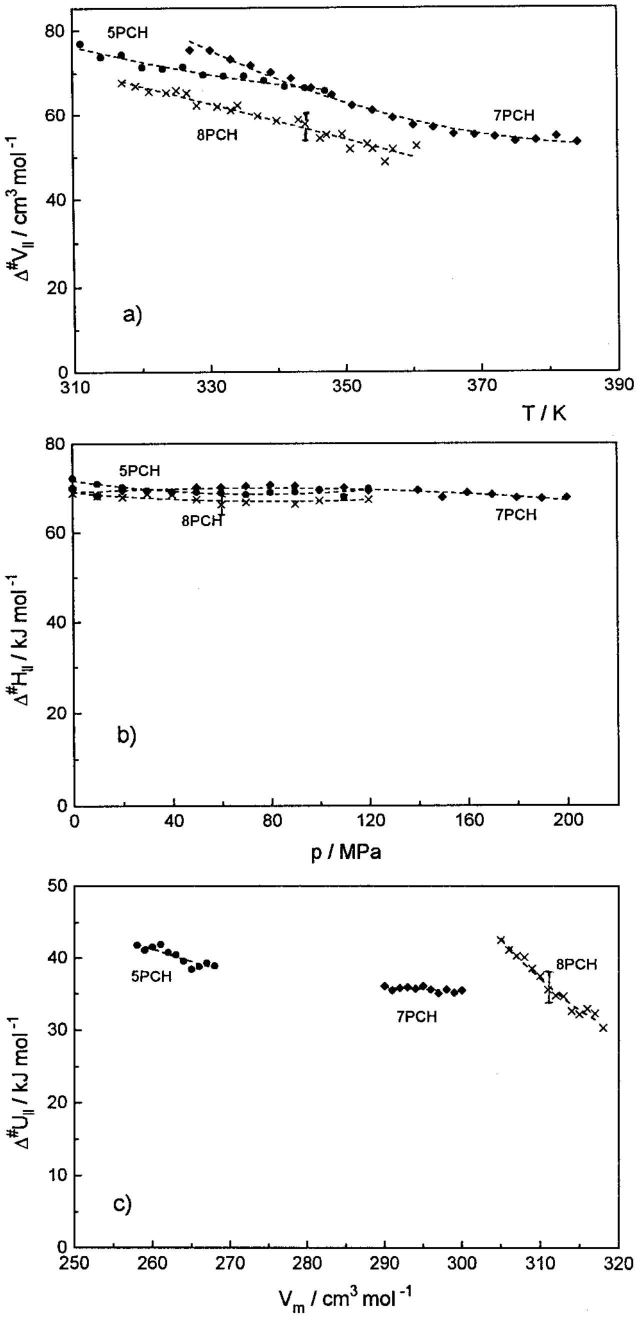

Figure 9. Comparison of the activation volume as a function of temperature (*a*), activation enthalpy as a function of pressure (*b*) and activation energy as a function of molar volume (*c*) in the nematic phase of three substances belonging to the same homologous series.

and $\varepsilon_{s2}-\varepsilon_{\infty}=1\cdot03$, which gives $\beta=31°$. This indicates that (at least in the isotropic phase) the molecular long axis is inclined from the *para*-axis of the benzene ring by this angle. Similar calculations for 7PCH based on the data of [14] lead to a similar value of $\beta=29°$ (the results obtained for 5PCH [20] indicate that β is smaller for this substance). In the case of *n*CB compounds, the h.f. relaxation process is considerably less visible in the TDS spectra of the isotropic phase [21]. We can conclude therefore that the PCH molecules are bent due to the flexible cyclohexyl ring.

The activation parameters calculated from the pressure and/or temperature dependences of the longitudinal relaxation times are presented in figures 8 and 9. They are compared with those obtained recently for other substances having the same length of the terminal groups (figure 8) or belonging to the same homologous series (figure 9). A common feature of these presentations is the decrease of all parameters if we move away from the N–I transition (compare figures 8 and 9 with the phase diagram, figure 1). Such behaviour is observed for all cyano compounds studied under high pressure [1–11], but not for a substance with another strong dipole group [22]. We attributed this effect to the dipole–dipole correlations which are well established for this class of compound. The increase of pressure causes a destabilization of the monomer–dimer equilibrium in a system and thus destroys the more voluminous associates of dimers. Therefore the decrease of the activation volume is always more pronounced than for the other parameters. Figure 8 also demonstrates a small influence of the molecular core on the values of the activation volume and enthalpy. However, this effect is distinctly more pronounced in the case of shorter molecules [1, 4, 11]. The activation volume for the isotropic phase of 8PCH is roughly 36 cm^3 mol^{-1} and does not differ from other similar substances [6, 11, 14, 21, 22].

The *n*PCH homologous series is one of very few for which the *PVT* data are available [12, 23]. Thanks to that, the volume effects in the activation barrier hindering the molecular rotations around the short axes can be established. Figure 9 (*c*) shows the activation energies for three substances studied under high pressure by the volumetric and dielectric methods. $\Delta^{\#}U_{\parallel}$ corresponds to the barrier experienced by molecules at constant volume. As can be seen from the figure, the activation energy is almost the same for the three *n*PCHs and consists only of *c.* 50% of the activation enthalpy [figure 9 (*b*)]. In spite of observed changes of all activation parameters within the nematic phase, the relation between them predicted by thermodynamics, $\Delta^{\#}H_{\parallel}=\Delta^{\#}U_{\parallel}+(\alpha/\beta)T\Delta^{\#}V_{\parallel}$, is fulfilled within the limit of the experimental errors (thermal expansivity α and isothermal compressibility β were obtained from the *PVT* data [12]).

It can be deduced from figures 4 and 7 that the l.f. relaxation time is distinctly retarded on passing through the isotropic–nematic phase transition. This well known phenomenon has been treated by Meier and Saupe in the concept of the retardation factor, $g_{\parallel}=\tau_{\parallel}/\tau_0$ [24]. τ_0 is the relaxation time with vanishing nematic potential q and in this work is obtained by an extrapolation from the $T(p)$-dependence of τ_{is}, as is shown in figure 7. The pressure dependence of the retardation factor within the nematic phase of 8PCH is presented in figure 10 (*a*). Two equations are employed which relate the retardation factor $g_{\parallel}$ to the nematic potential barrier parameter $\sigma=q/RT$:

$$g_{\parallel}=\frac{\tau_{\parallel}}{\tau_0}=\frac{\exp(\sigma)-1}{\sigma} \qquad (2)$$

$$g_{\parallel}=\frac{\tau_{\parallel}}{\tau_0}=\frac{\exp(\sigma)-1}{\sigma}\left[\frac{2}{1+1/\sigma}(\sigma/\pi)^{1/2}+2^{-\sigma}\right]^{-1}. \qquad (3)$$

The first one was obtained by Meier and Saupe [24], the second by Coffey *et al.* [25]. Both equations have been used to calculate the nematic potential q, see figure 10 (*b*). The q values after Coffey *et al.* are systematically larger than those after Meier and Saupe, but they both depend similarly on temperature and pressure. It should be pointed out that similarly to other substances [1], the nematic potential values obtained for 8PCH comprise 10÷20% of the activation enthalpies; thus, the contributions to the energy barrier from other sources (viscosity, volume effects, dipole–dipole associations, ...) dominate in the low frequency relaxation process in the nematic phase.

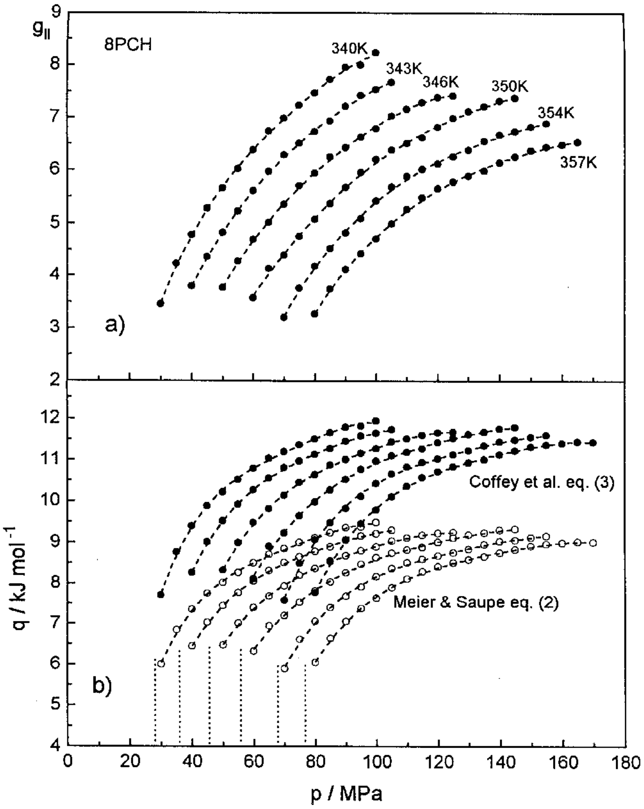

Figure 10. Pressure dependence of the retardation factor $g_{\parallel}$ (*a*) and the nematic potential q (*b*) according to Meier–Saupe (open points) and Coffey *et al.* (full points) formulae.

4.1. *Calculations of the order parameter S*

In the mean-field theory of the nematic state Maier and Saupe (MS) [26] assumed that the nematic potential q is proportional to the order parameter S

$$q=vS \qquad (4)$$

where the strength parameter v depends on the molar volume [1, 2, 27–29] and thus reflects the distance dependence of the interaction potential. The order parameter is defined as

$$S=(3\langle\cos^2\theta\rangle-1)/2 \qquad (5)$$

where θ is the angle between the molecular symmetry axis and the director **n**. In order to perform averaging $\langle\ldots\rangle$ the distribution function of the nematic order, $f(\theta)$, must be known. The authors proposed the following simple form

$$f(\theta)=f(0)\exp\left(-\frac{q}{k_{\mathrm{B}}T}\sin^2\theta\right)=f(0)\exp(-\sigma\sin^2\theta). \tag{6}$$

Thus, one has

$$\langle\cos^2\theta\rangle=\int_{-1}^{1}\mathrm{d}x\,x^2 f(x)\bigg/\int_{-1}^{1}\mathrm{d}x\,f(x) \tag{7}$$

with $x=\cos\theta$.

Recently Kalmykov and Coffey (KC) [30] have derived the relation between S and σ in a more general way. Starting from the Maier and Saupe interaction potential the authors applied the effective eigenvalue method and obtained the following analytical equation

$$S=\frac{3\exp(\sigma)}{4\sigma M\left(\frac{1}{2},\frac{3}{2},\sigma\right)}-\frac{3}{4\sigma}-\frac{1}{2} \tag{8}$$

where $M(\ ,\ ,\ )$ is the confluent hypergeometric function. The above relation can well be approximated by the relation [30]

$$\sigma\approx\frac{3S(5-\pi S)}{2(1-S^2)}. \tag{9}$$

Combining the experimental σ values as deduced from equations (2) and (3), respectively, with the formulae (5)–(7) and (9), it is possible, in principle, to calculate the order parameter S for the nematic phase. This idea was highlighted by Kresse [31] and recently applied by Jadżyn *et al.* [32, 33] for two nematics at a few temperatures. These authors performed the dielectric relaxation measurements over a broad range of frequencies in both the nematic and isotropic phases and could calculate the retardation factor $g_\|$ taking the measured $\tau_\|$ values, whereas τ_0 was obtained by extrapolation of $\tau_{\mathrm{is}}(T)$ to the nematic phase. The agreement with the results for S obtained by other experimental methods was within the limit of 20%.

In the case of our h.p. studies we use a quite different extrapolation method in obtaining the τ_0-values (see figure 7). In addition, we have many experimental points at each isotherm, so the behaviour of S over the whole range of the nematic phase can be observed. The vicinity of the N–I transition line where a strong change of S is observed in the pressure studies [1, 4, 27–29, 34] seems specially interesting. Moreover, our q values were calculated according to the two different theories from equations (2) and (3), respectively, and in addition they can be further treated by the corresponding two sets of formulae, equations (5)–(7) and (9).

Figure 11 presents, as an example, four sets of $S(p)$ data calculated from the q values shown in figure 10(*b*) (estimated uncertainty of S is $\pm0{\cdot}01$). The two upper sets correspond to Coffey *et al.* equation (3), and the two lower sets to Meier and Saupe equation (2). The full symbols correspond to the MS equations (5)–(7), and the open symbols to the KC equation (9) theoretical formulae. Striking features of this comparison are: a close similarity of the pressure dependence of S with the experimental $S(p)$ results obtained for other similar substances [1, 27–29, 34], and the fact that both sets of the data are fairly close over the whole range of the nematic phase of 8PCH in the case of the MS approach, while a large divergence is observed in the case of the KC formula (9) combined with the Coffey *et al.* formula (3). The latter seems to indicate a good equivalence of both mean-field theories [26, 30] for small σ only ($\sigma\leqslant3$).

In order to discuss which formula, equation (2) or (3), leads to better values of S, still further experimental results have to be considered. Unfortunately, no other data on the order parameter for 8PCH are available. However, a comparison of the present results with those obtained from the optical [27] and NMR [28, 29, 34] h.p. studies of related substances indicates that the Meier–Saupe formula (2) gives better S values, especially close to the clearing point where $S\approx0{\cdot}3$ seems to be more appropriate than $S\approx0{\cdot}4$ (see figure 11). Therefore, we recommend the results obtained with the aid of equation (2) for further consideration.

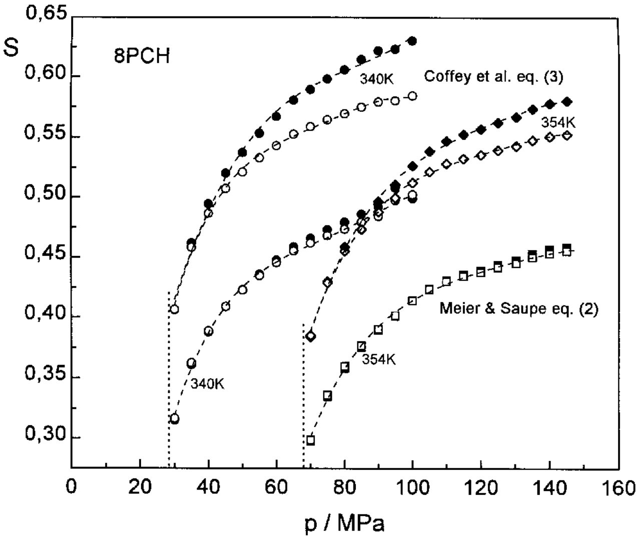

Figure 11. Comparison of two sets of order parameters versus pressure. Full symbols were calculated with the aid of the Maier–Saupe theory, open symbols were obtained from the Kalmykov–Coffey equation (9). Upper data were obtained with the use of equation (3), and lower data with equation (2).

In order to check whether both sets of S values behave similarly as a function of pressure the following formula was fitted to the experimental points

$$S(p) = S_0(p - p_{\mathrm{NI}})^{\gamma} \tag{10}$$

which is an analogue of the well known Haller relation describing the temperature dependence of S: $S(T) = S(0)$ $(T_{\mathrm{NI}} - T)^{\beta}$ where S_0, $S(0)$, β and γ are empirical parameters. Figure 12 shows that the fits are very good over the whole range of the nematic phase. The fitting parameters were S_0 and γ. S_0 decreases slightly with temperature (see inset of figure 12), whereas γ is practically constant. The dashed lines in figure 12 are the fits of equation (10) to the points with $\gamma = 0{\cdot}130$ ($\pm 0{\cdot}003$). Such a simple analytical formula might be useful for an analysis of different quantities dependent upon the order parameter.

Finally, in figure 13 we present the plot q versus S, see equation (4) which gives the strength parameter $v = 20 \pm 1\,\mathrm{kJ\,mol^{-1}}$. This value can be compared with those obtained for other substances [1]. In the case of nCBs, it is about 11–13 kJ mol^{-1}, whereas for 5PCH and 7PCH the v-values are *c.* 15–17 kJ mol^{-1} for the nematic potential obtained from Meier–Saupe formula (2), and *c.* 19 kJ mol^{-1} from equation (3) of Coffey *et al.* It should be pointed out, however, that in former studies the q and S data were taken from different experiments, whereas the present calculations are based on the same experimental results.

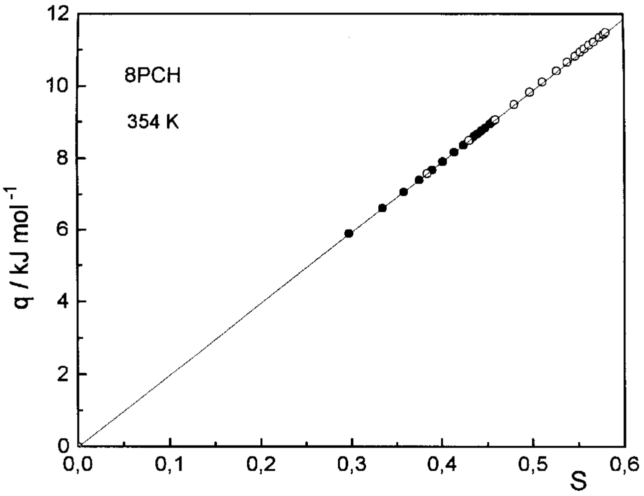

Figure 13. Nematic potential versus order parameter plots for 8PCH at 354 K. The S values correspond to the Maier–Saupe theory. Full points are based on equation (2), and open points on equation (3).

5. Conclusions

The dielectric studies of 8PCH performed over a broad range of frequency, temperature and pressure have brought out new information about: (i) the molecular structure, (ii) the reorientational dynamics of molecules in the isotropic and nematic phases, (iii) the influence of volume effects on the l.f. relaxation process in the nematic phase, (iv) the order parameter as a function of pressure. Reliable values and the correct pressure dependence of the order parameter obtained from the analysis of the relaxation data seem to justify the correctness of the extrapolation procedure we applied in the calculation of the retardation factor $g_{\parallel}$. At the same time this approach justifies the mean-field theories of the nematic state.

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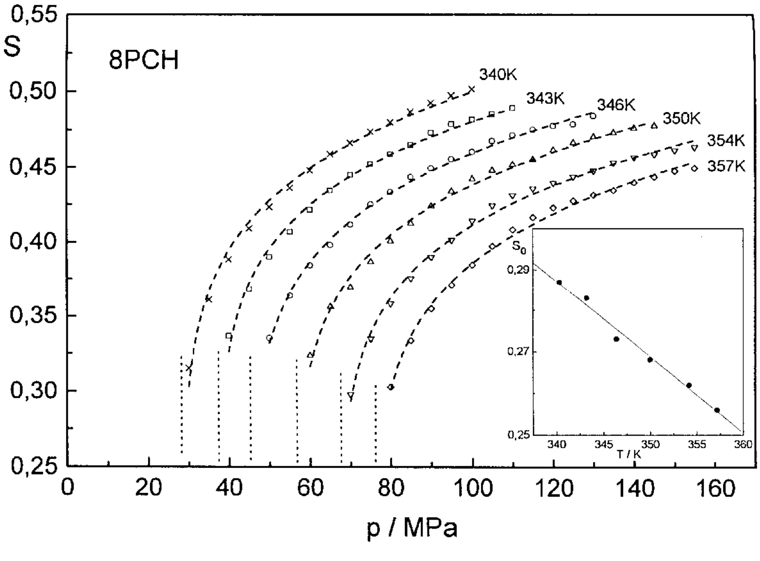

Figure 12. Order parameters versus p plots for several isotherms in the nematic phase of 8PCH according to the Maier–Saupe theory. The dashed lines are fits of the Haller-type formula (10) with $\gamma = 0{\cdot}13$. The inset shows the temperature dependence of the S_0 parameter. Vertical lines correspond to the N–I transition.

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