PVT Measurements on 4′-*n*-Octyl-Biphenyl-4-Carbonitrile (8CB) up to 300 MPa

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Z. Naturforsch. **53a**, 787–792 (1998); received July 10, 1998

P, V_m, T data have been measured for the smectic, nematic and isotropic phases of 4′-*n*-octyl-biphenyl-4-carbonitrile (8CB) in the temperature range 300–370 K and pressures up to 300 MPa. At atmospheric pressure all phase transitions appear to be of first order due to a discontinuity in the density. The volume change at the smectic A – nematic transition is only a tenth of the volume change at the clearing temperature. At moderate pressures below 80 MPa the S_A-N transition could be detected as a discontinuity in the period of oscillation in measurements with a high-pressure vibrating tube densimeter. At higher pressures the discontinuity seems to die away, possibly indicating a change from first order to second order transition. From the volume changes and the slopes of the transition lines we calculate the enthalpy changes at the phase transition. The p, V_m, T data enable us to calculate the volume part of the entropy and the molecular field parameter $\gamma = \partial \ln T_{NI} / \partial \ln V_{NI}$.

Key words: 8CB; High Pressure; pVT; Phase Transitions; Thermodynamics.

1. Introduction

In recent papers we reported p, V_m, T data for 5CB [1], 6CB and 7CB [2], which are typical representatives of liquid crystals with rod-like molecules, exhibiting nematic phases at moderate temperatures. In this paper we extend the investigation to 8CB, which displays additionally a smectic A phase (S_A). The nature of the S_A-nematic (N) transition is not clear [3]. In general it is described as being of second order, due to the vanishing enthalpy and volume change at this transition. Other authors proposed that the S_A-N transition possibly changes to second order at elevated pressures [4]. In the present work we perform careful volume measurements in the smectic, nematic and isotropic phases of 8CB. In particular the pressure dependence of S_A-N transition will be investigated.

2. Experimental

The high-pressure dilatometric cell has been described previously [1, 5]. In general the volume changes are recorded after equilibration of the temperature on decreasing the pressure. The densities at normal pressure are determined with a commercial vibrating-tube densimeter (Anton Paar DMA58). Additionally a high-pressure densimeter has been used in order to pursue the S_A-N transition at moderate pressures. To this end a special device was constructed in order to fill the high-viscous smectic sample into the measuring cell [6].

The 8CB (M=291.4 g mol^{-1}) samples were obtained from Merck and used without further purification. The liquid crystalline phases were not oriented in the dilatometer.

3. Results

In Fig. 1 the specific volume is plotted as a function of pressure and temperature. The largest step is observed at the transition from the crystal to the smectic A phase. The volume change at the nematic – isotropic transition is much smaller, nevertheless visible at all pressures. The volume change at the S_A-N transition (0.06 cm^3 mol^{-1} ~0.02%) is a magnitude smaller, just of the order of the detection limit; it is clearly detectable as a discontinuity in Fig. 2, where the specific volume is shown in function of temperature of atmospheric pressure. According to this discontinuity, the S_A-N transition is considered as a first order transition that has also been proposed by Leadbetter *et al.* [7]. Literature data at ambient pressure are reported by Dunmur and Miller [8], Łabno *et al.* [9], Shirakawa *et al.* [10], and Leadbetter *et al.* [7] and collected in Table 1. The best agreement is found with Dunmur and Miller [8]. The V (T) data at 1 atm have been fitted to the following polynomials:

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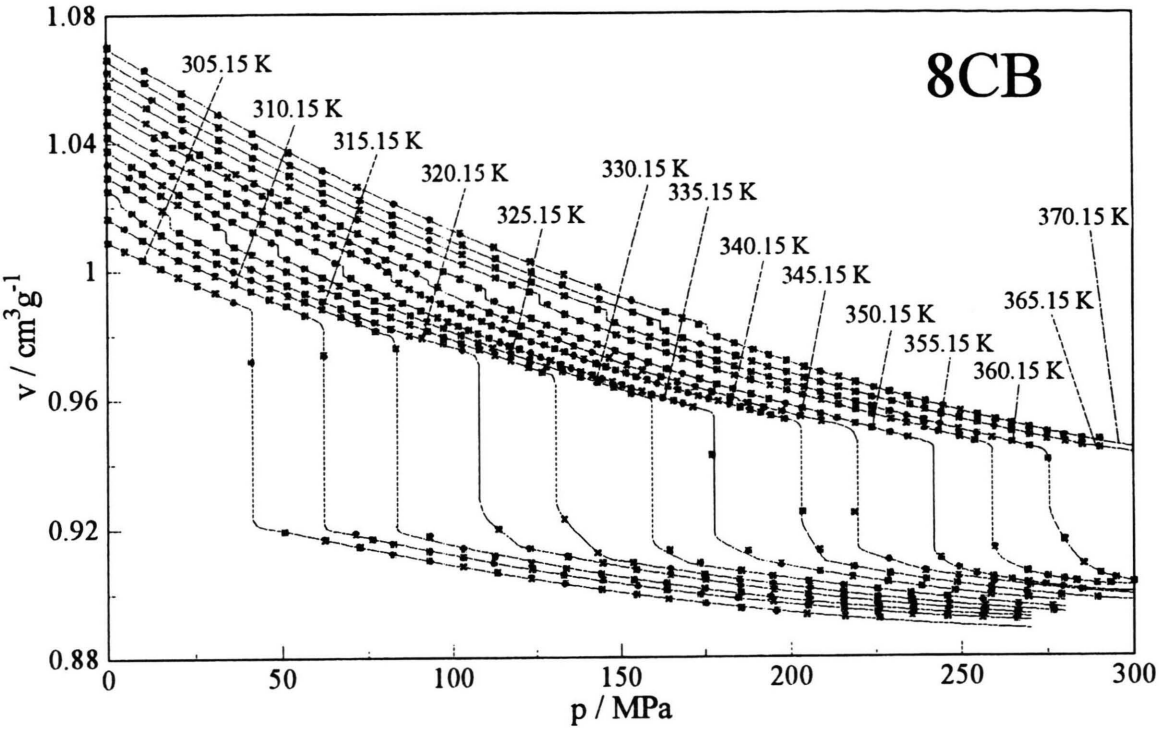

Fig. 1. Specific volumes of 8CB as a function of pressure, the steps in the isotherms refer to the transitions: cr $\rightarrow S_A$ and nematic $\rightarrow$ isotropic.

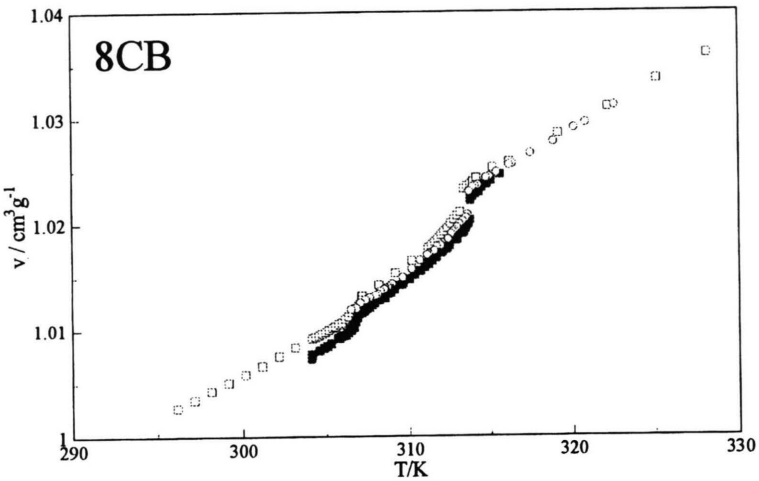

Fig. 2. Specific volumes of 8CB at atmospheric pressure, (□ this work, ■ Dunmur *et al.* [8], ○Łabno *et al.* [9].

Smectic A phase:

$$v/(\mathrm{cm}^3\cdot\mathrm{g}^{-1}) = 1.1947 - 2.065\cdot10^{-3}\,(T/\mathrm{K}) - 4.786\cdot10^{-6}\,(T/\mathrm{K})^2,$$

nematic phase:

$$v/(\mathrm{cm}^3\cdot\mathrm{g}^{-1}) = 2.5768 - 1.123\cdot10^{-2}\,(T/\mathrm{K}) + 2.000\cdot10^{-5}\,(T/\mathrm{K})^2,$$

isotropic phase:

$$v/(\mathrm{cm}^3\cdot\mathrm{g}^{-1}) = 0.7165 + 1.116\cdot10^{-3}\,(T/\mathrm{K}) - 4.320\cdot10^{-7}\,(T/\mathrm{K})^2.$$

The S_A-N transition could not be detected as a discontinuity in the high-pressure dilatometer. At most a break in the slope of the isotherms was visible at low pressures.

Table 1. Volume changes at 1 atm of the S_A-N and N-I transitions in comparison with literature.

Smectic A-nematic		Nematic-istotropic		Authors
T/K	ΔV/(cm^3 · mol^{-1})	T/K	ΔV/(cm^3 · mol^{-1})	
306.5	0.06	313.2	0.57	This work
		313.65	0.65	Łabno *et al.* [9]
306.8	0.09	313.8	0.51	Dunmur *et al.* [8]
		313.84	0.71	Shirakawa *et al.* [10]
306.7	0.14	313.7	0.95	Leadbetter *et al.* [7]

A better resolution is observed with the high-pressure vibrating tube densimeter. In Fig. 3 the S_A-N transition is seen as a discontinuity in the period of oscillation up to 40 MPa. At pressures higher than 80 MPa the S_A-N transition cannot be detected. The specific volume data are collected in detail in Table 2; a solid line in a column separates different phases.

The phase diagram is presented in Fig. 4, where also previous data obtained with DTA [11] and high-pressure optical measurements [12] have been included. The crystal – smectic A and smectic A – nematic phase boundaries converge, resulting in a triple point at $p = 300$ MPa, $T = 367$ K [13].

The pressure dependences of the phase transition temperatures have been fitted to polynomials and are collected in Table 3. There is no indication of metastable or reentrant phases, in agreement with a recent high-pressure X-ray study [14]. In [14] an anomaly in the layer spacing was observed at about 150 MPa for 8CB. Our dilatometric study does not exhibit any discontinuity in the isotherms.

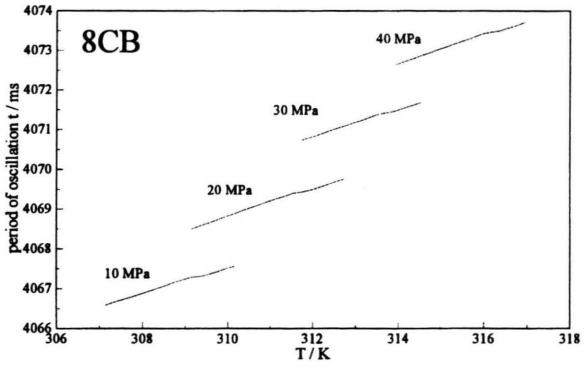

Fig. 3. Period of oscillation against temperature for various pressures showing the discontinuity due to the S_A-N transition.

The estimated volume changes, ΔV, and thermodynamic calculations of ΔH, and ΔS are presented in Table 4. Although the volume step ΔV_{NI} seems to be better defined than in the case for 5CB, we cannot assign a significant pressure dependence, let alone for the S_A-N transition. Anyway, the discontinuity in the density at the N-I transition seems not to die away with increasing pressure.

A lot of atmospheric pressure data are available for comparison; some literature data for the S_A-N and N-I transitions are collected in Table 5. The melting enthalpy (27.65 kJ/mol, calculated with the Clausius-Clapeyron equation) is somewhat larger than values reported by Coles *et al.* (23.43 kJ/mol [15]), Leadbetter *et al.* (23 kJ/mol [7], and Liebert *et al.* (25.17 kJ/mol [13]).

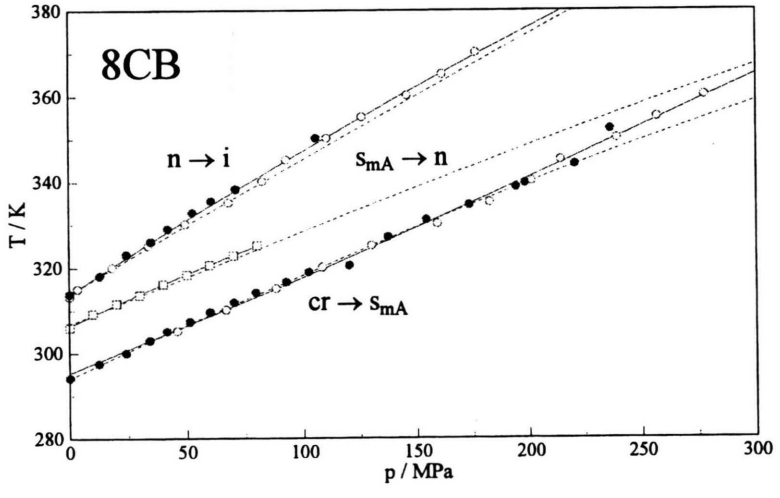

Fig. 4. Phase diagram of 8CB. ○, □ this work, ● DTA [11], - - - Cladis *et al.* [12].

Table 2a. Specific volumes ($g^{-1} \cdot cm^3$) of 8CB for the phases cr, S_A, N and I.

p/MPa	T/K						
	305.15	310.15	315.15	320.15	325.15	330.15	335.15
0.1	1.009	1.017	1.025	1.029	1.034	1.038	1.042
5	1.006	1.013	1.020	1.026	1.030	1.034	1.039
10	1.004	1.010	1.016	1.023	1.027	1.031	1.035
15	1.001	1.007	1.012	1.020	1.024	1.028	1.032
20	0.998	1.004	1.009	1.013	1.021	1.025	1.029
25	0.996	1.001	1.006	1.010	1.018	1.022	1.026
30	0.993	0.999	1.003	1.007	1.015	1.019	1.023
35	0.991	0.997	1.000	1.004	1.009	1.016	1.020
40	0.989	0.994	0.998	1.001	1.006	1.013	1.017
45	0.987	0.992	0.996	0.999	1.003	1.010	1.014
50	0.920	0.989	0.993	0.996	1.001	1.004	1.012
55	0.919	0.987	0.991	0.994	0.998	1.002	1.009
60	0.917	0.985	0.989	0.991	0.995	0.999	1.006
65	0.916	0.982	0.987	0.989	0.993	0.997	1.003
70	0.915	0.919	0.984	0.987	0.991	0.994	0.997
75	0.914	0.917	0.982	0.985	0.988	0.992	0.995
80	0.913	0.916	0.980	0.983	0.986	0.989	0.993
85	0.912	0.915	0.978	0.981	0.984	0.987	0.990
90	0.911	0.914	0.917	0.979	0.982	0.985	0.988
95	0.910	0.913	0.916	0.977	0.980	0.983	0.986
100	0.909	0.912	0.915	0.976	0.978	0.981	0.983
105	0.908	0.911	0.914	0.975	0.976	0.979	0.981
110	0.907	0.910	0.913	0.917	0.975	0.977	0.979
115	0.906	0.909	0.912	0.916	0.973	0.975	0.977
120	0.905	0.908	0.911	0.915	0.971	0.973	0.975
125	0.904	0.907	0.910	0.913	0.969	0.971	0.973
130	0.903	0.906	0.909	0.912	0.967	0.970	0.971
135	0.903	0.905	0.908	0.911	0.915	0.968	0.970
140	0.902	0.905	0.907	0.910	0.914	0.966	0.968
145	0.901	0.904	0.906	0.909	0.912	0.964	0.966
150	0.900	0.903	0.905	0.908	0.910	0.963	0.964
155	0.900	0.902	0.904	0.907	0.909	0.961	0.963
160	0.899	0.901	0.903	0.906	0.908	0.913	0.961
165	0.898	0.901	0.903	0.906	0.907	0.911	0.959
170	0.897	0.900	0.902	0.905	0.907	0.909	0.958
175	0.897	0.899	0.901	0.904	0.906	0.908	0.956
180	0.896	0.899	0.900	0.903	0.905	0.907	0.955
190	0.895	0.897	0.899	0.902	0.903	0.906	0.910
200	0.894	0.896	0.898	0.900	0.902	0.904	0.908
210	0.893	0.895	0.897	0.899	0.901	0.903	0.906
220	0.892	0.894	0.896	0.898	0.899	0.902	0.905
230	0.891	0.894	0.895	0.897	0.898	0.900	0.903
240	0.890	0.893	0.894	0.896	0.897	0.898	0.901
250	0.890	0.892	0.893	0.895	0.896	0.898	0.900
260	0.889	0.892	0.893	0.894	0.896	0.897	0.899
270	0.889	0.891	0.892	0.893	0.894	0.896	0.898

Table 2b. Specific volumes ($g^{-1} \cdot cm^3$) of 8CB for the phases cr, S_mA, N and I.

p/MPa	T/K						
	340.15	345.15	350.15	355.15	360.15	365.15	370.15
0.1	1.046	1.050	1.054	1.058	1.062	1.066	1.070
10	1.040	1.044	1.047	1.052	1.055	1.059	1.063
20	1.033	1.038	1.041	1.045	1.049	1.053	1.057
30	1.027	1.032	1.035	1.039	1.043	1.047	1.050
40	1.022	1.026	1.029	1.033	1.037	1.041	1.044
50	1.016	1.020	1.023	1.028	1.031	1.035	1.039
60	1.011	1.015	1.018	1.022	1.026	1.029	1.033
70	1.005	1.009	1.013	1.017	1.020	1.024	1.027
80	1.000	1.004	1.008	1.012	1.015	1.019	1.022
90	0.993	0.998	1.003	1.008	1.010	1.014	1.017
100	0.988	0.992	0.998	1.003	1.006	1.009	1.012
110	0.984	0.987	0.994	0.999	1.001	1.004	1.008
120	0.979	0.983	0.987	0.995	0.997	1.000	1.003
130	0.976	0.979	0.982	0.988	0.993	0.996	0.999
140	0.972	0.975	0.978	0.984	0.989	0.992	0.995
150	0.968	0.971	0.974	0.979	0.982	0.988	0.991
155	0.967	0.969	0.972	0.978	0.981	0.986	0.990
160	0.965	0.968	0.971	0.976	0.979	0.985	0.988
165	0.963	0.966	0.969	0.974	0.977	0.980	0.986
170	0.962	0.964	0.967	0.972	0.975	0.978	0.985
175	0.960	0.963	0.965	0.970	0.973	0.976	0.983
180	0.959	0.961	0.964	0.968	0.971	0.974	0.978
185	0.957	0.960	0.962	0.967	0.969	0.973	0.976
190	0.956	0.958	0.961	0.965	0.968	0.971	0.975
195	0.954	0.956	0.959	0.963	0.966	0.969	0.973
200	0.953	0.955	0.958	0.962	0.964	0.968	0.971
205	0.911	0.954	0.956	0.960	0.963	0.966	0.969
210	0.910	0.953	0.955	0.959	0.961	0.964	0.968
215	0.909	0.913	0.953	0.957	0.960	0.963	0.966
220	0.908	0.911	0.952	0.956	0.958	0.961	0.964
225	0.907	0.910	0.950	0.955	0.957	0.960	0.963
230	0.906	0.909	0.949	0.953	0.955	0.959	0.961
235	0.905	0.907	0.948	0.952	0.954	0.957	0.960
240	0.904	0.907	0.910	0.951	0.953	0.956	0.958
245	0.903	0.906	0.908	0.949	0.951	0.955	0.957
250	0.902	0.905	0.907	0.948	0.950	0.953	0.956
255	0.902	0.904	0.906	0.946	0.949	0.952	0.954
260	0.901	0.903	0.905	0.910	0.948	0.951	0.953
265	0.900	0.903	0.904	0.908	0.946	0.950	0.952
270	0.900	0.902	0.903	0.906	0.945	0.949	0.951
275	0.899	0.901	0.902	0.905	0.943	0.947	0.950
280	0.899	0.901	0.901	0.904	0.909	0.946	0.949
285	0.898	0.900	0.901	0.903	0.907	0.945	0.948
290	0.898	0.900	0.900	0.902	0.905	0.945	0.947

4. Discussion

Regarding the thermodynamic properties at the phase transitions the volume change at the S_A-N transition is of particular interest. Our findings as well as those of Dunmur *et al.* [7] for 8CB and Orwoll *et al.* [18] for 8OCB (they report a density change of $7 \cdot 10^{-5}$ cm^3 g^{-1} at the S_A-N transition) support its first order nature. However, Thoen *et al.* [3] report a second order transition.

Table 3. Transition Temperatures as a Function of Pressure for 8CB. $T/K = a + b \cdot p/MPa + c \cdot (p/MPa)^2$.

Transition	a	b	$10^4\, c$
cr → S_A	295.36	0.219	−0.45
S_A → N	306.33	0.261	−3.4
N → i	313.81	0.355	−2.19

At higher pressures the discontinuity seems to die away. Similar finding is reported for 8OCB with heat capacity measurements [19].

Table 4. Thermodynamic Properties of 8CB.

Phase Transition	T/K	p/MPa	ΔV_m/ ($cm^3 \cdot mol^{-1}$)	ΔH_m/ ($kJ \cdot mol^{-1}$)	ΔS_m/ ($J \cdot mol^{-1} \cdot K^{-1}$)
N→i	313.15	0.1	0.57	0.50	1.60
	315.15	3.5	0.93	0.83	2.63
	320.15	18.2	0.93	0.85	2.68
	325.15	33.7	0.87	0.83	2.56
	330.15	49.4	0.82	0.80	2.43
	335.15	68.0	0.44	0.45	1.34
	340.15	82.4	0.85	0.90	2.68
	345.15	92.6	0.85	0.92	2.68
	350.15	110.3	0.90	1.03	2.93
	355.15	125.8	0.82	0.96	2.72
	360.15	145.8	0.82	1.01	2.81
	365.15	161.3	0.82	1.05	2.88
	370.15	176.2	0.73	0.97	2.61
S_A→N	306.05	0.1	0.06	0.07	0.2
	309.25	10.0			
	311.65	20.0			
	313.65	30.0			
	316.25	40.0			
	318.45	50.0			
	320.65	60.0			
	322.85	70.0			
	325.15	80.0			
cr→S_A	294.50	0.1	20.56	27.65	93.88
	305.15	45.9	18.60	25.44	83.36
	310.15	66.8	17.71	23.47	75.69
	315.15	88.2	16.80	23.13	73.41
	320.15	108.3	15.94	22.78	71.16
	325.15	130.0	15.02	22.32	68.64
	330.15	159.1	13.78	21.48	65.06
	335.15	182.3	12.79	20.78	62.01
	340.15	201.0	11.99	20.21	59.43
	345.15	214.1	11.43	19.86	57.55
	350.15	239.2	10.36	18.84	53.79
	355.15	256.8	9.61	18.12	51.02
	360.15	277.8	8.72	17.13	47.55

Table 5. Enthalpy changes at 1 atm of the S_A-N and N-I transitions in comparison with literature.

Smectic A-nematic		Nematic-istotropic		Authors
T/K	ΔH/ ($kJ \cdot mol^{-1}$)	T/K	ΔH/ ($kJ \cdot mol^{-1}$)	
306.5	0.06	313.2	0.5	This work
308	0.04	313.4	0.669	Coles *et al.* [15]
306.7	0.20	313.7	0.70	Leadbetter *et al.* [7]
305.2	0.12	313.2	0.87	Liebert *et al.* [13]
305.0	0.10			Rojas *et al.* [16]
		313.75	0.67	Bauman *et al.* [17]

As in previous papers we can split the entropy change, ΔS_{tr}, at a first-order phase transition into a constant-volume (or configurational) part, and a dilatational part [1, 2]. The latter part is evaluated using our p, V_m, T data: $\Delta S_V = (\partial S/\partial V)_T \Delta V_{tr} = (\partial p/\partial T)_V \Delta V_{tr}$. Combining with the Clausius-Clapeyron equation $(\partial p/\partial T)_{tr} = \Delta S_{tr}/\Delta V_{tr}$ yields $\Delta S_{conf}/\Delta V_{tr} = [(\partial p/\partial T)_{tr} - (\partial p/\partial T)_V]$.

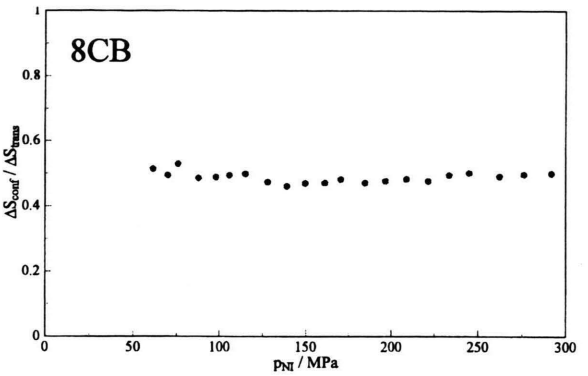

Fig. 5. Entropy separation for the nematic → isotropic transition of 8CB.

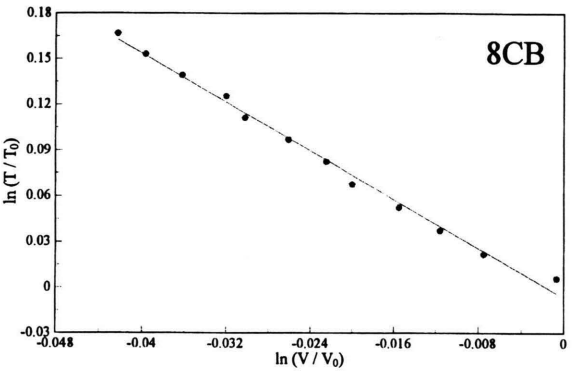

Fig. 6. Logarithm of the clearing temperature against the logarithm of the molar volume as a function of pressure for 8CB; T_0 and V_0 refer to atmospheric pressure.

Figure 5 shows that in agreement with previous finding the configurational part ΔS_{conf} amounts to approximately 50% of ΔS_{tr}.

The pressure dependence of the nematic → isotropic ($T_{NI}(p)$) phase transition can be combined with the p, V_m, T data, in order to determine the slope $\gamma = \partial \ln T_{NI}/\partial \ln V_{NI}$, which is related to the molecular field potential. Figure 6 shows a plot for 8CB, which yields $\gamma = 4$ for 8CB. This value is somewhat smaller than found for 5CB and 6CB, but still significantly exceeding 2 (that would correspond to only attractive forces).

Acknowledgement

Financial support of the Deutsche Forschungsgemeinschaft (Wu 97/10-1) and Fonds der Chemischen Industrie is gratefully acknowledged.

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