Dielectric Studies of trans,trans-4'-n-Pentyl-bicyclohexyl-4-carbonitrile (5 CCH) under High Pressure

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Dielectric studies on the static and complex permittivity have been performed on trans,trans-4'-n-pentyl-bicyclohexyl-4-carbonitrile (5 CCH) in the pressure range 0.1–200 MPa, the frequency range 1 kHz–13 MHz and the temperature range 300–390 K. Phase transitions between the isotropic, nematic, smectic B (metastable), and crystalline state have been recorded as steps in the static permittivity. Thus the phase diagram of 5 CCH was established. In particular the slow relaxation process in the nematic and smectic phase has been investigated. The dielectric relaxation time $\tau_{\parallel}$ increases by a constant factor of 210 on passing the nematic–smectic B phase transition. From the pressure and temperature dependences of τ we have calculated the activation volumes ($\Delta^{\neq} V/\text{cm}^3 \text{mol}^{-1} = 88{-}65$ (nematic), $= 70{-}45$ (smectic) and ≈ 32 for the isotropic phase) and activation enthalpies ($\Delta^{\neq} H/\text{kJ mol}^{-1} = 76{-}60$ (nematic), ≈ 60 (smectic) and ≈ 37 for the isotropic phase), respectively, which are compared with previous results on similar homologous series. The activation parameters increase significantly, when the rigid phenyl ring is replaced by the more flexible cyclohexyl ring.

Introduction

In the last years many dielectric studies under pressure have been performed on several liquid crystals, belonging to the series nCB (alkyl-cyano-biphenyls) [1–3] or nPCH (alkyl-cyclohexyl-benzonitriles) [4, 5]. The investigations are extended to the nOCB (alkyl-oxy-cyano-biphenyls) [6] and nCCH series (alkyl-bi-cyclohexyl-carbo-nitriles), in order to check the influence of different molecular cores on the dielectric properties. In fact the pressure dependence of both the static and complex permittivity give more insight into the molecular dynamics and the intermolecular potential [7–9].

The mentioned liquid crystals have their dipole moments mainly parallel to the long molecular axis that facilitates the interpretation of the dielectric relaxation, connected with the rotation about the short axis [10, 11]. The temperature and pressure dependence of the dielectric relaxation time yield the activation enthalpy $\Delta^{\neq} H_{\parallel} = R (\partial \ln \tau_{\parallel} / \partial T^{-1})_p$ and the activation volume, $\Delta^{\neq} V_{\parallel} = R T (\partial \ln \tau_{\parallel} / \partial p)_T$, respectively. A pronounced pressure dependence of $\Delta^{\neq} H_{\parallel}$ has been found in previous studies of nematic phases that was attributed to the breaking of antiparallelly oriented dipols.

Recently we compared the dielectric behaviour of 8 CB and 8 OCB [6], which both display a smectic A_d

phase. For both members the dielectric relaxation $\tau_{\parallel}$ changes practically continuously at the nematic–smectic A transition. However, for the smectic A_d phase the p, T-dependencies of the activation parameters for 8 OCB are opposite to 8 CB. In the present study we are curious to learn the dielectric properties of a smectic B phase.

1. Experimental

For the dielectric measurements a new high-pressure autoclave is employed that is described in [5, 12]. The pressure is transmitted by compressed silicon oil. The frequency dependence of the permittivity was measured with the impedance bridge Hewlett Packard 4192 A up to 13 MHz. In the nematic state the sample was oriented parallel to the probing electric field by superimposing a constant field of $E \sim 300$ V/cm. The accuracy for the temperature and pressure reading is supposed to be ± 0.2 K and ± 0.2 MPa, respectively. For details see [1–5]. The 5 CCH sample was obtained from Merck.

2. Results

2.1 Phase Behaviour

The polymorphism of 5 CCH at normal pressure was first noted by Eidenschink et al. [13] who men-

tioned a metastable smectic phase. Brownsey et al. identified the smectic phase as a bilayer smectic B structure [14]. Haase et al. investigated the crystal and molecular structure of three nCCHs [15]. Bartelt et al. performed high pressure phase studies on some nPCHs and nCCHs [16], however, the high pressure phase behaviour of 5CCH has not been reported in literature.

Figure 1 shows the phase diagram that has been established from dielectric permittivity measurements of the present work. The phase transitions between the isotropic, nematic, smectic (metastable), and crystalline state have been detected as steps in the static permittivity (compare Figs. 2 and 3 below). The smectic phase was only occasionally observed starting from the nematic phase, when the pressure was quickly increased (at constant temperature) in order to avoid crystallization. It was more difficult to obtain the smectic phase on cooling at constant pressure, especially at low pressures. Therefore transition points are lacking in the low pressure region. Only in few runs it was posible to stabilize the smectic phase down to 313 K at ambient pressure on cooling (see Figure 2). The smectic phase was never reached from the crystalline state on heating. That means, the smectic–crystal phase transition is monotropic, corroborating the metastability of the smectic B phase.

A monotropic smectic–smectic transition at 316 K and ambient pressure has been reported by Eidenschink et al. [13] that probably corresponds to the smectic–crystal transition at 313 K. However, in the present work we did not find any further indication of a second smectic phase. Once the smectic phase has been reached it transformed to the nematic phase on heating (or releasing the pressure) at the corresponding phase boundary, see Figure 1. Thus, the nematic–smectic transition is partially reversible. However, the "life-time" of the smectic phase is limited and recrystallization takes place very often. Moreover the $T(p)$ range, where the metastable smectic phase exists is rather small, that renders a thorough dielectric investigation rather difficult.

The phase transition lines for 5CCH can be represented by polynomials, see Table 1. The crystal→nematic transition is not strictly monotropic. However, the transition points were reproducible on heating only, because on cooling the nematic phase either crystallizes at a lower temperature or transforms to the smectic B phase.
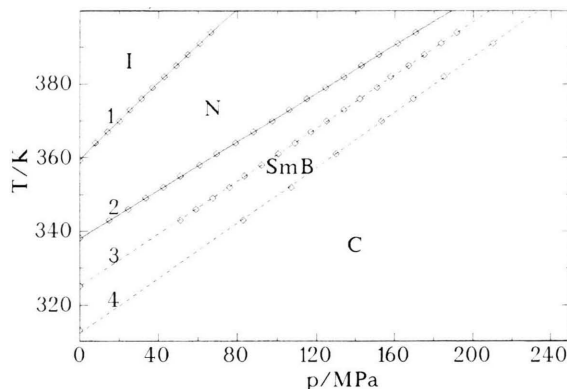

Fig. 1. Temperature-pressure phase diagram for 5CCH. The numbers of the phase boundaries correspond to Table 1.
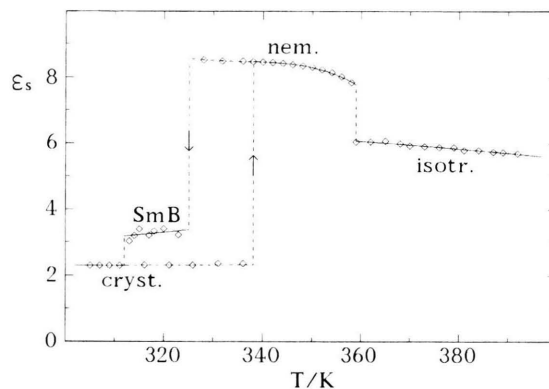

Fig. 2. Static permittivity as a function of temperature at normal pressure in the nematic, smectic B and isotropic phases. The arrows show cooling ↓ and heating ↑ runs.
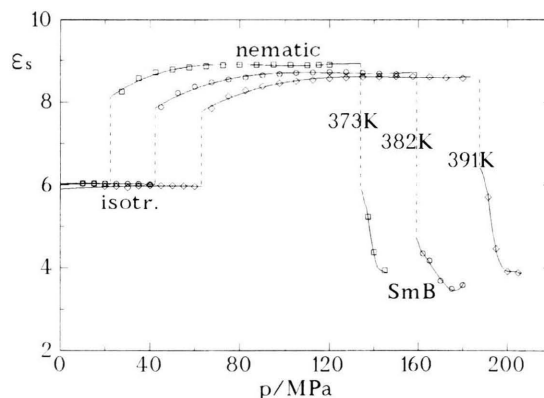

Fig. 3. Static permittivity as a function of pressure in the nematic, smectic B and isotropic phases.

Table 1. Pressure dependence of the phase transition temperatures of 5CCH.

1) nematic ↔ isotropic	$T/K = 359.5 + 0.5357\ (p/MPa)$ $- 2.867 \cdot 10^{-4}\ (p/MPa)^2$
2) crystal → nematic	$T/K = 338.0 + 0.3300\ (p/MPa)$ $- 0.114 \cdot 10^{-4}\ (p/MPa)^2$
3) nematic ↔ smectic	$T/K = 325.1 + 0.3548\ (p/MPa)$ $+ 0.24 \cdot 10^{-4}\ (p/MPa)^2$
4) smectic → crystal	$T/K = 313 + 0.372\ (p/MPa)$

2.2 Dielectric Measurements

Static Permittivity

Figure 2 shows the static permittivities of the nematic and smectic phases, $\varepsilon_{\parallel}$, and of the isotropic phase, ε_{iso}, at atmospheric pressure, which are comparable with results from Bradshaw et al. [17]. The pressure dependence of the static permittivity is presented in Figure 3. In general the measurements were performed on changing the pressure at constant temperature. Due to the small $T(p)$ region of the smectic phase and the frequent recrystallization, a significant T, p-dependence of ε cannot be quoted.

Dielectric Relaxation

The frequency dependence of the real and imaginary part of the complex permittivity, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, is displayed in Figs. 4a, b for three state points in the neighboorhood of the nematic–smectic phase transition. At 120 MPa there is a strong loss peak in the MHz range, corresponding to the $\tau_{\parallel}$-relaxation process in the nematic phase. At slightly higher pressures (125.5 MPa) this loss peak is considerably reduced in favour to the appearance of a second loss curve in the kHz range. Finally, at 140 MPa, only this low-frequency peak is visible, that must be attributed to the slow $\tau_{\parallel}$-relaxation process in the smectic B phase, connected with rotations around the short molecular axis in the hexagonal arrangement of the molecules. The simultaneous observation of two loss curves at 125.5 MPa is apparently caused by the coexistence of nematic and smectic phase. Obviously the frequency of maximum loss changes by more than two orders of magnitude at the nematic–smectic B transition, in contrast to the practically continuous change at a nematic–smectic A transition [3, 6]. Similar strong shifts in the dielectric relaxation frequency have been reported by Kresse et al. for various smectic (Sm B, I, E, F) liquid crystals [18, 19].
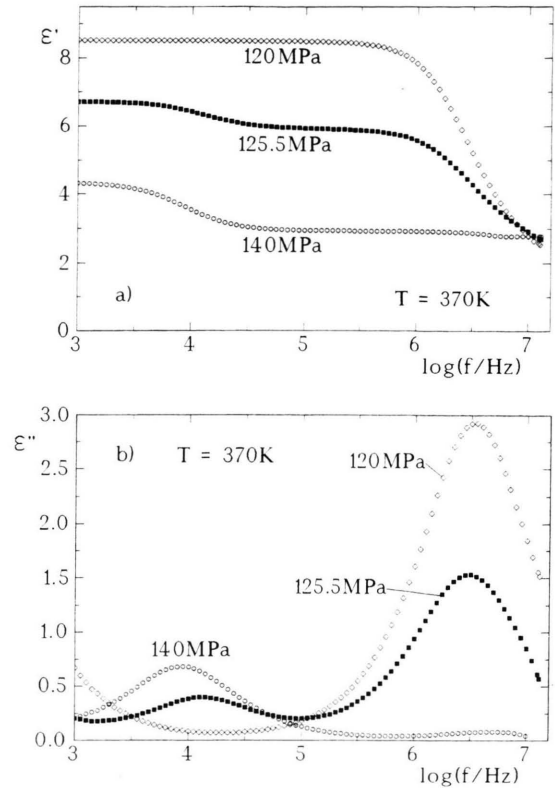

Fig. 4. a) Real (ε') and b) imaginary part (ε'') as a function of frequency at 370 K for three different pressures near the nematic–smectic B phase transition.
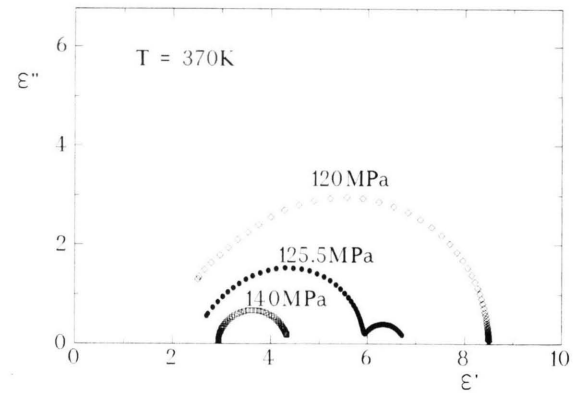

Fig. 5. Cole-Cole plots for the state points of Figure 4.

The respective Cole-Cole plots are presented in Fig. 5, which are close to a semicircle, in accordance with previous results for nematic LCs. Accurate fitting [20] of the loss curves yield Jonscher parameters m, $1 - n \approx 1$, corresponding to a single Debye relaxation process for both the nematic and smectic phase.

The dielectric relaxation time τ (calculated from the reciprocal frequency of maximum loss) is presented in Fig. 6 in a semilogarithmic scale as a function of the pressure, showing the shifts of τ at the nematic–smectic and nematic–isotropic phase transitions. In particular the strong jump of $\tau_\parallel$ at the nematic–smectic B transition is of interest, which is shown in more detail in Figure 7. It can be seen that τ remains constant on both sides of the phase transition, whereas as slight increase of τ along the smectic A–nematic phase transition line was found for 8CB [3] and 8OCB [6]. The relaxation times for 5CCH at the phase boundary are: nematic: $\tau_\parallel = 6.83 \cdot 10^{-8}$ s, smectic: $\tau_\parallel = 1.44 \cdot 10^{-5}$ s, thus also the ratio $\tau_{smect}/\tau_{nem} = 210$ is independent of pressure.
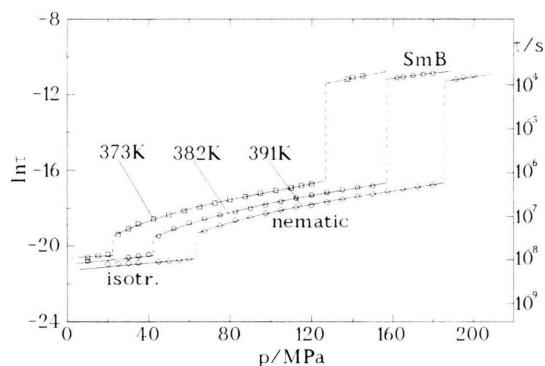

Fig. 6. Logarithm of the dielectric relaxation times as a function of pressure for three different temperatures in the nematic, smectic B and isotropic phases.
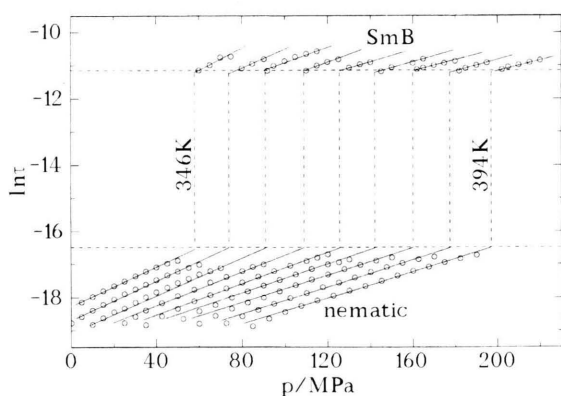

Fig. 7. Logarithm of the dielectric relaxation times as a function of pressure in the neighbourhood the nematic–smectic B phase transition. The temperatures vary in steps of 6 K from 346 to 394 K.

In the isotropic phase we could only measure the pressure dependence of the low frequency part of the loss curves, due to limitations of our impedance bridge. The absolute values for the relaxation times τ_{iso} are available at atmospheric pressure from recent TDS measurements [21] which are extrapolated to higher pressures according to the present work. Again τ seems to remain constant along the phase boundary, in agreement with findings for the nematic–isotropic transition of previously studies liquid crystals. The temperature and pressure dependences of τ yield the activation parameters in the usual way [1–8].

3. Discussion

3.1 Activation Parameters

In Figs. 8 and 9 we have plotted the activation volume, $\Delta^{\neq} V = R\,T(\partial \ln \tau_\parallel / \partial p)_T$, and the activation enthalpy, $\Delta^{\neq} H = R(\partial \ln \tau_\parallel / \partial T^{-1})_p$, for 5CCH for the nematic, smectic and isotropic phases. With the use of Gestblom's data [21] we find $\Delta^{\neq} H = 35$ kJ · mol^{-1} for the isotropic phase at 1 atm. According to our high pressure measurements we estimate $\Delta^{\neq} V_{iso} \approx 32$ cm^3 · mol^{-1} and $\Delta^{\neq} H_{iso} \approx 37$ kJ · mol^{-1}. The decrease of $\Delta^{\neq} V_\parallel$ (88–65 cm^3 · mol^{-1}) and $\Delta^{\neq} H_\parallel$ (76–60 kJ · mol^{-1}) in the nematic phase with rising temperature or pressure has also been noticed for various nCBs, that is attributed to the destruction of antiparallely oriented dipoles. Increasing pressure probably destroys the more voluminous associates of dimers. The activation parameters for the smectic phase ($\Delta^{\neq} V_\parallel = 70$–45 cm^3 · mol^{-1}, $\Delta^{\neq} H_\parallel \approx 60$ kJ · mol^{-1}) are significantly smaller than for the nematic phase, in accordance with findings for 8CB and 8OCB and other liquid crystals with smectic A phases [6, 22]. However, the $T(p)$-dependences of the activation parameters are similar for both the nematic and smectic phase. In a previous study of 8CB an opposite pressure dependence has been found for the smectic A phase [3].

In Figs. 10 and 11 we compare the activation parameters for the nematic phases of 5CCH, 5PCH and 5CB, in order to check the influence of different molecular cores. Clearly, the $\Delta^{\neq} V_\parallel$ and $\Delta^{\neq} H_\parallel$-values increase when we replace one or both rigid phenyl rings by cyclohexyl. This could be connected with the higher flexibility of the cyclohexyl ring that needs more space for the reorientation than the rigid benzene ring. On the other hand the pressure dependence
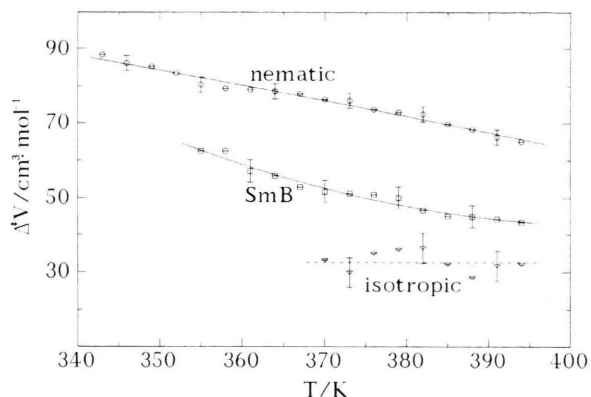
Fig. 8. Activation volumes as a function of temperature for the nematic, smectic B and isotropic phases.
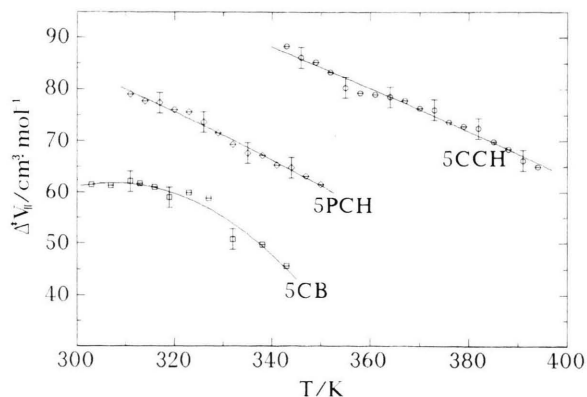

Fig. 10. Comparison of activation volumes for the nematic phases of 5CCH, 5PCH and 5CB.
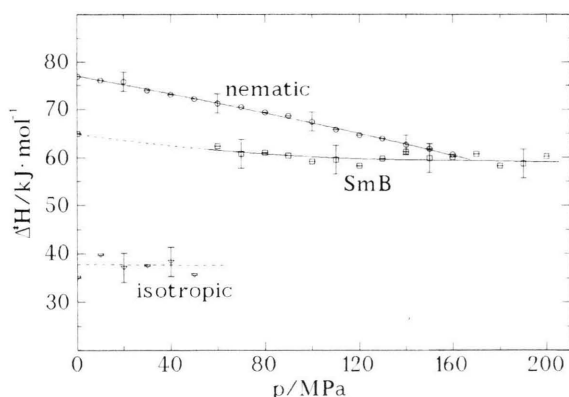

Fig. 9. Activation enthalpies as a function of pressure for the nematic, smectic B and isotropic phases.
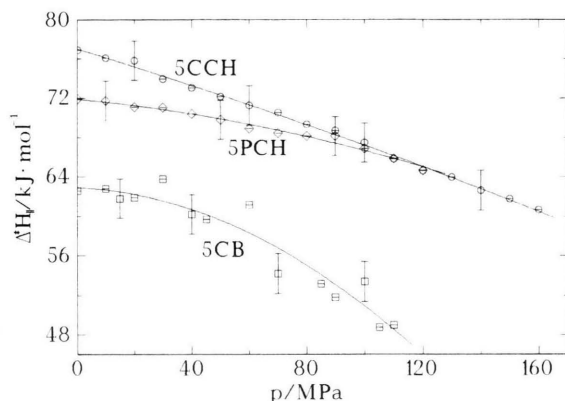

Fig. 11. Comparison of activation enthalpies for the nematic phases of 5CCH, 5PCH and 5CB.

of $\Delta^{\neq} H_{\parallel}$ is much less pronounced for 5PCH compared with 5CB or 5CCH. The weaker pressure dependence for 5PCH could reflect stronger dipole-dipole interactions, so that the dimers cannot be so easily destroyed with pressure. Due to dielectric studies of Dunmur et al. the strength of association is weaker for 5CCH than for 5CB [23]. Possible changes in the molecular environment have to be taken into consideration at a phase transition. Wilson et al. have performed a molecular dynamics computer simulation for 5CCH in the nematic and isotropic phases [24]. They found changes in the degree of gauche conformations and in the shape of the rod-like mesogen, when going from the isotropic to the nematic phase.

3.2 Retardation Factors and Nematic Potential

For a detailed discussion of the shift of the relaxation times at the nematic–isotropic phase transition Meier and Saupe introduced the concept of retardation factors, $g_{\parallel} = \tau_{\parallel}/\tau_0$ [25]. τ_0 is the relaxation time at a hypothetical state with vanishing nematic potential [10, 11] that can be obtained by an appropriate extrapolation from the isotropic phase. The $g_{\parallel}$-factors increase from ca. 6 to ca. 25 with rising pressure and decreasing temperature, see Table 2. The $T(p)$-dependencies of $g_{\parallel}$ are the same as previously found for the nCB [1–3] and nPCH [4, 5] series. However, the absolute values increase in the order nCB, nPCH and

Table 2. Retardation factors $g_{||}$ for different temperatures and pressures.

p/MPa	T/K				
	370	376	382	388	394
30	5.64				
40	7.77	5.87			
50	9.68	7.92	5.81		
60	11.47	9.68	7.77		
70	13.20	11.70	9.49	7.85	
80	15.33	13.33	11.13	9.58	6.96
90	17.46	15.49	12.94	11.02	8.76
100	19.49	17.46	14.73	12.55	10.38
110	21.54	19.69	16.61	14.15	11.94
120	23.57	21.98	18.54	15.96	13.33
130		24.05	20.49	17.64	14.88
140			22.42	19.69	16.44
150		24.05		21.54	17.99
160				23.34	19.49
170				25.28	21.33
180					22.87
190					24.29
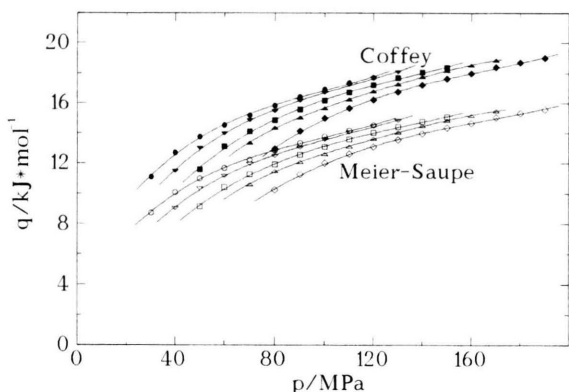
Fig. 12. Nematic potential q as a function of pressure after Meier et al. (open symbols) and Coffey et al. (black points).

nCCH, similar to the trend observed for the activation quantities.

Two equations are employed which relate the retardation factor $g_{||}$ with the nematic potential barrier parameter $\sigma = q/(R\,T)$:

$$g_{||} = \frac{e^{\sigma} - 1}{\sigma}, \tag{1}$$

$$g_{||} = \frac{e^{\sigma} - 1}{\sigma} \left(\frac{2}{1 + 1/\sigma} \sqrt{\sigma/\pi} + 2^{-\sigma} \right)^{-1}. \tag{2}$$

The first equation was derived by Meier and Saupe assuming a simple form of the orientational distribution function [25]. The second equation has been established by Coffey et al. who employed a sophistical mathematical treatment to solve the rotation in a uniaxial potential [26]. Both equations have been used to calculate the nematic potential q, see Figure 12. The q-values after Coffey et al. are systematically larger than after Meier and Saupe, similar to previous calculations for 7 PCH [5] and 8 OCB [6]. Again we find a trend of increasing values when we compare results for 5 CB, 5 PCH and 5 CCH. Apparently these common trends for the activation quantities, the $g_{||}$-factors, and the q-values have the same origin, namely the successive substitution of the phenyl ring by cyclohexyl in the molecular core.

Acknowledgements

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