Differential Thermal Analysis (DTA) and Dielectric Studies of 4-(trans-4-Heptyl-Cyclohexyl)-benzonitrile (7PCH) under High Pressure

T. Brückert, D. Büsing, and A. Würflinger
Physical Chemistry II, Ruhr-University, D-44780 Bochum, Germany

S. Urban
Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Kraków 16, Poland

Z. Naturforsch. **50a,** 977–983 (1995); received August 25, 1995

With the aid of DTA the phase diagram of 4-(trans-4-heptyl-cyclohexyl)-benzonitrile, 7PCH, was redetermined. Dielectric studies on the static and complex permittivity have been performed on 7PCH in the pressure range 0.1–220 MPa, the frequency range 1 kHz–13 MHz and the temperature range 290–380 K. For the slow relaxation process in the nematic phase, characterized by the relaxation time τ_{II}, we have calculated the activation volume, $\Delta^{\neq} V_{II}$, of about 80 to 60 cm^3/mol (decreasing with increasing temperature), and the activation enthalpy, $\Delta^{\neq} H_{II}$, of approximately 70 kJ/mol. The isochoric activation energy, $\Delta^{\neq} U_{II}$, amounts to about 36 kJ/mol. The pressure dependence of $\Delta^{\neq} H_{II}$ is less pronounced compared with previous findings for 5PCH and 7CB. Estimates of τ_0 (extrapolated from the relaxation time in the isotropic phase) allow the calculation of the retardation factor $g_{II} = \tau_{II}/\tau_0$ that is analysed in terms of theories of Martin-Meier-Saupe and Coffey in order to evaluate the nematic potential q. Using data for the order parameter S from NMR studies it was possible to determine the strength of the interaction potential in the nematic phase and to check the relation $q \sim S$ which is valid at p=const., but not at V=const. The results are compared with recent findings for other homologous series.

Key words: Dielectric Relaxation, High Pressure, Liquid Crystals, Activation Parameters, Phase Transitions.

1. Introduction

Dielectric properties of liquid crystals (LCs) are important for many industrial and scientific applications [1]. In the last years a growing interest of dielectric studies under pressure can be noticed [2–5]. In fact the pressure dependence of both the static and complex permittivity yield valuable information about activation quantities and the intermolecular potential [6–11]. Recently we started to investigate the alkyl-cyclohexyl-benzonitrile series with 5PCH [11–12]. The results are compared with previous detailed studies of the alkyl-cyano-biphenyls, nCBs [5–10], in order to check the influence of different molecular frames on the dielectric properties.

Both series are described in the literature as being characterized by the formation of antiparallel dimers in the nematic state [13–16]. Nevertheless noticeable differences in the dielectric behaviour have been observed for 5PCH and 5CB [11]. In the present study we extend the investigation to 7PCH in order to get more insight in the dynamics of the reorientational behaviour in the nematic state.

The temperature and pressure dependence of the dielectric relaxation time does not only allow to calculate the activation parameters ($\Delta^{\neq} H_{II}$, $\Delta^{\neq} U_{II}$, $\Delta^{\neq} V_{II}$), but also retardation factors g_{II} and then to evaluate the nematic potential q according to relations derived by Meier and Saupe [17, 18] and Coffey et al. [19–21].

2. Experimental

The experimental set-up for the high-pressure DTA has been described in [22]. For the dielectric measurements a new high-pressure autoclave is employed that was recently developed for ultrasonic measurements [23], see Figure 1. The pressure vessel is made of copper beryllium alloy and closed by a Bridgman piston for the electrical feed-throughs. Some changes in the dielectric cell and the lead connections were necessary for the dielectric studies at somewhat higher temperatures [24]. The pressure is transmitted by compressed silicon oil using a hand-operated pump. In previous dielectric measurements the pressure transmitting gas

---

Reprint requests to Prof. A. Würflinger

0932-0784 / 95 / 1100-0977 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72027 Tübingen

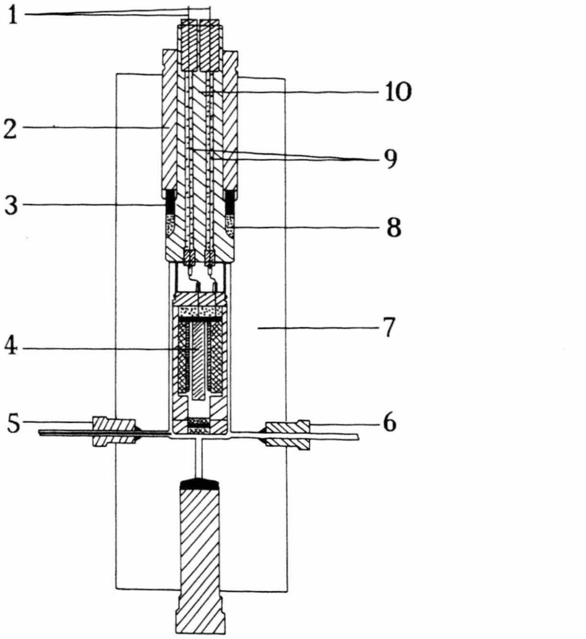

Fig. 1. High pressure set up for dielectric measurements – 1: connections for the electrical leads, 2: screw, 3: pressure ring, 4: three terminal capacitor, 5: screw with thermocouple, 6: inlet for the pressurizing medium, 7: high pressure vessel, 8: sealing, 9: electrical feed-throughs, 10: Bridgman piston.

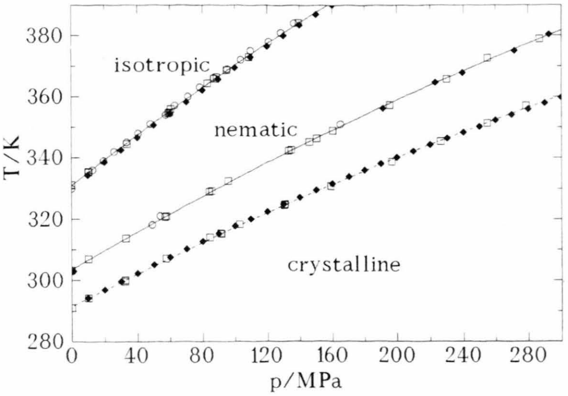

Fig. 2. Temperature-pressure phase diagram for 7PCH, □ = DTA, ○ = dielectric measurements, ◆ = [26].

caused often leakages, so that many runs were necessary in order to obtain reproducable results. The new set-up facilitates the measurements considerably. 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. For details see [6–11]. The 7PCH sample was obtained from Merck.

3. Results

3.1 Phase Behaviour

7PCH reveals a remarkable polymorphism at ambient pressure that has been thoroughly studied by Haase and Pendzialek [25]. These authors report four crystalline phases, some of which occur only as metastable phases. The phase behaviour of 7PCH at elevated pressures has partly been determined by Friedrich et al. [26], reporting also metastable phase transitions. However, the exact knowledge of the phase boundaries is important for performing the dielectric measurements. Therefore the phase diagam of 7PCH was redetermined with the help of DTA. Figure 2 shows the phase boundaries, including also data from the dielectric measurements. The pressure dependence of the clearing temperature is well established with both experimental procedures. However, the lower phase transition line (C_{II}-N after [25]) could not be detected by the dielectric method. Obviously the crystalline form C_{II} belongs to a metastable phase. Contrary to Friedrich we could observe both transition lines C_I-N and C_{II}-N at lower pressures, depending on the thermal treatment. However, these transitions did not appear in the same run.

The phase transition lines for 7PCH can be represented by polynomials:

$C_{II} \rightarrow$ nematic:
$$T(\mathrm{K}) = 291.4 + 0.272\,(\mathrm{p/MPa}) - 1.40 \cdot 10^{-4}\,(\mathrm{p/MPa})^2,$$
$C_I \rightarrow$ nematic:
$$T(\mathrm{K}) = 303.5 + 0.311\,(\mathrm{p/MPa}) - 1.68 \cdot 10^{-4}\,(\mathrm{p/MPa})^2,$$
nematic → isotr.:
$$T(\mathrm{K}) = 331.0 + 0.420\,(\mathrm{p/MPa}) - 2.86 \cdot 10^{-4}\,(\mathrm{p/MPa})^2.$$

Some thermodynamic data at normal pressure are compiled in Table 1. The volume changes have been calculated using the Clausius-Clapeyron equation. The transition enthalpies were taken from [25].

Table 1. Thermodynamic Properties of 7PCH at 1 atm.

Transition	T/K	ΔH/kJ mol^{-1}	ΔV/cm^3 mol^{-1}
$N \rightarrow I$	330.9	1.0	1.27
$C_I \rightarrow N$	303.3	25.5	26.2
$C_{II} \rightarrow N$	290.7	19.0	17.8
$C_{III} \rightarrow N$	289.3	19.6	18.4

3.2 Dielectric Measurements

Static Permittivity

At atmospheric pressure the static permittivity of the nematic phase, $\varepsilon_{\mathrm{s}\parallel}$, is higher than in measurements where the sample is oriented with a magnetic field [14, 27, 28]. A detailed discussion will be given in a forthcoming paper [29]. The temperature dependence for ε_{S} in the isotropic phase reveals a small maximum a few degrees above the clearing temperature that has also been reported for other nematic LCs with strong dipole moments [30, 31].

The pressure dependence of the static permittivity is shown in Figure 3. The measurements were performed on decreasing the pressure starting from points close to the nematic-solid phase boundary. In the neighbourhood of the clearing temperature the permittivity drops distinctly to smaller values. The variation of ε in the isotropic phase is not strong, but clearly visible in Figure 4. All isotherms for $\varepsilon(p)$ in the isotropic phase reveal a maximum at ca. 40 MPa below the N-I transition line, similar to the behaviour of $\varepsilon(T)$ at ambient pressure. Such a maximum as a function of pressure has been resolved for the first time, due to the improved high-pressure set-up that enables us to extend the measurements to higher temperatures.

The static permittivity for 7PCH is significantly smaller ($\sim 15\%$) than that for 5PCH. For the molar susceptibility $(\varepsilon-1)M/\varrho$ (calculated with density data from Kuss [32]) this difference is appreciably reduced ($\sim 2\%$). Nevertheless there remains an influence of the alkyl chain length that cannot be solely explained by the different molar mass or densities [33]. Apparently the longer alkyl chain performs motions with larger amplitudes that smears out the position of the main molecular axis and causes a looser packing in the nematic phase [34]. Striking differences in the association behaviour of 5PCH and 7PCH have also been observed by Majumder et al. [35] in dielectric studies of diluted solutions.

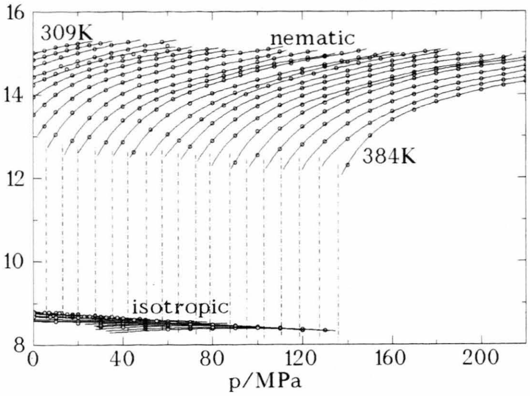

Fig. 3. Static permittivity as a function of pressure in the nematic and isotropic phase of 7PCH; the temperatures for the different isotherms vary in steps of 3 K.

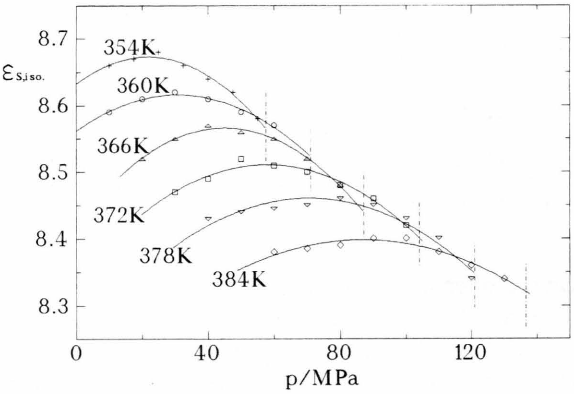

Fig. 4. Static permittivity as a function of pressure for selected isotherms in the isotropic phase of 7PCH.

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 Figure 5a. With increasing pressure the frequency of maximum loss, $f_{\max}=1/(2\pi\tau_{\parallel})$, is shifted to lower values. The Cole-Cole plots (Fig. 5b) show that the relaxation in the nematic phase is very close to a single Debye process, in accordance with previous results for nematic LCs. Nevertheless we prefer to fit the loss curves with the Jonscher equation that is an unambigous and convenient way to determine the dielectric relaxation time τ.

The dielectric relaxation time τ is presented in Fig. 6 in a semilogarithmic scale as a function of the pressure. There is a considerable shift of τ at the nematic-isotropic phase transition. In the isotropic phase we can only measure the low frequency part of the loss curves, due to limitations of our impedance bridge. Therefore we have taken relaxation times τ_{iso} from recent TDS measurements at atmospheric pressure [29] and extrapolated them to higher pressures

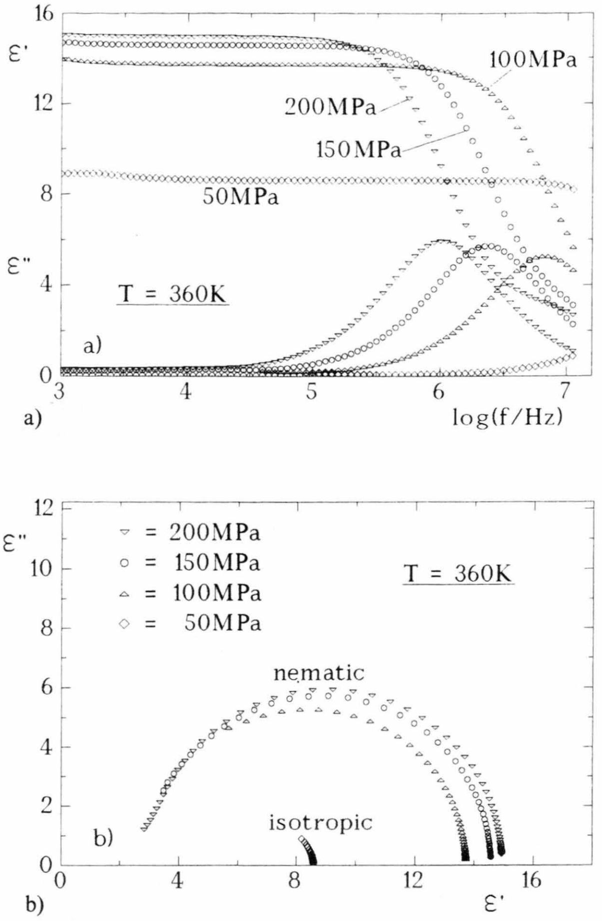

Fig. 5. a) Dielectric dispersion (ε') and absorption (ε'') as a function of pressure at $T = 360$ K, b) Cole-Cole plots for different pressures at $T = 360$ K.

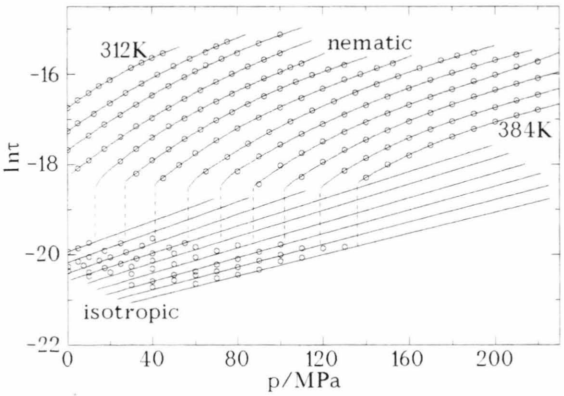

Fig. 6. Logarithm of the dielectric relaxation times as a function of pressure for different temperatures in the nematic and isotropic phase of 7PCH; the temperatures for the different isotherms vary in steps of 6 K.

according to the observed pressure dependence of the measured spectra. The temperature and pressure dependences of τ yield the activation parameters in the usual way [6–11].

4. Discussion

4.1 Dielectric Behaviour

Liquid crystals with strongly polar end groups like CN or NO_2 exhibit a tendency to form antiparallel dimers that appreciably influence their dielectric properties. Thus the effective dipole moment is reduced resulting in a Kirkwood-g-factor less than unity. The usefulness of the Onsager equation being doubtful for anisotropic systems [5], we shall discuss the observed effects only qualitatively.

The maximum of $\varepsilon_{S,\,\mathrm{iso}}(T)$ in ambient pressure measurements was attributed to an increase of the number of dimers (with decreasing temperature) in a dynamic monomer-dimer equilibrium [30, 31]. Additionally, some fluctuations of the nematic clusters embedded to the isotropic liquid near the transition temperature may also influence the static permittivity [31]. In our studies the pressure was decreased at $T = \mathrm{const}$ within the isotropic phase starting from p_{NI}. According to the phase diagram this corresponds to an increase of T at $p = \mathrm{const}$ starting from T_{NI}. Thus both observed maxima have the same origin, i.e. breaking of the dipole-dipole associations of the molecules caused by appropriate temperature or pressure changes. A more thorough discussion will be given elsewhere [33].

4.2 Activation Parameters

In Figs. 7 and 8 we have plotted the activation volume, $\Delta^{\neq} V = RT(\partial \ln\tau/\partial p)_T$, and the activation enthalpy, $\Delta^{\neq} H = R(\partial \ln\tau/\partial T^{-1})_p$, for 7PCH both for the nematic and isotropic phase. The decrease of $\Delta^{\neq} V_{\mathrm{II}}$ with rising temperature is quite normal, but the plateau at higher temperatures has not been observed for other related liquid crystals. The small decrease of $\Delta^{\neq} V_{\mathrm{II}}$ with temperature in the isotropic phase is of the order of the experimental error and therefore neglected. That is, we use a constant value of 37 $\mathrm{cm}^3\,\mathrm{mol}^{-1}$ for the evaluation of the retardation factors (see below).

The activation enthalpy $\Delta^{\neq} H_{\mathrm{II}}$ remains practically constant, whereas a distinct decrease was observed for the n-CB series [6–10]. The isochoric activation en-

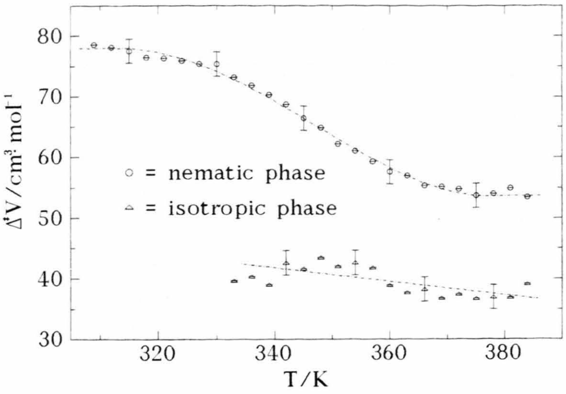

Fig. 7. Activation volumes as a function of temperature for the nematic and isotropic phase of 7PCH.

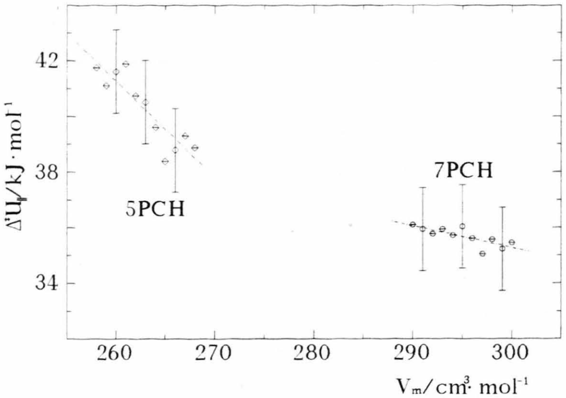

Fig. 9. Activation energies as a function of the molar volume of the nematic phases of 7PCH and 5PCH.

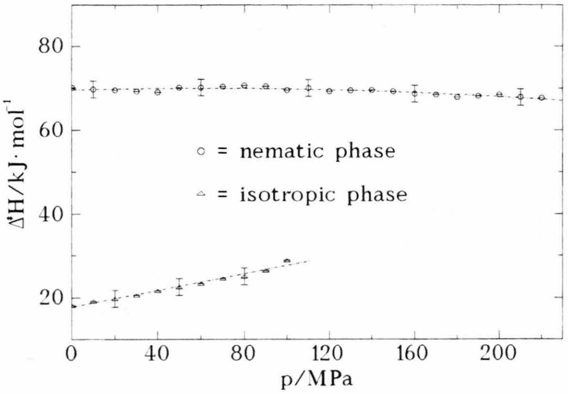

Fig. 8. Activation enthalpies as a function of pressure for the nematic and isotropic phase of 7PCH.

ergy, $\Delta^{\neq} U_{\mathrm{II}} = R(\partial \ln \tau_{\mathrm{II}} / \partial T^{-1})_{\mathrm{V}}$, calculated with pVT data from Kuss [32], exhibits even an opposite density dependence than the *n*-CBs, although less pronounced as for 5PCH (Figure 9). Anyway, the large non-zero $\Delta^{\neq} U_{\mathrm{II}}$ – values indicate that the τ_{II}-relaxation process cannot be explained only by volume effects [36].

For the *n*-CBs the peculiar pressure dependence has been discussed in the frame of a monomer-dimer equilibrium. Increasing pressure destroys more or less associates of antiparallel dimers thus reducing the activation enthalpy with pressure. Because the formation of antiparallel dimers is also accepted for the *n*-PCH series [13–16, 30, 31], we believe that the weak pressure dependence of $\Delta^{\neq} H_{\mathrm{II}}$ is caused by stronger dipole-dipole interactions, so that the dimers cannot so easily be destroyed with rising pressure. Similar differences are also observed for the pressure dependence of the static permittivity, when we compare the *n*-CB and *n*-PCH series [33].

4.3 Retardation Factors and Nematic Potential

Two main factors are responsible for the considerable slowing-down of the low-frequency relaxation process when passing the isotropic – nematic phase transition: The appearance of the nematic potential and the change in the viscosity. According to the Maier-Saupe mean field theory [37] the nematic potential q is proportional to the order parameter $S = \langle (3\cos^2\theta - 1)/2 \rangle$, where θ is the angle between the main molecular axis and the director: $q = vS$. The interaction coefficient v, being a measure of the strength of the molecular interactions in the nematic phase, is supposed to be independent of temperature, but it depends on the molar volume. The dielectric relaxation studies can give valuable information about q and v [33], provided S is available as a function of temperature and pressure.

In order to characterize quantitatively the changes in the relaxation times Meier and Saupe introduced the concept of retardation factors, $g_{\mathrm{II}} = \tau_{\mathrm{II}}/\tau_0$, where τ_0 is the relaxation time at $q = 0$ [17, 18]. Strictly speaking τ_0 can only be measured in the isotropic phase. However, we can assume a hypothetical state with $q = 0$ for T/p-conditions within the nematic phase. Then τ_0 is obtained by an extrapolation from the $T(p)$-dependence of τ_{iso}. The g_{II}-factors change between ca. 4 close to T_{NI} and ca. 14 close to the freezing line. Two equations are employed which relate the retardation factor

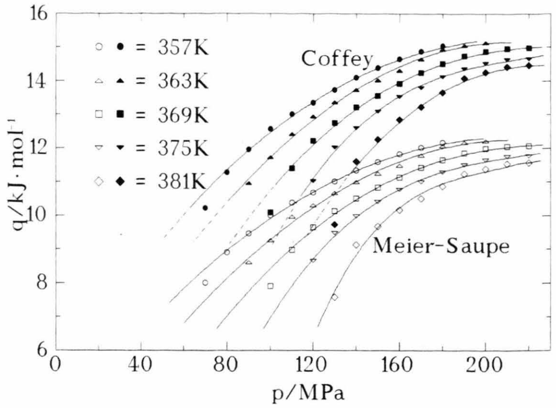

Fig. 10. Nematic potential q as a function of pressure after Meier et al. and Coffey et al.

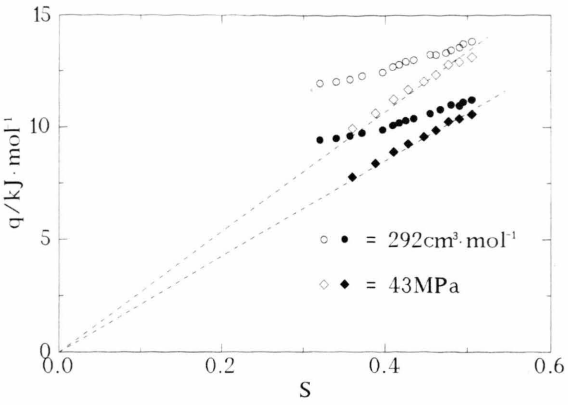

Fig. 11. Nematic potential q as a function of the order parameter S at $p=\text{const}$ and $V=\text{const}$; *black points*: Meier et al. [17], *open points*: Coffey et al. [19–21].

g_{II} with the nematic potential barrier parameter $\sigma=q/(RT)$:

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

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

The first one was obtained by Meier and Saupe [17] with simplified assumptions about the form of the orientational distribution function, the second one is more general and was derived by Coffey et al. [19–21], who considered a single axis rotator in a uniaxial potential.

Both equations have been used to calculate the nematic potential q, see Fig. 10. The q-values after Coffey et al. are systematically larger than after Meier and Saupe, but they both depend similarly on temperature and pressure. In order to check the proportionality between q and S, we use data obtained by Emsley et al. [38] at $p=43$ MPa and $V=292\ \mathrm{cm^3\,mol^{-1}}$. Figure 11 shows that both sets of q-values give nice proportionality to S at $p=\text{const}$, but not at $V=\text{const}$. From the slopes we obtain the strength parameter $v=21.5$ kJ/mol for (1) and 27.0 kJ/mol for (2). However, because the order parameters were obtained from NMR measurements of a biaxial solute dissolved in a nematic solvent, they seem to be underestimated. As will be outlined in [29], the strength parameters should be divided by a factor of 1.4, yielding $v=15.4$ and 19.3 kJ/mol, respectively. These values are still larger than those found for nCBs [33, 39] and nOCBs [33, 40].

Acknowledgement

Financial support of the Deutsche Forschungsgemeinschaft (Wu 97/8-1 & 2) and Fonds der Chemischen Industrie is gratefully acknowledged.

[1] Bunsen-meeting, Leipzig 1993, Neue Eigenschaften und Anwendungen von Flüssigkristallen, Ber. Bunsenges. Phys. Chem. **97**(10), 1169 (1993).
[2] A. Würflinger, Int. Rev. Phys. Chem. **12,** 89 (1993).
[3] R. Shashidhar, in "Phase transitions in liquid crystals" ed. S. Martellucci, Plenum Press, A. N. Chester (1992), p. 245.
[4] C. Carboni, H. F. Gleeson, J. W. Goodby, and A. J. Slaney, Liq. Cryst. **14,** 1991 (1993).
[5] S. Urban, Z. Naturforsch. **50a,** 826 (1995).
[6] H. G. Kreul, S. Urban, and A. Würflinger, Phys. Rev. A, **45,** 8624 (1992).
[7] S. Urban, H. G. Kreul, and A. Würflinger, Liq. Cryst. **12,** 921 (1992).
[8] S. Urban, T. Brückert, and A. Würflinger, Liq. Cryst. **15,** 919 (1993).
[9] T. Brückert, A. Würflinger, and S. Urban, Ber. Bunsenges. Phys. Chem. **97,** 1209 (1993).
[10] S. Urban, T. Brückert, and A. Würflinger, Z. Naturforsch. **49a,** 552 (1994).
[11] T. Brückert, D. Büsing, A. Würflinger, and S. Urban, Mol. Cryst. Liq. Cryst. **262,** 209 (1995).
[12] B. Gestblom and S. Urban, Z. Naturforsch. **50a,** 595 (1995).
[13] S. Y. Yakovenko, A. A. Minko, G. Krömer, and A. Geiger, Liq. Cryst. **17,** 127 (1994).
[14] P. Kedziora and J. Jadzyn, Mol. Cryst. Liq. Cryst. **249,** 105 (1994).

[15] V. S. Rachkevich, S. Ye. Yakovenko, and J. Pelzl, Liq. Cryst. **15,** 591 (1993).

[16] S. Urban, E. Novotna, H. Kresse, and R. Dabrowski, Mol. Cryst. Liq. Cryst. **262,** 257 (1995).

[17] G. Meier and A. Saupe, Mol. Cryst. **1,** 515 (1966).

[18] A. J. Martin, G. Meier, and A. Saupe, Symp. Faraday Soc. **5,** 119 (1971).

[19] W. T. Coffey, Yu. P. Kalmykov, and E. S. Massawe, Adv. Chem. Phys. **85,** 667 (1993).

[20] W. T. Coffey, D. S. F. Crothers, Yu. P. Kalmykov, and J. T. Waldron, Physica A **213,** 551 (1995).

[21] W. T. Coffey, Yu. P. Kalmykov, and J. T. Waldron, Liq. Cryst. **18,** 677 (1995).

[22] A. Würflinger, Ber. Bunsenges. Phys. Chem. **79,** 1195 (1975).

[23] R. Ledwig, Doctoral Thesis, University of Bochum, 1986; R. Ledwig and A. Würflinger, J. Chem. Soc. Faraday Trans. 2, **83,** 655 (1987).

[24] T. Brückert, Doctoral Thesis, University of Bochum, in preparation.

[25] W. Haase and R. Pendzialek, Mol. Cryst. Liq. Cryst. **97,** 209 (1983).

[26] J. Friedrich, Diplom Thesis, University of Bochum, 1985; A. Bartelt, G. M. Schneider, Mol. Cryst. Liq. Cryst. **173,** 75 (1989); G. M. Schneider, A. Bartelt, J. Friedrich, H. Reisig, and A. Rothert, Physica **139 & 140B,** 616 (1986).

[27] S. Sen, K. Kali, S. K. Roy, and S. B. Roy, Mol. Cryst. Liq. Cryst. **126,** 269 (1985).

[28] H. Schad and M. A. Osman, J. Chem. Phys. **75,** 880 (1981).

[29] S. Urban, B. Gestblom, T. Brückert, and A. Würflinger, to be published.

[30] M. J. Bradshaw and E. P. Raynes, Mol. Cryst. Liq. Cryst. Lett. **72,** 73 (1981).

[31] J. Thoen and G. Menu, Mol. Cryst. Liq. Cryst. **97,** 163 (1983).

[32] E. Kuss, Mol. Cryst. Liq. Cryst. **76,** 199 (1981).

[33] S. Urban and A. Würflinger, Adv. Chem. Phys., submitted.

[34] V. V. Belyaev, M. F. Grebenkin, and V. F. Petrov, Zhurn. Fiz. Khim. **64,** 958 (1990).

[35] T. P. Majumder, S. K. Roy, and M. Mitra, Mol. Cryst. Liq. Cryst. **261,** 41 (1995).

[36] G. Williams, Trans. Faraday Soc. **60,** 1548 (1964).

[37] W. Maier and A. Saupe, Z. Naturforsch. **14a,** 982 (1959); **15,** 287 (1960). G. R. Luckhurst and G. W. Gray, The Molecular Physics of Liquid Crystals, Academic Press, New York 1979.

[38] J. W. Emsley, G. R. Luckhurst, and S. W. Smith, Mol. Phys. **70,** 967 (1980).

[39] C. J. R. Counsell, J. W. Emsley, N. J. Heaton, and G. R. Luckhurst, Mol. Phys. **54,** 847 (1985).

[40] C. J. R. Counsell, J. W. Emsley, G. R. Luckhurst, and H. S. Sachdev, Mol. Phys. **63,** 33 (1988).