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PVT measurements on *n*-octyl-isothiocyanato-biphenyl (8BT) at elevated pressures

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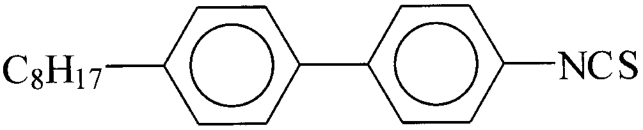
For the first time pressure-volume-temperature (PVT) measurements for the crystal-like smectic E phase have been performed. The phase diagram of 4′-*n*-octyl-4-isothiocyanato-biphenyl 8BT has been recently established using differential thermal analysis up to 250 MPa. 8BT exhibits a splitting of the clearing line above 170 MPa. PVT data have been measured in the same pressure range for temperatures between 313 and 393 K. Volume and enthalpy changes accompanying the clearing line of 8BT are also presented. The configurational part of the entropy change at the CrE–I transition of 8BT amounts to ≈ 60%. Using the PVT data and recently published dielectric relaxation results, the isochoric activation energy was calculated (giving ≈ 50% of the activation enthalpy); this is compared with analogous results for other liquid crystals.

1. Introduction

Knowledge of the volumetric behaviour and PVT data for liquid crystals is important both for technical applications and theoretical treatments. The pressure dependence of physical properties provides a better understanding of the intermolecular interactions and steric conditions [1–3]. Thermal methods are particularly useful for establishing the phase diagrams under high pressure [4–10]. Volumetric properties have been investigated in the past for various liquid crystals [9–12], particularly for laterally aryl-branched [13, 14], nematic [11, 15, 16], and smectic A liquid crystals [17]. In the present work we present PVT data for 4′-*n*-octyl-4-isothiocyanatobiphenyl 8BT, which has a crystal like smectic E phase, whose phase diagram and dielectric behaviour were recently reported [18]. It has the following chemical structure:



2. Experimental

A recently developed PVT apparatus [13, 19] was employed to determine the specific volumes of 8BT between 313 and 393 K. The sample is enclosed in a container of stainless steel, which is closed by a moving piston; any volume change of the sample causes a movement of the piston, whose position is recorded with an induction coil. Usually the measurement is carried out at constant temperature. Increasing and decreasing pressure cycles are necessary in order to determine the hysteresis pressure. For details of the calibration and evaluation see [19–21]. The atmospheric pressure densities have been measured with a vibrating tube densimeter (Anton Paar DMA 60) [14]. The 8BT sample was obtained from R. Dąbrowski, Institute of Chemistry, Military University of Technology (Warsaw, Poland). It was produced as reported previously [18, 22].

Moreover, a few transition points have been remeasured with differential thermal analysis (DTA), in order to clarify the behaviour around a recently reported triple point [18]. The transition temperatures are usually obtained from DTA heating runs [17, 18] and from decreasing pressure cycles along an isotherm in PVT measurements. However, the CrE phase of 8BT exhibits a strong tendency to supercool, corresponding to a strong superpressurizing in the isothermal PVT measurements,

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thus extending the smectic phase region to considerably higher pressures and lower temperatures. Therefore in the present work we evaluate the PVT data preferentially along rising pressure cycles.

3. Results

3.1. *Phase diagram*

The phase diagram of 8BT as established by DTA and PVT measurements is presented in figure 1. The phase transitions reported in [18] were fitted to polynomials, where the clearing line above and below the triple point (T_{tr}) was represented by one equation: $T_{\mathrm{cl}}(^{\circ}\mathrm{C}) = 67.9 + 0.237p + 8.09 \times 10^{-5}p^2$ (p in MPa). Unfortunately the quadratic term had the wrong sign, and thus the calculated clearing temperatures were much too low. Moreover we think that the fitting should be performed separately for the branches above and below the triple point, because the slope of the phase lines changes discontinuously at T_{tr} [23]. The new fitting yields (T in K, p in MPa): (a) below T_{tr}: $T_{\mathrm{cl}} = 341.03 + 0.269p - 1.245 \times 10^{-4}p^2$; (b) above T_{tr}: $T_{\mathrm{cl}} = 332.0 + 0.2954p$; for the short parts $T > T_{\mathrm{tr}}$ linear equations are sufficient. The reported equation for $T_{\mathrm{E\text{-}N}}$ remains essentially unchanged: $T_{\mathrm{E\text{-}N}} = 348.7 + 0.207p$ (except that the temperatures are now in K). The initial slope of the clearing line ($\mathrm{d}T/\mathrm{d}p = 0.269\ \mathrm{K\,MPa^{-1}}$) is significant, when the Clausius–Clapeyron equation is employed, see below.

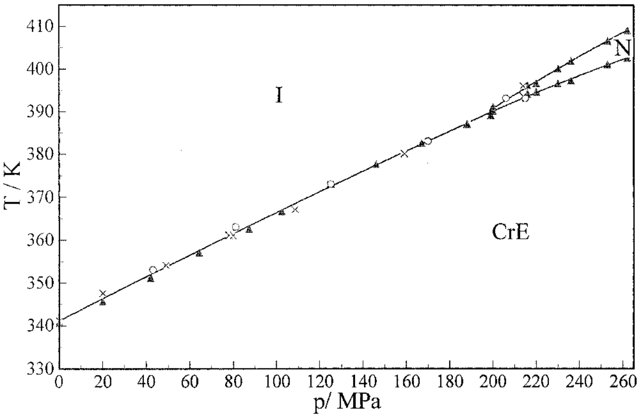

Figure 1. Pressure dependence of the clearing line, as obtained by DTA (▲ [18], × this work) and PVT measurements (○).

3.2. *PVT measurements*

The PVT measurements were started in the CrE region for temperatures between 313.15 and 343.15 K in steps of 10 K. In this range the measured volume changes were linked to atmospheric pressure densities [14] of the E phase. (For the 343.15 K isotherm the density was slightly extrapolated from lower temperatures). For higher temperatures, all isotherms display clearly the CrE–isotropic transition (see figure 2), and therefore densities of the isotropic phase (at 1 atm) are needed to adjust the volumes along the measured isotherm. However, Schmalfuss [14] determined only in a small temperature region of the isotropic phase the densities, which showed an unusually strong decrease of ρ with T. Therefore a different approach was applied. The present PVT cell allows repeated measurements with one filling. Thus the measured isotherms are linked to each other, provided that the experimental conditions (position and thermostatting of the induction coil etc.) are the same for all runs. Then the volume change due to a temperature change can be calculated with the aid of an 'isobaric calibration' [19–21]. In such a way, the specific volumes

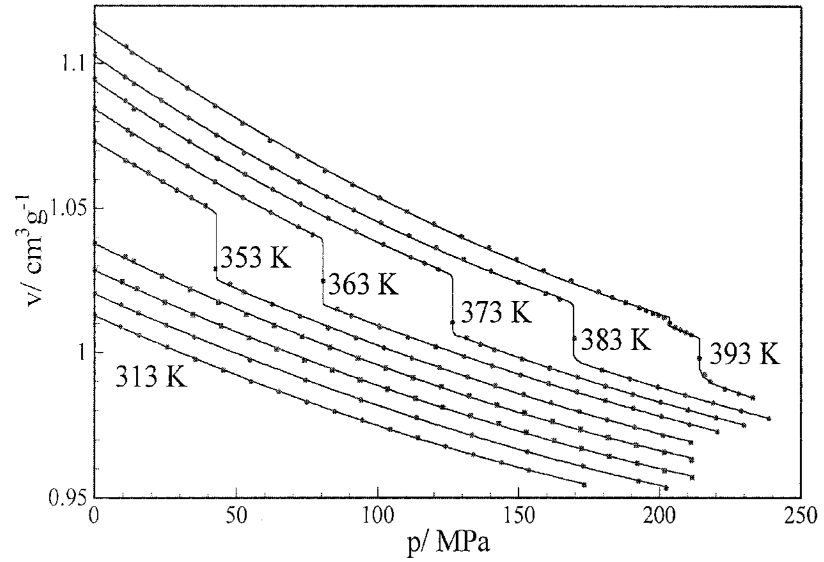

Figure 2. Specific volumes of 8BT as a function of pressure; the steps in the isotherms refer to the transition CrE → I.

for $T > 343.15$ K were obtained. Only for the highest temperature (393.15 K) was the $v(p)$ isotherm adjusted with the isochore at $v = 1.05\,\mathrm{cm^3\,g^{-1}}$.

Figure 2 shows the specific volumes as a function of pressure, the steps indicating the transition CrE–isotropic. At 393.15 K an additional small step can be observed, corroborating the splitting of the clearing line as detected by DTA [18]. Each isotherm within one phase was fitted to a polynomial of second order, separately for the CrE and isotropic phases, yielding the volume changes at the transition pressure. The $v(p)$ isotherms of the isotropic region extrapolated to ambient pressure give the specific volume (or density ρ) at 1 atm. Figure 3 shows the density at 353.15 K, agreeing with Schmalfuss [14], but the slope $\mathrm{d}\rho/\mathrm{d}T$ is much flatter, in reasonable agreement with results for other liquid crystals.

The $v(p)$ isotherms enable us to calculate isochoric lines, which are plotted in figure 4. They are practically straight lines both for the CrE and isotropic phases. This allows us to extrapolate the PVT data to 303.15 K for the evaluation of dielectric measurements (see below). The parameters of the linear equations: $T/K = a + b \times p$ MPa, for the isochores are presented in table 1. The parameter b represents the slope $(\partial T/\partial p)v$ which varies systematically as a function of v in both phases, showing the good correlation of the PVT data.

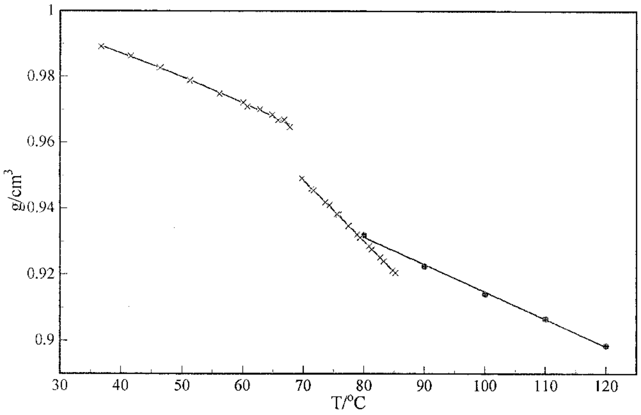

Figure 3. Densities of 8BT at ambient pressure, × [14], ● this work.

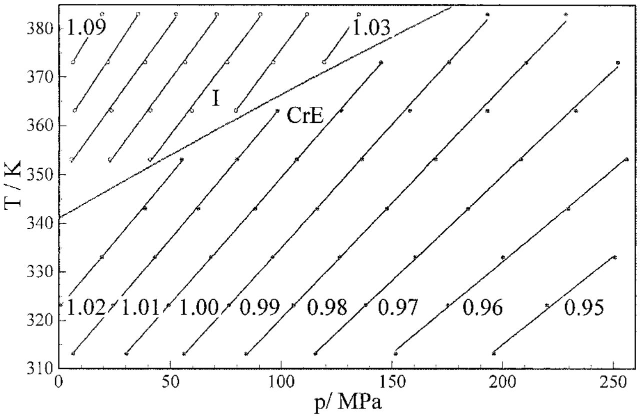

Figure 4. Isochores for the smectic and isotropic phases of 8BT in steps of $0.01\,\mathrm{cm^3\,g^{-1}}$. The lower right part of the phase region belongs to the supercooled or superpressurized CrE phase.

Using the Clausius–Clapeyron equation: $\mathrm{d}p/\mathrm{d}T = \Delta S/\Delta V = \Delta H/(T\Delta V)$, enthalpy changes too are obtained. Some thermodynamic results are given in table 2. The ΔH value at 1 atm can be compared with DSC measurements [22]: $\Delta H_{\mathrm{cl}} = 10.13\,\mathrm{kJ\,mol^{-1}}$ which agrees with table 2. The ΔV value at 1 atm has been extrapolated from the high pressure data. The accuracy of the specific volumes is estimated to be *c.* 0.1% and that of the volume changes $> 1\%$. This is caused by the difficulty of defining the onset of the phase transition in the $v(p)$ plot which often reveals a pretransitional effect. Correspondingly, the inaccuracy for ΔH will be larger, adding the errors for ΔV, T and $\mathrm{d}T/\mathrm{d}p$ in the Clausius–Clepeyron equation.

4. Discussion

4.1. *Appearance of a new LC phase*

The most interesting feature of the phase diagram is the appearance of a pressure-induced phase. Optical or

Table 1. Parameters of the equations for the isochores: $T/K = a + b \times p\,\mathrm{MPa^{-1}}$.

CrE phase			isotropic phase		
$v/\mathrm{cm^3\,g^{-1}}$	a	b	$v/\mathrm{cm^3\,g^{-1}}$	a	b
0.95	242.01	0.36524	1.02	295.27	0.54348
0.96	256.22	0.37988	1.03	297.16	0.63694
0.97	263.43	0.43213	1.04	313.77	0.62047
0.98	272.73	0.47679	1.05	327.88	0.60513
0.99	284.56	0.50488	1.06	338.25	0.62612
1.00	297.48	0.51991	1.07	348.98	0.63785
1.01	309.75	0.54203	1.08	358.08	0.70111
1.02	322.60	0.54756	1.09	368.30	0.76923

Table 2. Thermodynamic properties of 8BT ($M = 323\,\mathrm{g\,mol^{-1}}$).

T/K	p/MPa	$\Delta V/$ $\mathrm{cm^3\,g^{-1}}$	$\Delta H/$ $\mathrm{kJ\,mol^{-1}}$	$\Delta S/$ $\mathrm{J\,K^{-1}\,mol^{-1}}$
CrE → I				
341.00	0.1	0.0250	10.24	30.03
353.15	43.0	0.0238	10.52	29.79
363.15	81.0	0.0227	10.71	29.49
373.15	125.0	0.0206	10.44	27.99
383.15	170.0	0.0202	11.04	28.82
CrE → N				
393.15	215.0	0.0150	9.19	23.38
N → I				
393.15	207.0	0.0020	0.86	2.19

spectroscopic methods at high pressures are not available in our laboratory, but the pressure-induced phase transition has now been confirmed by the PVT measurements. In [17], the possibility of the appearance of pressure-induced nematic phases was discussed. It was argued that a sufficiently high temperature and pressure can destroy the smectic structure and induce a phase similar to high pressure re-entrant nematic phases [24, 25]. The small and large steps in the $v(p)$ plot at 393 K correlate well with the thermal effects observed in the DTA measurements (cf. figure 2 of the DTA peaks in [18]) corresponding to the sequence: isotropic–induced (N?)–CrE phase.

4.2. *Volume dependence of the clearing line*

The PVT data for 8BT enable us to compare the $(\partial p/\partial T)_v$ of isochoric lines with the slope of the CrE–isotropic transition. As in previous papers [12–17], we estimate the configurational part of the entropy change: $\Delta S_{\mathrm{conf}}/\Delta S_{\mathrm{tr}} = [(\partial p/\partial T)_{\mathrm{tr}} - (\partial p/\partial T)_v]/(\partial p/\partial T)_{\mathrm{tr}} \approx 0.6$. This value is significantly higher than that found for alkylcyanobiphenyls and 6DBT [17]. It corresponds rather to findings for laterally aryl-branched liquid crystals [13]. Values between 0.4 and 0.6 were found by Abe *et al.* [26]. On the other hand, Daoudi *et al.* found much smaller values for dilaterally substituted nematogens using the thermobarometric method [10]. This result is connected with high values found for $(\partial T/\partial p)^{\mathrm{NI}}$ that may imply a lower minimum density required for the nematic order. The strong volume dependence of the entropy is explained by the more bulky molecules having a relatively large excluded volume. In the case of 8BT and the previously investigated laterally branched mesogens, the 'free volume' and hence the volume-dependent part of the entropy are much smaller.

PVT measurements enable analysis of the interaction potentials involved in the isotropic–nematic transition [1, 12, 27]. Maier and Saupe considered only the attractive part of the interaction potential of the nematic state resulting in $T_{\mathrm{Is\text{-}N}} \sim V_{\mathrm{Is\text{-}N}}^{-\gamma}$ with $\gamma = 2$ [28]. However, for many rod-like nematogens, the parameter $\gamma = -\partial \ln T_{\mathrm{NI}}/\partial \ln V_{\mathrm{NI}}$, is distinctly larger than 2 [1, 12], showing that the repulsive interaction part must also be taken into account. Applying this approach for an isotropic–smectic type transition as well, one obtains $\gamma = 2.7$ for the CrE–I transition of 8BT. This relatively small value is similar to findings for laterally aryl-branched liquid crystals [13].

4.3. *Calculation of the isochoric activation energy*

A recent dielectric relaxation study of 8BT yielded the longitudinal relaxation times as functions of temperature up to 345 K and pressures up to 120 MPa. This enabled us to derive the activation enthalpy $\Delta H^{\#} = R(\partial \ln \tau_{\|}/\partial T^{-1})_p$ and the activation volume $\Delta V^{\#} = RT(\partial \ln \tau_{\|}/\partial p)_T$ [18]. Using the PVT data, we can calculate additionally the activation energy $\Delta U^{\#} = R(\partial \ln \tau_{\|}/\partial T^{-1})_V$ for selected specific volumes. To this end we use a cross plot of $\ln \tau_{\|}$ as a function of pressure and appropriate isochores marked by dashed lines in figure 5. The corrresponding activation plots are presented in figure 6. This is the first such finding for a crystal-like E phase. The $\Delta H^{\#}$ and $\Delta U^{\#}$ values are interrelated by the PVT data: $\Delta H^{\#} = \Delta U^{\#} + (\partial p/\partial T)_V T \Delta V^{\#}$, showing that $\Delta U^{\#}$ must be smaller than $\Delta H^{\#}$ (for details of the relations see [1]). We compare the results with

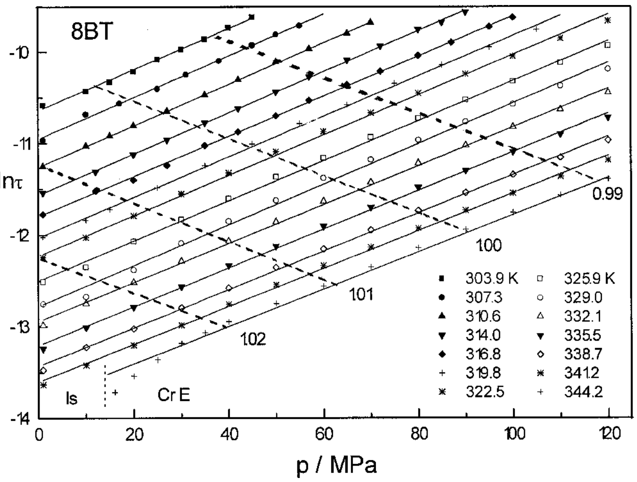

Figure 5. Pressure dependence of the longitudinal relaxation time (in logarithmic scale) for the crystal E phase (CrE) of 8BT (taken from [18]) with four isochores (v in $\mathrm{cm}^3\,\mathrm{g}^{-1}$) marked by dashed lines.

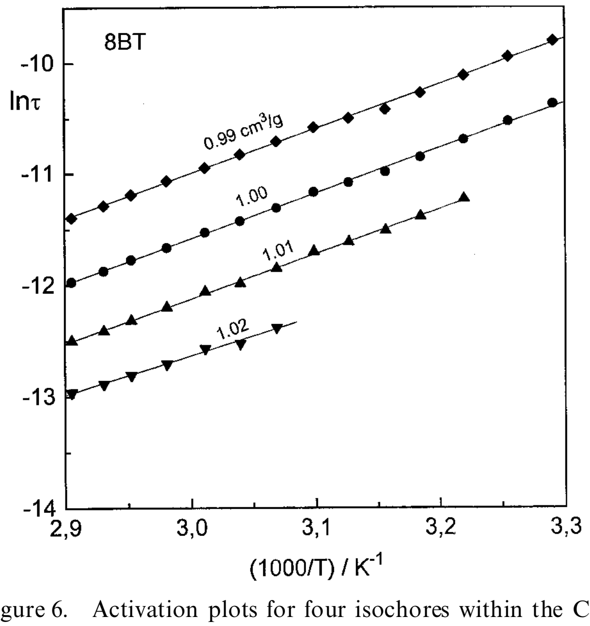

Figure 6. Activation plots for four isochores within the CrE phase of 8BT. The points were taken from figure 5.

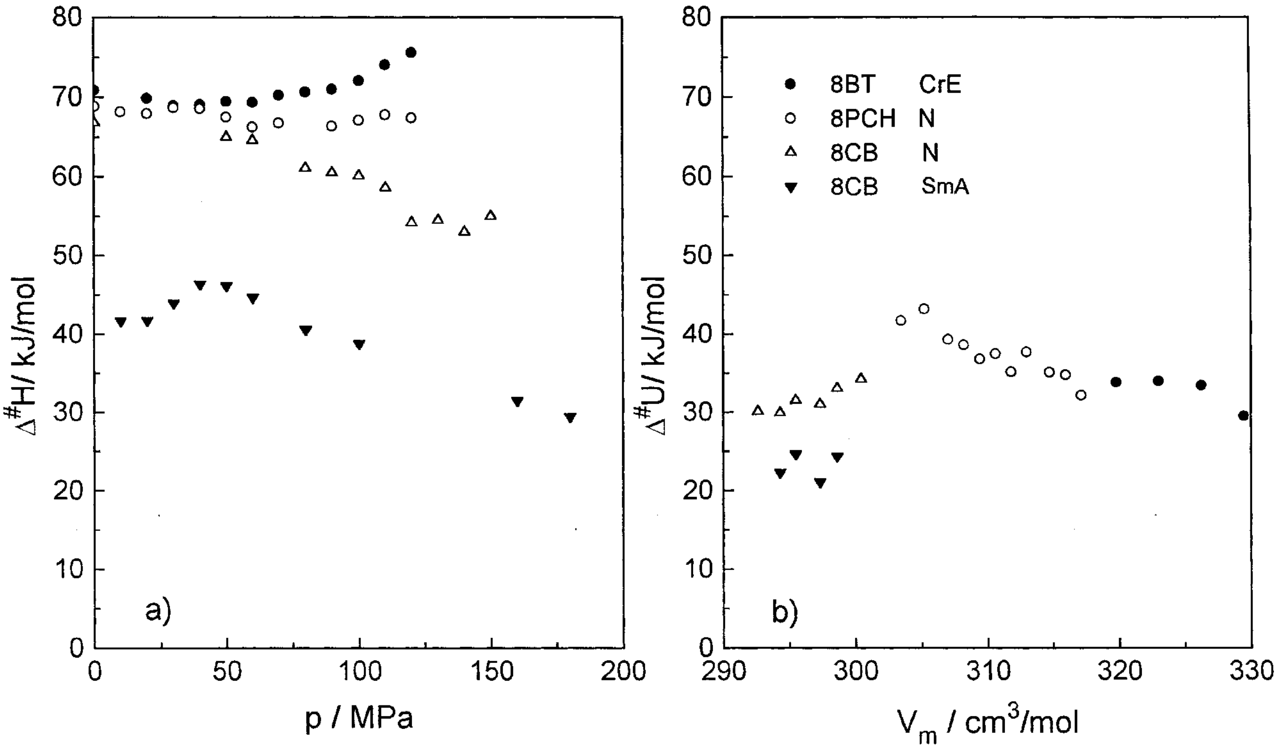

Figure 7. Comparison of (*a*) the activation enthalpies (as a function of pressure), and (*b*) the activation energies (as a function of volume) of 8BT (CrE phase), 8PCH (N phase) and 8CB (N and SmA$_d$ phase).

those for two other octyl compounds, 8PCH and 8CB [29, 30], see figure 7. Two facts are worth mentioning: (i) the activation parameters are very close for such different phases as the nematic and CrE phases, and (ii) independently of the LC phase (nematic, smectic A$_d$ or crystalline E) the activation energy amounts to approximately half of the activation enthalpy. This indicates that both temperature and volume effects determine the molecular rotations around the short axes in LC phases to the same extent.

5. Conclusions

For the first time, PVT measurements have been made for the crystal-like smectic E phase. The results obtained can be summarized as follows. The splitting of the clearing line observed in the DTA studies has now been corroborated in the volume measurements. A small step in the $v(p)$ plot on the $T = 393$ K isotherm corresponds well with a small thermal effect accompanying the transition from the induced phase to the isotropic phase [18]. This suggests that one is dealing with a liquid-like LC phase (probably nematic). The configurational part of the entropy of transition between the CrE and I phases is markedly larger than in the cases of transitions from liquid-like phases to the isotropic phase in similar substances. The interaction potential parameter $\gamma = 2.7$ for 8BT is considerably smaller than values obtained for 8CB [16] and 8PCH [15] ($\gamma = 4.0$ and 3.4, respectively). The activation parameters $\Delta H^{\#}$ and $\Delta U^{\#}$ for 8BT are close to the values obtained for similar substances exhibiting liquid-like phases, with the same relation between them.

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References

[1] Urban, S., and Würflinger, A., 1997, *Adv. chem. Phys.*, **98**, 143.

[2] Brückert, T., Büsing, D., Urban, S., and Würflinger, A., 1998, *Proc. SPIE*, **3318**, 198.

[3] Shashidhar, R., 1992, in *Phase Transitions in Liquid Crystals*, edited by S. Martellucci and A. N. Chester (Plenum Press), p. 245.

[4] Chandrasekhar, S., and Shashidhar, R., 1979, in *Advances in Liquid Crystals*, Vol. 4, edited by G. H. Brown (London: Academic Press), p. 84.

[5] Schmidt, C., Rittmeier-Kettner, M., Becker, H., Ellert, J., Krombach, R., and Schneider, G. M., 1994, *Thermochim. Acta*, **238**, 321.

[6] SCHNEIDER, G. M., BARTELT, A., FRIEDRICH, J., REISIG, H., and ROTHERT, A., 1986, *Physica*, **139&140B,** 616.

[7] HARTMANN, M., JENAU, M., WÜRFLINGER, A., GODLEWSKA, M., and URBAN, S., 1992, *Z. Physik. Chem.*, **177,** 195.

[8] MAEDA, Y., RAO, D. S. S., PRASAD, S. K., CHANDRASEKHAR, S., and KUMAR, S., 2001, *Liq. Cryst.*, **28,** 1679.

[9] VAN HECKE, G. R., 2001, in *Physical Properties of Liquid Crystals: Nematics*, EMIS Datareview Series, Vol. 25, edited by D. A. Dunmur, A. Fukuda, and G. R. Luckhurst (London: Institute of Electrical Engineers), p. 127.

[10] DAOUDI, A., LONGUEMART, S., ROUSSEL, F., KOLINSKY, C., and BAYLE, J. P., 2001, *Liq. Cryst.*, **28,** 291.

[11] WEDLER, W., 1998, in *Handbook of Liquid Crystals*, Vol. 1, edited by D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, and V. Vill (Weinheim: Wiley-VCH), p. 350.

[12] WÜRFLINGER, A., and SANDMANN, M., 2001, in *Physical Properties of Liquid Crystals: Nematics*, EMIS Datareview Series, Vol. 25, edited by D. A. Dunmur, A. Fukuda, and G. R. Luckhurst (London: Institute of Electrical Engineers), p. 151.

[13] WÜRFLINGER, A., SANDMANN, M., and WEISSFLOG, W., 2000, *Z. Naturforsch.*, **55a,** 823; WÜRFLINGER, A., and WEISSFLOG, W., 2000, *Z. Naturforsch.*, **55a,** 936.

[14] SCHMALFUSS, H., WEISSFLOG, W., WÜRFLINGER, A., MASBERG, S., and SCHNEIDER, G. M., 2001, *Z. Naturforsch.*, **56a,** 262.

[15] SANDMANN, M., HAMANN, F., and WÜRFLINGER, A., 1999, *Z. Naturforsch.*, **54a,** 281; SANDMANN, M., HAMANN, F., and WÜRFLINGER, A., 1997, *Z. Naturforsch.*, **52a,** 739.

[16] SANDMANN, M., and WÜRFLINGER, A., 1998, *Z. Naturforsch.*, **53a,** 233, 787.

[17] WÜRFLINGER, A., and URBAN, S., 2001, *Phys. Chem. chem. Phys.*, **3,** 3727.

[18] URBAN, S., WÜRFLINGER, A., and KOCOT, A., 2001, *Liq. Cryst.*, **28,** 1331.

[19] SANDMANN, M., 1998, PhD thesis, University of Bochum, Germany.

[20] JENAU, M., 1996, PhD thesis, University of Bochum, Germany.

[21] LANDAU, R., and WÜRFLINGER, A., 1980, *Rev. sci. Instrum.*, **51,** 533.

[22] URBAN, S., CZUPRYŃSKI, K., DĄBROWSKI, R., GESTBLOM, B., JANIK, J., KRESSE, H., and SCHMALFUSS, H., 2001, *Liq. Cryst.*, **28,** 691.

[23] WÜRFLINGER, A., and SCHNEIDER, G. M., 1973, *Ber. Bunsenges. Phys. Chem.*, **77,** 121.

[24] CLADIS, P. E., 1998, in *Handbook of Liquid Crystals*, Vol. 1, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (Weinheim: Wiley-VCH), Chap. 6.4.

[25] DROZD-RZOSKA, A., RZOSKA, S. J., and ZIOŁO, J., 2000, *Phys. Rev. E*, **61,** 5349; DROZD-RZOSKA, A., RZOSKA, S. J., and CZUPRYŃSKI, K., 2000, *Phys. Rev. E*, **61,** 5355.

[26] ABE, A., and NAM, SU Y., 1995, *Macromolecules*, **28,** 90; ABE, A., and NAM, SU Y., 1996, *Macromolecules*, **29,** 3337.

[27] ICHIMURA, H., SHIRAKAWA, T., TOKUDA, T., and SEIMIYA, T., 1983, *Bull. Chem. Soc. Jpn.*, **56,** 2238.

[28] MAIER, W., and SAUPE, A., 1959, *Z. Naturforsch.*, **14a,** 882; MAIER, W., and SAUPE, A., 1960, *Z. Naturforsch.*, **15a,** 287.

[29] MARKWICK, P., URBAN, S., and WÜRFLINGER, A., 1999, *Z. Naturforsch.*, **54a,** 275.

[30] URBAN, S., BÜSING, D., WÜRFLINGER, A., and GESTBLOM, B., 1998, *Liq. Cryst.*, **25,** 253.