

Volumetric study of *n*-octyloxy-cyanobiphenyl (8OCB)

C. Michael Roland^a, Daniel Fragiadakis^a, Debjani Roy^a and Stanisław Urban^{b*}

^aChemistry Division, Naval Research Laboratory, 20375 Washington, DC, USA; ^bInstitute of Physics, Jagiellonian University, 30-059 Krakow, Poland

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Volumetric measurements were carried out on *n*-octyloxy-cyanobiphenyl (8OCB) over temperatures from ambient to 150°C at pressures up to 200 MPa, encompassing the liquid, nematic and smectic liquid crystalline, and crystal states. From the step changes in volume at the transitions, the phase boundaries and the associated activation enthalpies and energies were determined. The results are consistent with prior studies that were limited to a narrower range of thermodynamic conditions. The thermodynamic potential parameter, Γ , found for the isotropic–nematic transition, =3.15, is significantly smaller than the scaling exponent γ (=4.4) that superposes the longitudinal relaxation times in the nematic state. From this non-equivalence, we conclude that the order parameter must vary with pressure along the clearing line. By comparing the phase behaviour of the nematic state for isochoric and isobaric conditions, the relative contribution of volume was determined to be less than the effect of thermal energy on the thermodynamic stability.

Keywords: specific volume; high pressure; interaction potential; 8OCB

1. Introduction

The relationship between pressure, P , volume, V , and temperature, T ; that is, the equation of state, $V(P, T)$, is essential to understanding the physical properties of condensed matter under different thermodynamic conditions. This is seen in studies of calamitic liquid crystals (LCs) using hydrostatic pressure, which number in the hundreds (for reviews see [1–7]). From PVT data combined with dielectric relaxation times measured in various LC phases, the phase behaviour, nematic order parameter, and the dielectric tensor permittivity components of nematics have been determined. Especially important in understanding LCs is characterisation of the interaction potential in the LC phases. The thermodynamic potential parameter Γ is defined as

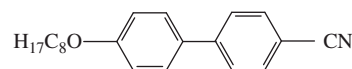
$$\Gamma = - \left(\frac{d \log(T_c/T_0)}{d \log(V_c/V_0)} \right)_P \quad (1)$$

where T_c and V_c refer to the respective temperature and specific volume along the pressure-dependent phase boundary (T_0 and V_0 correspond to ambient pressure). Dynamical quantities (relaxation time τ , viscosity, diffusion constant, etc.) have been reported for isobaric, isochoric, and isothermal conditions [2,3,5–7], enabling determination, via the thermodynamic scaling

$$\tau = f(TV^\gamma) \quad (2)$$

of the interaction parameter γ characterising the steepness of the intermolecular potential [5–12]. The possible equivalence of the two potential parameters, Γ and γ , was discussed in refs. [5–7,13].

n-Octyloxy-cyanobiphenyl (8OCB, molar mass = 307.4 g/mol),



exhibits isotropic (I), nematic (N), smectic A_d (S_{Ad}), and crystalline (Cr) phases, as revealed by numerous studies performed at ambient pressure (for example [14,15]), as well as at elevated pressure [16–22]. Cladis [16] discovered the re-entrant phenomenon (reemergence of a nematic phase at a lower temperature than a more ordered smectic state) in the pressure–temperature phase diagram. Above about 160 MPa, the sequence of transitions on cooling follows:



However, the metastable nature of this phenomenon makes observation difficult. Specific volume was measured in three studies [17,19,22], in which the focus was on determination of the thermodynamic parameters accompanying the phase transitions. With these in mind, we decided to perform PVT measurements over broad temperature and pressure ranges, to allow us to analyse the dielectric relaxation times obtained by the Bochum

*Corresponding author. Email: ufurban@cyf-kr.edu.pl

group [20,21]. Our aim is to apply thermodynamic scaling of the relaxation times, Equation (2), in order to determine the interaction parameter characterising the steepness of the interaction potential ([5–7,23] and references therein).

2. Experimental

The 8OCB sample was synthesised by Prof. R. Dąbrowski's group at the Institute of Chemistry, Military University of Technology, Warsaw, Poland. Its purity was higher than 99.9%. The volume change of a ~ 1 ml sample was measured as a function of pressure and temperature with a Gnomix instrument [23], utilising mercury as the confining fluid. At each pressure, the sample was cooled at $0.5^\circ\text{C}/\text{min}$ from above the clearing temperature to 20°C . During the ensuing isobaric run, the pressure was raised prior to increasing the temperature to an initial value in the range from 90 to 140°C depending on the pressure. The differential volume data were converted to specific volume using the specific gravity determined at ambient conditions.

3. Results

In Figure 1a are the isobaric $V(T)$ data for heating runs, with examples of the strong supercooling during both heating and cooling illustrated in Figure 1b. The transitions I–N and S_A –Cr are readily apparent as step changes in the specific volume. However, the transition S_A –N is not detected in our measurements, contrary to other studies [14,19–22]. The line separating the S_A –N phases was drawn according to the results of Brückert et al. [20,21]. The pressure dependence of the volume

change at the Cr– S_A transition on cooling and heating the 8OCB are shown in the inset to Figure 1b.

In Figure 2, the $T(P)$ phase diagram based on the PVT measurements is compared with the dielectric data obtained from Brückert et al. [20,21] and Johnson and Collings [17]. There is good agreement only for the N–I transition. Quadratic polynomial fits to the PVT results yield (T in K, P in MPa):

N–I

$$T = 354.6 + 0.351P - 2.00 \times 10^{-4}P^2 \text{ [this work]}$$

$$T = 352.6 + 0.354P - 2.42 \times 10^{-4}P^2 \text{ [17]}$$

$$T = 353.7 + 0.346P - 0.86 \times 10^{-4}P^2 \text{ [20,21]}$$

S_A –N

$$T = 339.6 + 0.166P - 2.88 \times 10^{-4}P^2 \text{ [17]}$$

$$T = 339.5 + 0.192P - 4.82 \times 10^{-4}P^2 \text{ [20,21]}$$

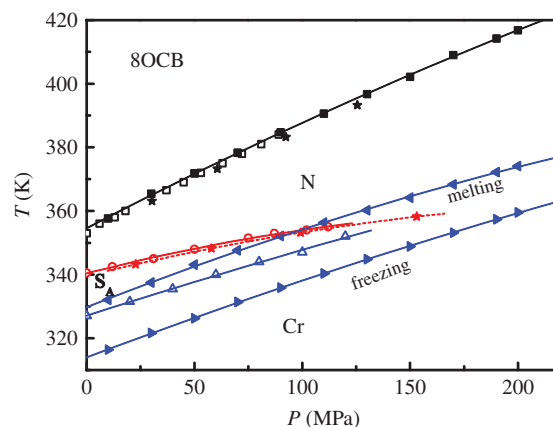
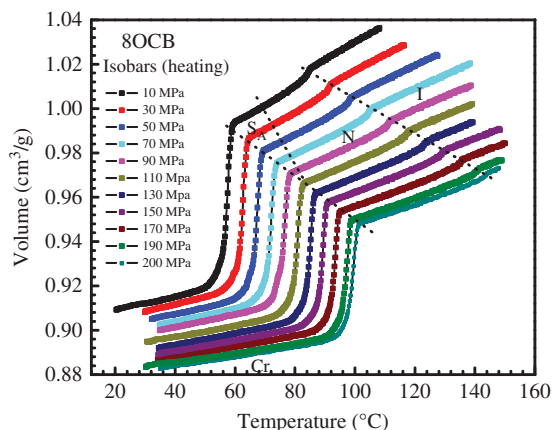
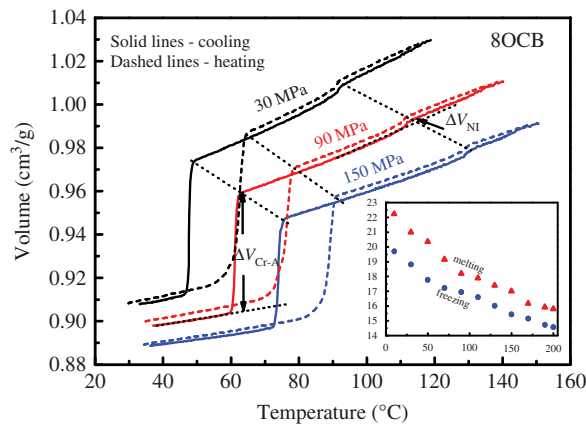


Figure 2. (colour online) Phase diagram of 8OCB determined from the PVT (full symbols), along with literature results (stars: Johnson and Collings [17]; open symbols: Brückert et al. [20,21]).



(a)



(b)

Figure 1. (colour online) (a) Isobaric specific volume for 8OCB on heating (the line separating S_A and N phases from ref. [21]). (b) Typical results for the irreversible behaviour of the volume on heating and cooling, with the volume changes at the phase transitions denoted by arrows. Inset shows the pressure dependence of the volume changes at the Cr– S_A transition.

$$\begin{aligned} \text{Cr-S}_A \\ T &= 329.7 + 0.268P - 2.37 \times 10^{-4}P^2 \text{ melting} \\ &\text{[this work]} \\ T &= 314.0 + 0.255P - 1.41 \times 10^{-4}P^2 \text{ freezing} \\ &\text{[this work]} \end{aligned}$$

Note from linear fits Cusmin et al. [22] reported pressure coefficients equal to 0.307 and 0.300 K/MPa for the N–I and Cr–S_A transitions, respectively, which are within 12% of the values herein at low pressure.

In Figure 3 is a double logarithmic plot for the N–I transition according to Equation (1), yielding the thermodynamic potential parameter $\Gamma = 3.15$. There is good agreement of the present data with the results of Johnson and Collings [17].

The longitudinal relaxation times were measured by Brückert et al. [20,21] in the nematic and smectic phases of 8OCB. Because of the narrow range and pressure-limited character of the S_A phase (Figure 2), only data for the N phase are included in our present analysis. Figure 4 shows a semi-logarithmic plot of τ vs. P for 12 isotherms within the N phase. From Arrhenius plots for isobaric and isochoric conditions (Figure 5) the respective activation enthalpy and energy were obtained

$$\text{Activation enthalpy: } \Delta H = R \left(\frac{\partial \ln \tau}{\partial \ln(1/T)} \right)_P \quad (3)$$

$$\text{Activation energy: } \Delta U = R \left(\frac{\partial \ln \tau}{\partial \ln(1/T)} \right)_V \quad (4)$$

The former is considerably larger, as found for other LC materials [2,5–12,24,25]. Figure 6 compares the two quantities for the N phase of 8OCB and 8CB [26]. ΔH is roughly two times larger, indicating

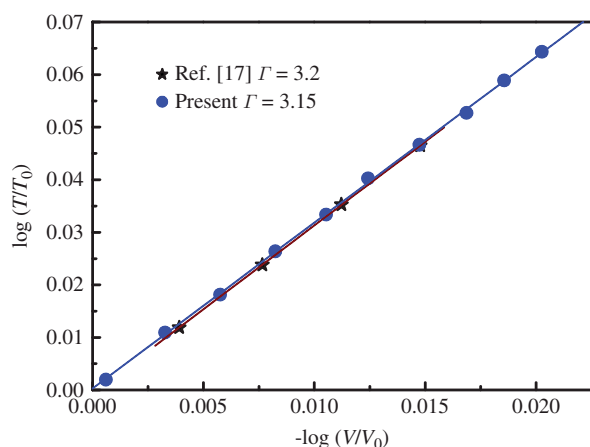


Figure 3. (colour online) Clearing temperature versus volume for the N–I transition determined herein (circles) and determined by Johnson and Collings [17] (stars). The Γ values are indicated.

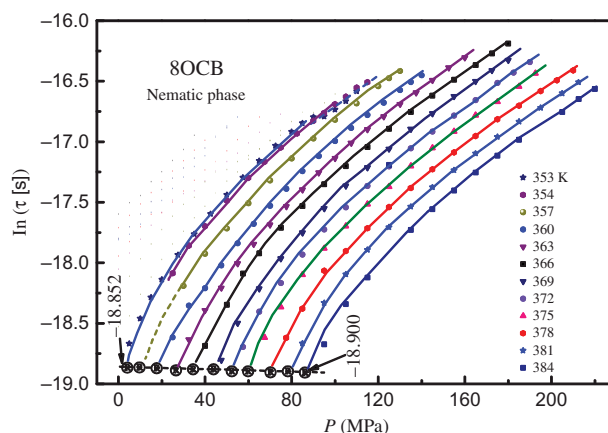


Figure 4. (colour online) Longitudinal relaxation time for the nematic phase of 8OCB at several isotherms. The values extrapolated to the clearing line are marked (Brückert et al. [20,21]).

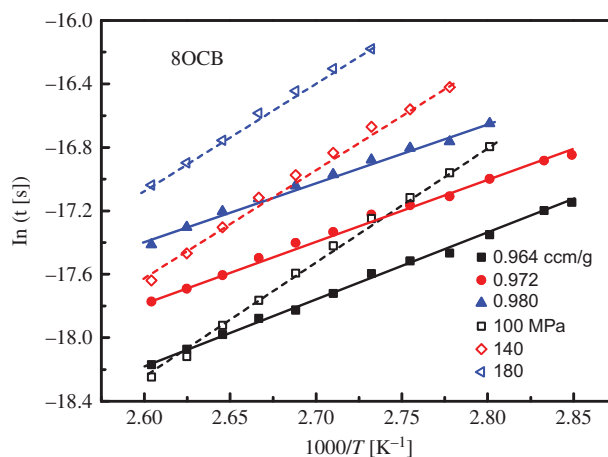


Figure 5. (colour online) Arrhenius plots for three isochors (full symbols) and three isobars (open symbols) in the nematic phase of 8OCB. The slopes yield the respective activation energy and activation enthalpy.

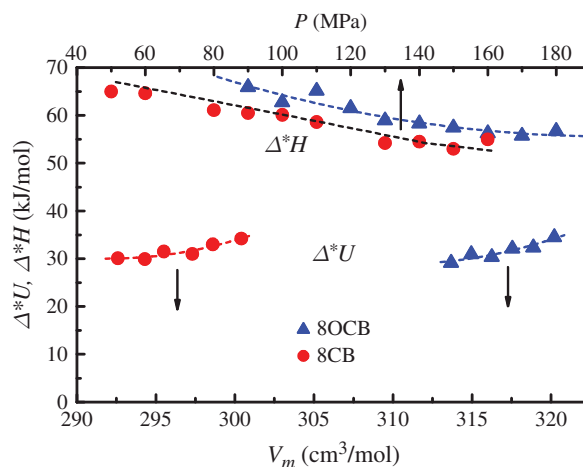


Figure 6. (colour online) Activation enthalpy for different isobars and activation energy for different isochors within the nematic phase of 8OCB (triangles) and 8CB (circles) [26].

that thermal energy and volume govern equivalently rotation about the short molecular axis ('flip-flop' motion). A decrease in the activation enthalpy for state points more distant from the isotropic–nematic phase boundary is a typical feature of compounds having the strongly polar CN group, responsible for antiparallel associations of the molecules [2,24,25].

4. Discussion

8OCB belongs to the well-known family of cyanobiphenyl compounds, whose properties have been studied for many years. Many physical properties of the cyanobiphenyl compounds are determined by strong dipole–dipole intermolecular associations [2]. Depending on the lateral tail (*n*-alkyl in *n*CB or *n*-alkoxy in *n*OCB), the properties differ slightly. For short tails, $n \leq 7$, only the nematic phase appears. For $n = 8$ and 9 the smectic A phase follows the N phase, while for larger n only the smectic phase exists, although the N phase can be induced at high pressures [22,27]. Both, 8OCB (Figure 2) and 8CB [28] show a limited stability of the S_A phase at higher pressure (for the latter at distinctly higher pressure).

As is shown in Figures 1 and 2 herein, the phase transition I–N is reproduced accurately by different experiments, consistent with the absence of any supercooling effect. The N– S_A transition is the second order type and can barely be detected experimentally. The Cr– S_A transition is readily supercooled or superpressed. The volume change at the I–N transition is small, $\Delta V_{NI} = 0.80$ ml/mol and pressure independent within the error (± 0.2 ml/mol). In contrast, ΔV_{CrA} decreases markedly with pressure for both the melting and freezing processes (see inset to Figure 1b). Such a tendency has also been observed for 8CB with comparable ΔV_{CrA} values [28]. Cusmin et al. [22] obtained similar volume changes for both transitions, 0.42 and 24.19 ml/mol, respectively, and noted a small discontinuity in the molar volume at the N– S_A transition. Orwoll et al. [19] reported 0.46 ml/mol for the I–N transition.

Combining the slope of the I–N transition line, $(\partial T/\partial P)_{tr}$, with the isochoric slopes within the N phase, $(\partial T/\partial P)_V$, the isochoric (configurational) entropy component ΔS_{conf} of the total entropy change at the I–N transition, ΔS_{tr} , can be estimated:

$$\Delta S_{conf}/\Delta S_{tr} = 1 - \left(\frac{\partial T}{\partial P}\right)_{tr} / \left(\frac{\partial T}{\partial P}\right)_V \quad (5)$$

(for details see refs. [4,7,19]). In Figure 7 are the plots for 8OCB showing that the slopes differ considerably. Within the N phase $(\partial T/\partial P)_V$ decreases slightly with increasing pressure (decreasing

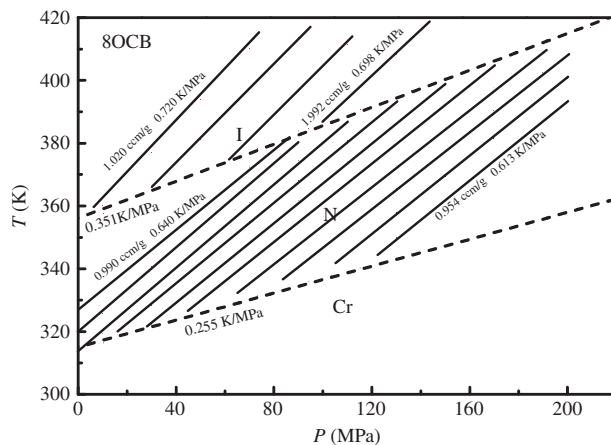


Figure 7. Isochors (solid lines) in the nematic and isotropic phase of 8OCB determined from the PVT results (in steps of 0.006 ml/g). Transition lines are denoted by the dashed lines.

volume). Taking the averages, $(\partial T/\partial P)_V = 0.636$ and $(\partial T/\partial P)_{tr} = 0.351$ K/MPa, we obtain $\Delta S_{conf}/\Delta S_{tr} = 0.448$. Thus, the entropy of disordering is less than half the total entropy change, similar to the behaviour of other LCs [4,7].

It has been shown that the scaling relation, Equation (2), originally proposed for glass-forming liquids and polymers ([23,29] and references therein), is applicable to the longitudinal relaxation times in various types of LCs [5–12]. As shown in Figure 8 (lower curve), the values of τ in Figures 4 and 5 superpose to form a master curve when plotted versus the scaling variable TV^γ , with the value $\gamma = 4.2$ the same as determined for 8CB [8]. The γ parameter from Equation (2) can be sensibly related to the intermolecular potential [30,31] (the dynamic quantity is expressed in reduced units [32]). For the relaxation time (the same applies to the viscosity [33]):

$$\begin{aligned} \tau^* &= \nu^{-1/3} (k_B T/m)^{1/2} \tau \\ \tau^* &\sim V_m^{-1/3} T^{1/2} \tau \end{aligned} \quad (6)$$

where ν and m are molecular volume and mass, and V_m is the molar volume. The upper curve in Figure 8 shows the result of scaling using these reduced units. The scatter of points is slightly reduced, with almost the same scaling exponent, $\gamma^* = 4.4$.

Although the potential parameters obtained herein for the nematic phase of 8OCB, γ and Γ , have magnitudes similar to those for other LC compounds [6,7,34], the value extracted from scaling of the dynamics, $\gamma^* = 4.4$, is significantly larger than the thermodynamic potential parameter, $\Gamma = 3.15$ (Figure 3). In the context of Maier–Saupe theory of the nematic state [35], equivalency of these two parameters implies

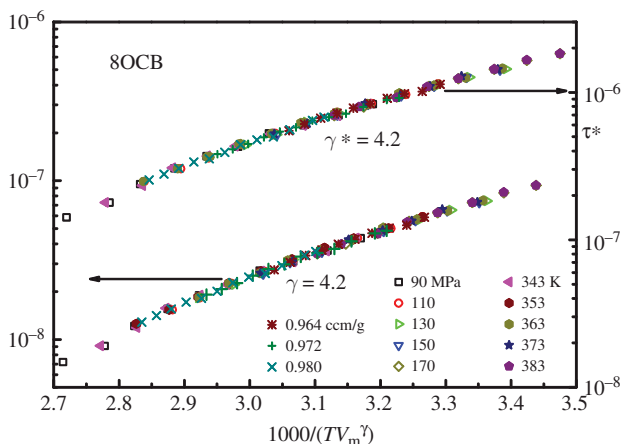


Figure 8. (colour online) Scaling of the longitudinal relaxation times in the nematic phase of 8OCB. The γ value corresponds to the experimental data (Equation (2)); γ^* corresponds to the reduced relaxation times (Equation (6)).

the order parameter, S , is constant along the clearing line [9]. This issue was analysed recently in detail by Satoh [13], who performed molecular dynamic simulations based on the simple Maier–Saupe potential [35]. The conclusions of this work included [13] the fact that a stronger attractive term in the potential increased the magnitude of Γ , and that the range of the nematic phase was three times greater for isochoric as compared to isobaric conditions. The simulations also confirmed that a necessary condition for $\Gamma = \gamma$ is a stable order parameter along the clearing line.

It is known from the Maier–Saupe theory that the longitudinal relaxation time is directly connected to the order parameter [36]. A small pressure dependence of τ extrapolated to the clearing line (Figure 4) may indicate that S_{NI} is not strictly pressure-independent, which would account for the difference observed herein in the values of Γ and γ . Concerning the differences in the range of the N phase for 8OCB herein, we find for heating that the isochoric ΔT ($V = 0.968$ ml/g) equals 64.7 K, whereas the isobaric ΔT ($P = 130$ MPa) equals 36.9 K. The ratio is 1.8 (the cooling data give a similar value), substantially less than the factor of 3 seen in the simulations. The difference is due to the smaller potential parameter for the simulated liquids ($\Gamma \sim 2$ [13]), reflecting a weaker effect of volume.

5. Conclusions

From the analyses herein we conclude the following concerning the behaviour of 8OCB:

- (1) The thermodynamic potential parameter Γ ($=3.15$) evaluated from the phase behaviour of

the nematic state was significantly smaller than the scaling exponent γ ($=4.4$) obtained by superpositioning the longitudinal relaxation times. This implies that the order parameter varies with pressure along the clearing line.

- (2) The configurational entropy change is $\sim 45\%$ of the total excess entropy accompanying the isotropic–nematic transition, a value consistent with other LC.
- (3) The range of stability of the nematic phase is 1.8 times broader for isochoric conditions versus an isobaric change in temperature. This effect of volume changes is consistent with the magnitude of the potential parameter for 8OCB.

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