DTA and *pVT* Measurements on 4-cyanobenzyl-5-(4-*n*-octyloxybenzoyloxy)-2-undecyloxybenzoate up to 250 MPa and 383 K

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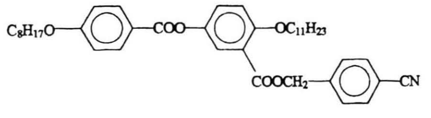
The phase diagram of 4-cyanobenzyl-5-(4-*n*-octyloxybenzoyloxy)-2-undecyloxybenzoate (4CNOUB) has been established with differential thermal analysis (DTA). The pressure range for the smectic A phase is limited, resulting in a triple point at 165 MPa and 378.26 K. p, V_m, T data have been measured for the smectic and istotropic phases of 4CNOUB between 243 and 383 K and up to 250 MPa. The volume changes accompanying the crystal – smectic and scmectic – isotropic transitions have been determined. The corresponding enthalpy changes have been calculated using the Clausius-Clapeyron equation. The p, V_m, T data enable also to estimate the volume entropy for the smectic – isotropic transition and the volume dependence of the clearing temperature.

Key words: Aryl-branched Liquid Crystals; High Pressure; *pVT*; Phase Transitions; Thermodynamics.

1. Introduction

In a preceding paper we reported p, V_m, T data for 3-cyanobenzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoate (3CNBOB) [1], which revealed features different from conventional rod-like liquid crystals. 3CNBOB was a representative of laterally aryl-substituted three-ring mesogens [2, 3]. The clearing temperatures of such compounds are unexpectedly high. One reason might be an intercalated packing of these molecules in smectic layers to reach a high packing density [4]. Also two-ring mesogens can be laterally substituted by phenyl containing groups [5]. As an example we consider 4-cyanobenzyl 5-(4-*n*-octoloxybenzoyloxy)-2-undecyloxybenzoate (4CNOUB), whose chemical structure is shown in Figure 1. The synthesis was performed as described for the unsaturated derivatives [6]. In the last reaction step, 4-cyanobenzyl 2-hydroxy-5-(4-*n*-octyloxybenzoyloxy) benzoate was alkylated with undecanol-1 by means of the Mitsunobu-reaction.

4-cyanobenzyl-5-(4-n-octyloxybenzoyloxy)-2-undecyloxy-benzoate



Cr$_1$ 35 Cr$_2$ 61 SmA 76.05 I M = 655 g mol^{-1}

Fig. 1. Structure of 4CNOUB.

2. Experimental

2.1. *Differential Thermal Analysis*

Two high-pressure devices, described in [7, 8], have been employed. The temperatures were measured with thermocouples. The DTA thermograms were displayed with a two-pen recorder or registered on-line with the aid of a personal computer. Both heating (1–2 K/min) and cooling runs were performed.

2.2. *pVT Measurements*

Two high-pressure dilatometers have been used. The older one is pressurized with compressed gas [9]. The new one is similarly constructed, but the pressure is transmitted by compressed oil [1, 10]. The new device enables us to achieve higher temperatures and to measure several isotherms with the same filling of the dilatometric cell. The densities at 1 atm were measured by Schmalfuß with a vibrating tube densimeter Anton Paar DMA 60 [11].

3. Results

3.1. *Measurements at Atmospheric Pressure*

Figure 2 shows a DSC measurement carried out in Halle. At ~ 60 K 4CNOUB melts to a smectic A phase, at ~ 76 K the clearing temperature is observed. On decreasing temperature the smectic phase can be considerably supercooled and crystallizes only reluctantly.

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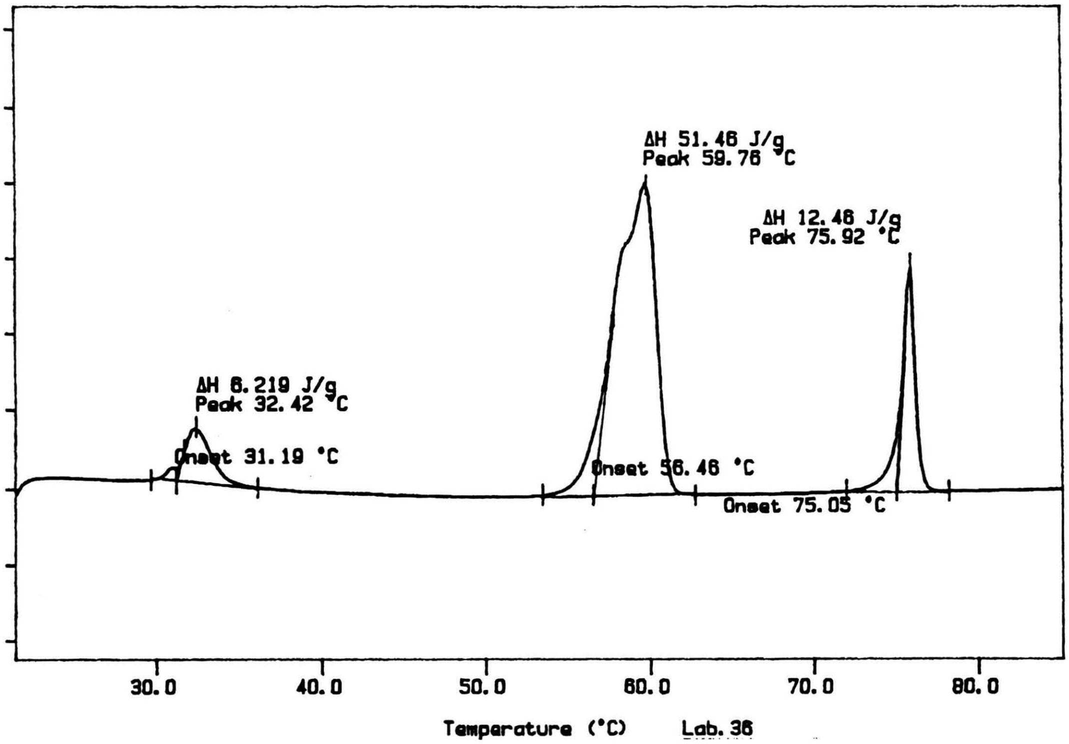

Fig. 2. DSC traces at atmospheric pressure for a not annealed sample of 4CNOUB.

Obviously metastable phases are formed which cause additional transitions on reheating (~ 35 K), cf. also the high-pressure results. The occurrence of several metastable phases has also been noted for other laterally aryl-branched liquid crystals [3].

In Fig. 3 the specific volume is presented as a function of temperature at 1 atm [11]. The volume step at the clearing temperature, $\Delta V_{\mathrm{SmA-I}} = 0.00765\ \mathrm{cm^3\ g^{-1}}$, is distinctly larger than $\Delta V_{\mathrm{NI}} \sim 0.002\ \mathrm{cm^3\ g^{-1}}$ for nematogens [12–14].

3.2. High-pressure DTA Measurements

Figure 4 shows DTA traces at moderate and higher pressure. Two peaks are observed at 63 MPa, corresponding to the melting curve (Cr–SmA) and the clearing line (SmA–Is). With increasing pressure the transition lines converge and intersect at a triple point at 165 MPa and 378.26 K. At 245 MPa only one peak is observed due to the melting Cr–Is. Thus the phase diagram was established (Fig. 5). The transition lines have been fitted to the polynomials:

$$\text{Cr–SmA:}\ T/\mathrm{K} = 331.4 + 0.3127\, p/\mathrm{MPa} - 1.7287 \cdot 10^{-4} (p/\mathrm{MPa})^2 \quad (p < p_{\mathrm{Triple}\,p.})$$

$$\text{SmA–Is:}\ T/\mathrm{K} = 348.3 + 0.1924\, p/\mathrm{MPa} - 6.6074 \cdot 10^{-5} (p/\mathrm{MPa})^2 \quad (p < p_{\mathrm{Triple}\,p.})$$

$$\text{Cr–Is:}\ T/\mathrm{K} = 344.1 + 0.2074\, p/\mathrm{MPa} \quad (p > p_{\mathrm{Triple}\,p.})$$

$$\text{Is–SmA:}\ T/\mathrm{K} = 351.2 + 0.1625\, p/\mathrm{MPa} \quad (p > p_{\mathrm{Triple}\,p.})$$

The DTA peaks obtained on cooling are also displayed in Figure 4. There is only little supercooling (≤ 1 K) of the Is–SmA transition. However, the freezing (SmA–Cr) could not be detected. Even above the triple point freezing is not observed. On cooling the isotropic liquid a transition occurred at lower temperatures with a heat effect distinctly smaller than the enthalpy of melting. This transition (indicated as a dashed line in Fig. 5) is also observed on reheating and looks very similar to the smectic-isotropic transition observed at lower pressures. It seems that the smectic phase exists also above the triple point as a metastable phase. The sample had to be annealed for several hours (or even overnight) at sufficiently low temperatures in order to reproduce the melting temperatures.

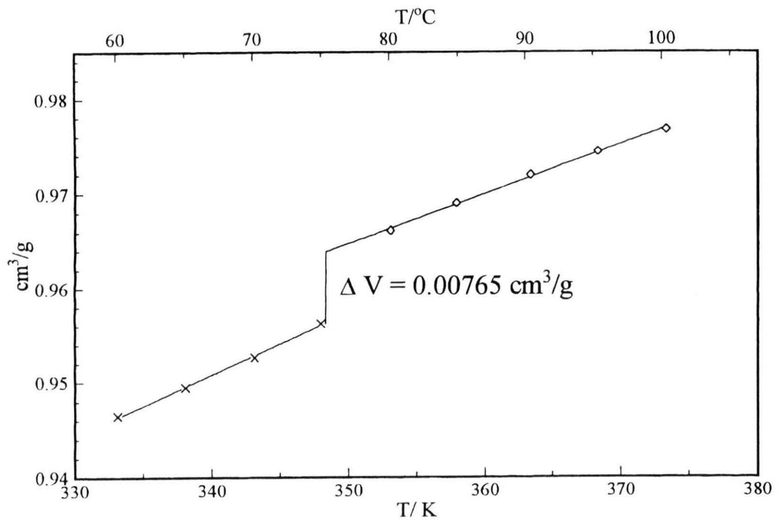

Fig. 3. Specific volume vs. temperature of 4CNOUB at atmospheric pressure after [11].

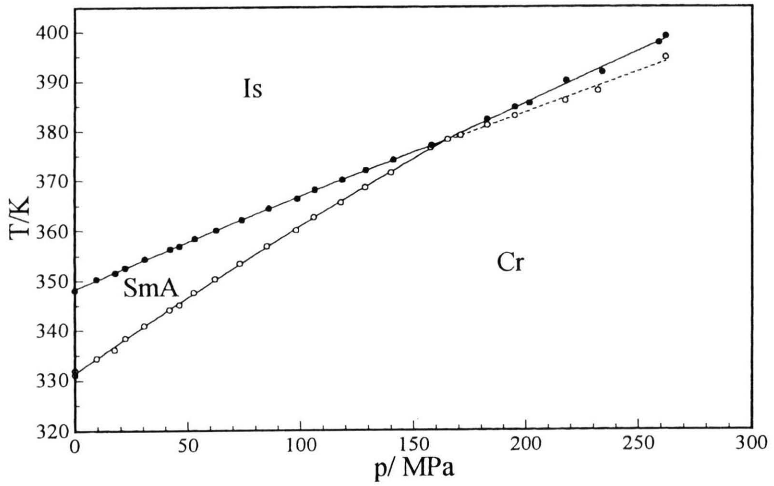

Fig. 5. Phase diagram of 4CNOUB. The dashed line presents the Is → SmA transition observed on cooling.

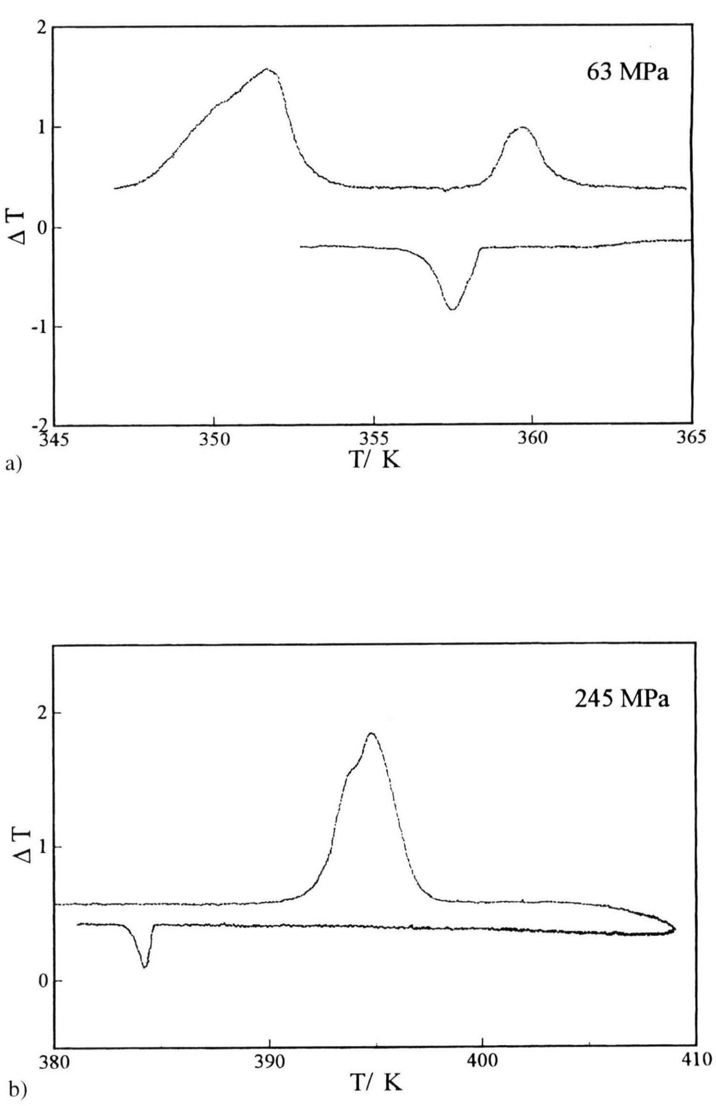

Fig. 4. DTA traces a) below, b) above the triple point. Lower curves correspond to cooling.

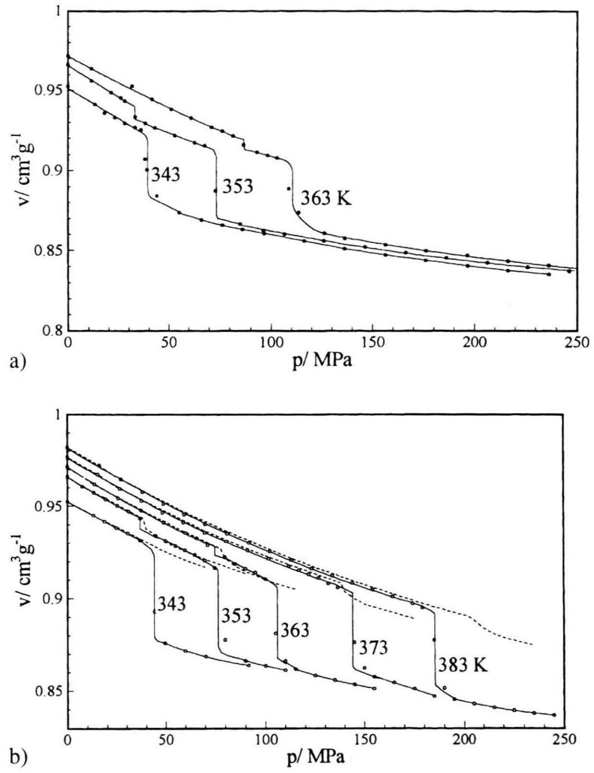

Fig. 6. Specific volumes of 4CNOUB as a function of pressure, a) gascompressed apparatus, b) oil-compressed apparatus; the steps in the isotherm refer to the transitions Cr → SmA and SmA → Is. The dashed lines were observed in rising pressure runs.

3.3. High-pressure Volume Measurements

In Fig. 6 the specific volume is plotted as a function of pressure for various temperatures. Clearly two different steps can be discerned corresponding to the melting and the clearing temperature, respectively. In general the isotherms are recorded on decreasing the pressure (Fig. 6a). In Fig. 6b isotherms are also shown for increasing pressure runs. Compressing – decompressing cycles are necessary for the determination of the hysteresis pressure [9, 10]. Apart from that, Fig. 6b shows the isotropic – smectic transition (dashed lines) for all isotherms. For $T \leq 363$ K the Is–SmA (and SmA-Is) step occurs at pressures lower than the melting pressure, in accordance with the phase diagram. At 373 K, just below the triple point melting and clearing cannot be separated on decreasing pressure, but with rising pressure the Is–SmA transition is visible. At 383 K the Is-SmA transition takes place at a pressure distinctly higher than the melting pressure. This superpressing effect corresponds to the supercooling effect observed in the DTA measurements.

The volume steps displayed in Fig. 6 enable the calculation of the enthalpy change with the aid of the Clausius-Clapeyron equation. Some thermodynamic data are gathered in Table 1, using averaged values from runs with both pVT devices. The high pressure results are in reasonable correspondence with atmospheric data taken from Figs. 2 and 3. Due to the insufficient resolution of the Cr–SmA–Is transitions at 373 K the observed volume step was attributed to a Cr–Is transition, although it is below the triple point.

4. Discussion

4-cyanobenzyl-5-(4-*n*-octyloxybenzoyloxy)-2-undecyloxybenzoate can be compared with 4-cyanobenzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoate (4CNBOB), whose high pressure phase behaviour was recently studied with DTA [3] and DSC [15]. Both liquid crystals exhibit the phase sequency crystal – smectic A – isotropic and similar transition enthalpies (for 4CNBOB [15]: $\Delta H_{\text{Cr-SmA}} = 35\ \text{J} \cdot \text{g}^{-1}$, $\Delta H_{\text{SmA-I}} = 11\ \text{J} \cdot \text{g}^{-1}$). The slope of the SmA– Is transition is for 4CNOUB significantly

Table 1. Thermodynamic properties of 4-cyanobenzyl-5-(4-*n*-octyloxybenzoyloxy)-2-undecyloxybenzoate.

T/K	Cr → S_mA			S_mA→ isotr.		
	p/MPa	ΔV/cm$^3 \cdot$ g^{-1}	ΔH/J $\cdot$ g^{-1}	p/MPa	ΔV/cm$^3 \cdot$ g^{-1}	ΔH/J $\cdot$ g^{-1}
	0.1		51.46	0.1	0.00765	12.46
343.15	38	0.045	51.6			
353.15	73	0.044	54.7	33	0.0072	13.5
363.15	110	0.042	55.2	87	0.0057	11.2
	Cr → isotr.			Isotr. → S_mA		
373.15	145	0.043	61.0	140	0.006	14
383.15	188	0.046	85.5	210	0.006	14

smaller $(\partial T/\partial p) = 0.192$ K/MPa) than for 4CNBOB (0.241 K/MPa), whereas the slopes of the melting curves are similar. Thus the smectic phase is pressure-limited for 4CNOUB, contrary to 4CNBOB. Recent DTA measurements on other liquid crystals of conventional shape yielded larger slopes for the SmA–Is transition as well [16].

As in previous papers we estimate the configurational part of the transition entropy by comparing the slopes of isochoric lines, $(\partial p/\partial T)_V$, with the slope of the clearing line [13, 14]. In the present work we find: $(\partial p/\partial T)_V \approx 1.2$ MPa/K for the smectic phase and ≈ 0.9 MPa/K for the isotropic phase. The slope of the SmA–Is transition line $(\partial T/\partial p)_{\text{SmA–Is}}$ varies, $(0.19 \div 0.17)$ K/MPa, in the pressure range in question, resulting in $\Delta S_{\text{conf}}/\Delta S_{\text{tr}} = [(\partial p/\partial T)_{\text{SmA–Is}} - (\partial p/\partial T)_V]/(\partial p/\partial T)_{\text{SmA–Is}} \approx 0.8$. The same high value was found for the nematic-isotropic transition in the laterally aryl-branched 3CNBOB [1], whereas Daoudi et al. report high values for the volume entropy $(\Delta S_{\text{NI}})_d = \Delta S_{\text{tr}} - \Delta S_{\text{conf}}$ of laterally substituted nematogens [17]. Also the variation of the density along the clearing line, $-\partial \ln T_{\text{SmA–I}}/\partial \ln V_{\text{SmA–I}} = 1.3$ is very similar to that for 3CNBOB: $-\partial \ln T_{\text{NI}}/\partial \ln V_{\text{NI}} = 1.35$. Again we conclude that the transition to the isotropic phase is not associated with a certain specific volume, discounting steric conditions for the onset of the NI or SmA–I transitions in a laterally aryl-branched liquid. On the other hand, the compressibilities of 4CNOUB and 3CNBOB are similar to those of conventional rod-like nematogens, being of the order of $\approx 5 \cdot 10^{-4}$ MPa^{-1} [13, 14, 18].

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