Volumetric Study of the Nematic−Smectic-A$_d$−Reentrant Nematic Phase Transitions in the 8OCB + 6OCB Mixture

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High-resolution volumetric measurements were performed near the nematic to smectic-A$_d$ and the smectic-A$_d$ to reentrant nematic phase transitions. The changes in slope of a temperature dependence of density, $\rho(T)$, at both of the transitions were detected. The thermal expansion coefficient, $\alpha_p(T)$, at the smectic-A$_d$ to reentrant nematic transition revealed a positive deviation from a smooth background. This result, although not found in the earlier calorimetric measurements and inconsistent with the earlier density measurements, as well as with an intuition, is discussed and proved as consistent with the conclusions derived from $p(T)$ and $T(x)$ phase diagrams where $(dp/dT)_{crit}$ changes sign to negative at a singular point and again to positive at x_{max} point.

I. Introduction

Liquid crystalline materials on cooling from an isotropic phase (I) usually exhibit a sequence of the mesomorphic phases such as nematic (N), smectic-A (SmA), smectic-C (SmC), and other more ordered smectic phases. In some polar compounds, which exhibit a partial bilayer smectic-A$_d$ phase (SmA$_d$), an unusual sequence I−N−SmA$_d$−N$_r$ with a *reappearing* nematic phase, called reentrant nematic (N$_r$), has been found and well-established experimentally.[1−4]

Since the discovery of the reentrant nematic phase in a mixture of polar liquid crystals by Cladis[1] in 1975 the phenomenon of reentrance has become the topic of numerous theoretical and experimental studies. Soon after its first discovery, the reentrant nematic phase was also found in pure (*n*-octyloxy)cyanobiphenyl (8OCB) at high pressures[2] and in mixtures[3,4] of 8OCB with the homologous (*n*-hexyloxy)-cyanobiphenyl (6OCB) at 1 atm. 8OCB and 6OCB + 8OCB mixtures have become very thoroughly investigated liquid crystalline systems.[2−12] Later, the reentrant nematic was found in many other substances and systems, even in a pure substance at atmospheric pressure.[5] References to most of the experimental and theoretical papers on this subject can be found in an extensive overview by Cladis.[6] Many papers concern thermo-dynamic investigations of the phase transitions: nematic to smectic-A$_d$ (N−SmA$_d$) and smectic-A$_d$ to reentrant nematic (SmA$_d$−N$_r$). The thermal dependence of isobaric heat capacity, $C_p(T)$, is the most frequently investigated thermodynamic quantity, but we will refer here only to those measurements[7−9,12−14] that attempt to detect the SmA$_d$−N$_r$ transition. Molar volume or density is the other important thermodynamic parameter, but for the transitions under consideration, only three works, to the best of our knowledge, seem important: the density, ρ, measured as a function of temperature and composition[3,4] and the volume measured as a function of pressure.[11] Very precise X-ray investigations of the 8OCB + 6OCB system for different concentrations were carried out by Kortan et al.[12] From the X-ray scattering measurements the authors[12] were able to calculate correlation lengths $\xi_{||}(T)$ and $\xi_\perp(T)$ for the SmA$_d$ phase near both the transitions and to extract the critical
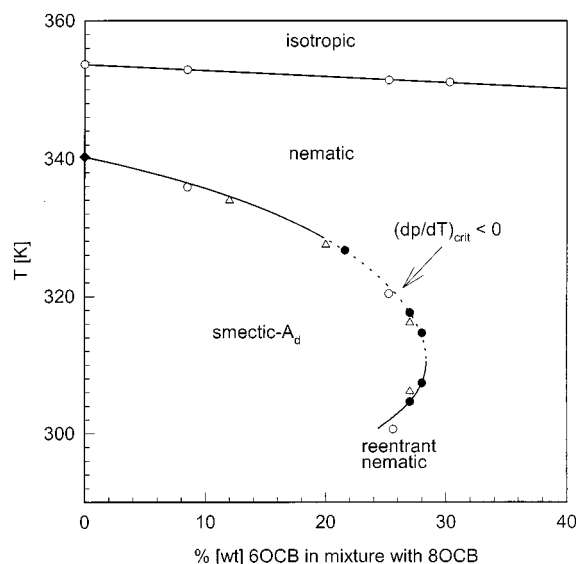
Figure 1. Temperatures of the phase transitions for different compositions of 6OCB in the 8OCB + 6OCB mixture obtained by different authors: (○) F. R. Bouchet et al.;[3] (△) K. J. Lushington et al.;[9] (●) this work; (◆) overlapping points of all above authors. The line through the points measured in the present work serves as a guide for the eye, and its dotted part shows the range of a boundary line of the N−SmA$_d$ transition where $(dp/dT)_{crit} < 0$.

exponents $\nu_{||}$ and $\nu_\perp$, respectively. All above-mentioned results will be discussed in the present paper.

As can be seen from the $T−x$ phase diagram shown in Figure 1 or from the schematic $p−T$ phase diagram in Figure 2, any point in the reentrant nematic can be reached in a continuous manner, i.e. without necessarily passing through the phase transitions, from any point in the high-temperature nematic. Then, when the phase transitions occur with, e.g., decreasing temperature, they should cause the two *changes* in "opposite directions" from the standpoint of molecular order and ther-modynamics. Chen et al.[10] found such behavior of birefringence studied for the 8OCB + 6OCB mixture at a 6OCB concentration equal to 27.0 wt %. They revealed that there is no discontinuity in birefringence, Δn, at both transitions but pretransitional effects
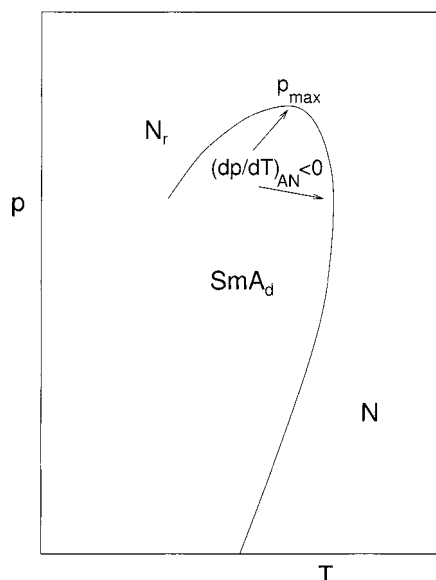
Figure 2. Schematic $p(T)$ phase diagram for the pure substance exhibiting a reentrant nematic phase at elevated pressures.

Figure 3. Sketch of the three different possibilities for the changes in density (curves a, c, and e) and in thermal expansion (curves b, d, and e) with temperature at the N−SmA$_d$ and SmA$_d$−N$_r$ phase transitions. The broken line depicts the necessity for *a continuity* of the nematic phase (see text).

show "opposite directions". It means that the quantities $\delta(\Delta n)$, defined as the differences between the Δn values extrapolated to the transition temperature as linear with temperature when far from the transition, have opposite signs. It is known that the changes in birefringence, Δn, are related to the changes in order parameter and density. Chen et al.[10] also proved optical identity of high- and low-temperature nematic phases by light scattering intensity measurements.

Similarly, the density measurements performed by Bouchet and Cladis[3] with the aid of a Paar instrument (vibrating oscillator filled with a sample) gave a relative increase of density at the *entrance* to the SmA$_d$ phase and a relative decrease of density at the *reentrance* to the N$_r$ phase, in relation to the linear background. Such a result, shown schematically in Figure 3 as curves a and b, is consistent with an intuition (mentioned above *continuity* of the nematic phase represented on curves a, c, and e by the dotted lines) and with above considerations but contradicts the thermodynamic analysis of the $p-T$ phase diagram given by Clark[15] on the basis of data from ref 2. This contradiction is a reason for the present work, and the region of the phase diagram where $(dp/dT)_{crit}$ changes sign to negative and again to positive is of our main interest. The aim of the present paper is to show by the precise volumetric measurements that the N−SmA$_d$ and SmA$_d$−N$_r$ phase transitions are continuous and that negative $(dp/dT)_{crit}$ is related to the differences in a behavior of the isobaric thermal expansion, $\alpha_p(T)$, at the phase transitions.

It was already proved that our very precise dilatometer with improved procedure described by Żywociński et al.[16] can be successfully applied for investigations of very weak continuous phase transitions,[17,18] even classical second-order ones (according to Ehrenfest's classification), like some of the SmA−SmC transitions.[16,19] Direct and precise measurements of volume in a vicinity of the phase transition give one of the best methods, in addition to adiabatic or ac-calorimetry, to distinguish whether the transition is of the first order or continuous and yet, if continuous, whether classical second order or critical.

In a theoretical approach to the reentrant nematic phenomenon, the first attempt was made by Pershan and Prost,[20] who derived a parabolic equation for the $p(T)$ coexistence line from the Landau theory with an assumption of optimum density stabilizing a smectic order. They allowed the phase transitions
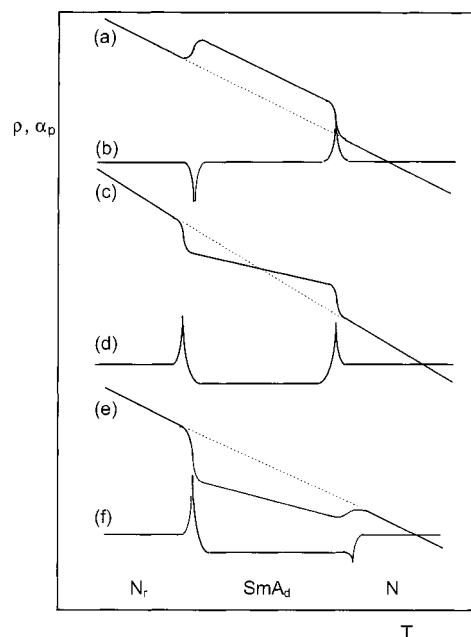
to be either first or second order. However, the model applied to $p-T$ data from ref 2 did not give a very good fit[20] and the assumption about optimum density was not supported by later measurements of volume as a function of pressure for 8OCB.[11] Apparently, the better results were obtained by Klug and Whalley,[21] who fitted the results from ref 2 with an equation of ellipse. Their equation was derived with an assumption of the first-order transitions along the coexistence line using an expansion of the molar Gibbs free energy difference between the two phases in a Taylor series. Independently, Clark[15] derived the same equation and fitted the same data.[2] A very detailed thermodynamic analysis of the $p-T$ phase diagram, considering the regions where a change of volume and a change of entropy at the phase transitions are expected to change their signs, was also given.[15] This early analysis by Clark and by Klug and Whalley[21] is not rigorous, since it is based on the incorrect assumption that N−SmA transitions are first order and Clark uses the Clapeyron equation.

Among the microscopic theories, "a frustrated spin-gas model" presented by Berker and Walker[22] should be mentioned as the most successful in reproducing the reentrant behavior. Phase diagrams, even with multiple reentrances,[23] identical with experimental $p-T$ diagrams were calculated. With this model Indekeu et al.[13] were able to calculate the temperature dependence of specific heat, $C_p(T)$, at both transitions, N−SmA$_d$ and SmA$_d$−N$_r$. Their theoretical results were confirmed experimentally in the same work.[13] An important result is that both singularities of $C_p(T)$ show peaks of the second-order transitions, i.e., positive deviations from the background, despite Clark's analysis[15] of negative $(dp/dT)_{crit}$. The same result was obtained recently for a two-component system with a closed reentrant nematic region.[14] A behavior with closed reentrant nematic region and bilayer smectic below was recently reproduced theoretically with a model of associating cylindrical molecules.[24] This model incorporating association due to the hydrogen bonding can also reproduce a simple reentrant behavior.[25] Although hydrogen bonding is not responsible for the nematic

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reentrance in the system considered in this work, association caused by strong dipolar interactions gives the same effect.

This paper is organized in three sections. In section II, part A the dilatometric measurements for the 8OCB + 6OCB mixture, not supporting the density measurements,[3] are presented and discussed on the grounds of classical thermodynamics. Doubtful density measurements[3] with the commercial Paar densimeter were reproduced and are also presented in section II part B. Discrepancies between the two methods are further proved in the case of the well-known SmA_d-N phase transition in 8OCB and a simplified explanation of the reasons originating from the viscosity changes is also given. Section III gives a broad discussion of the negative slope of the boundary line in the $p-T$ phase diagram and its relation to the thermodynamic properties of the phases resulting from the Pippard equation.[26] Discussion, conclusions, and summary are given in Section III.

II. Experiment and Results

The compounds studied, 8OCB (M_8 = 307.440 g/mol) and 6OCB (M_6 = 279.384 g/mol), were synthesized and purified by "ZD Chemipan", Warsaw, and were used without any further purification. The high purity of the samples was confirmed by a narrow temperature range ($\leq$0.05 K) of the two-phase region at the nematic-to-isotropic phase transitions.

A. Dilatometric Measurements. In our previous works[16,18] a very precise dilatometer that allows for volume measurements with a resolution slightly better than 0.1 ppm was used. That dilatometer could not been used here because of a wide temperature range to cover to investigate both transitions, i.e., $N-SmA_d$ and SmA_d-N_r, in the same run. An older glass dilatometer (without a pressure jacket) with a calibrated volume of ca. 5.6 cm³ and with a capillary 0.5 mm in diameter and 37 cm long, was used. Although the detailed experimental procedure was described earlier,[16] we have to mention some of the most important details. A known amount of mercury was placed at the bottom of the dilatometer and filled the capillary during measurements. The capillary was connected to the assembly of manometers for compensation of changing hydrostatic pressure of the mercury column. The corrections for compressibility of the sample caused by approximate compensation with an external manometer were made. Temperature of a 70 dm³ water bath was controlled with a precision of ±0.2 mK. The resolution of the dilatometer is estimated as ca. 1 ppm due to the temperature fluctuations (even very small) and a changing shape of mercury meniscus. The sample was degassed by 3-fold heating to the isotropic phase and solidification under vacuum, and next it was introduced as the nematic phase into the dilatometer, still under vacuum. The amount of the sample was ca. 4.8 g and the concentration of 6OCB in the system studied here was 26.97 wt % 6OCB in a 8OCB + 6OCB mixture (mole fraction x_{6OCB} = 0.2889), which is very close to the composition studied by Bouchet and Cladis[3] and by Chen et al.[10]

Experimental points were measured with relatively big temperature steps, about 0.5 K, because of very small effects of each temperature change. The sample was always kept for at least 1 h at constant temperature before the readings were taken. The measurements were first collected during the cooling run and the next four points were repeated during heating. To show the $\rho(T)$ curve on the graph with a resolution comparable to the resolution of our experiments, an arbitrary background linear with temperature had to be subtracted. The results of volumetric measurements corrected to p = 1.013 bar and calculated as the temperature dependence of density deviations from a background are presented in Figure 4. The phase
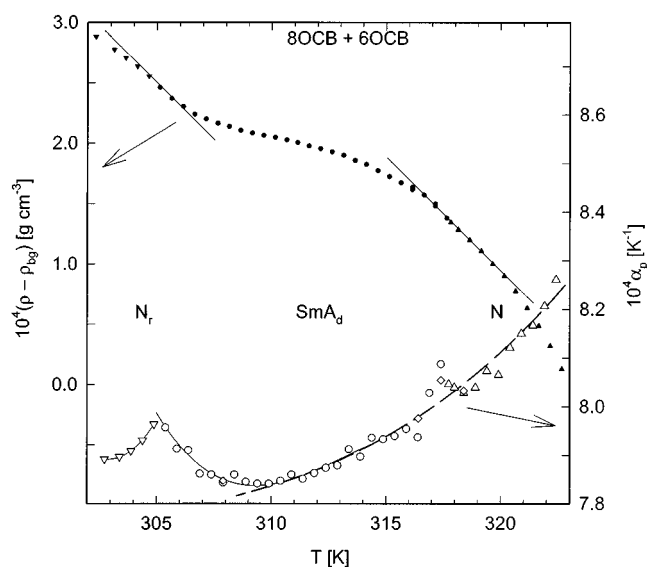
Figure 4. Thermal dependence of density (solid symbols) and thermal expansion coefficient (open symbols) for the mixture of 26.97 wt % 6OCB in 8OCB + 6OCB. Density data measured in the high-resolution dilatometer are presented as the differences between the direct density data and the linear background, ρ_{bg} = 1.28015−8.05 × $10^{-4}T$, multiplied by 10000; points of the lower curve present the thermal expansion coefficients $\bar{\alpha}_p = (-1/\bar{\rho})(\Delta\rho/\Delta T)_p$ calculated from the pairs of neighboring data points; the lines serve just as a guide for the eye (see text). Key: (▼, ▽) nematic-reentrant; (●, ○) smectic-A_d; (▲, △) nematic; (◇) thermal expansion coefficients calculated for four points repeated during heating.

transitions are clearly discernible here as the two changes in slope of the $\rho(T)$ curve, resulting in the thermal expansion of the SmA_d phase being lower than the thermal expansion of both nematic phases, N and N_r. Two auxiliary lines have been drawn through the points close to both the transitions to illustrate the clear point of inflection at $T(SmA_d-N_r) \cong 305$ K and the apparent absence of a point of inflection at $T(SmA_d-N) \cong 317.4$ K, as seen with a hot-stage polarizing microscope. For data analysis the mean values of $\bar{\alpha}_p = (-1/\bar{\rho})(\Delta\rho/\Delta T)_p$ were calculated successively from the pairs of neighboring data points and results are shown as a lower plot in Figure 4. A dashed line in this plot is a curve calculated as a wing of the N−I transition and together with the solid lines near the SmA_d-N_r transition serves just as a guide for the eye. The points of $\bar{\alpha}_p$ in the region of the SmA_d-N transition are more scattered, but we have no good explanation why these data seem noisier. Three points in this region were repeated during heating, and one of them deviates in the same direction as the point formerly measured.

No attempts to fit the data were taken because of the limited number of points and the very weak pretransitional effects. Also a calculation of the thermal expansion coefficients as analytical derivatives of a fitted equation would smear the real picture depending on the form of the equation. Nevertheless, the plot of $\bar{\alpha}_p(T)$ exhibits a clear and broad peak of the SmA_d-N_r phase transition. The other peak at the SmA_d-N phase transition deviates in the same direction from a smooth background, but the deviation of the highest calculated value of $\bar{\alpha}_p$ is as small as about 1%. It hardly exceeds the experimental scatter, so the "critical anomaly" near $T(SmA_d$-N) is too small to be established. The behavior around the SmA_d-N transition and the lack of the clear anomaly in $\alpha_p(T)$ near the SmA_d-N transition is the most difficult and one of the most interesting aspects of the present measurements and will be discussed in the context of negative $(dp/dT)_{crit}$. The above result seriously contradicts the
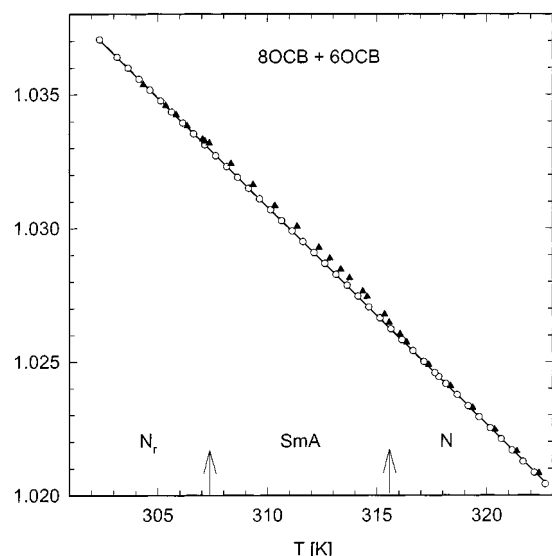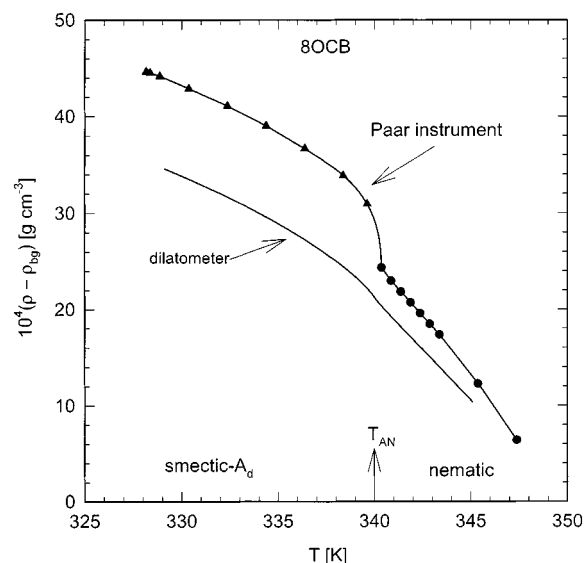
Figure 5. Comparison of the "apparent density" data measured with the Paar instrument for 28.02 wt % 6OCB in the 8OCB + 6OCB mixture (solid triangles) with the true density data from the dilatometer for 26.97 wt % 6OCB in the 8OCB + 6OCB mixture (open circles). The arrows at the bottom show the transition temperatures determined with a hot-stage polarizing microscope for 28.02 wt % 6OCB, only.

Figure 6. Comparison of the "apparent density" data measured with the Paar instrument for pure 8OCB (solid symbols) with the true density data from the dilatometer (solid line). The curve representing dilatometric measurements was calculated from earlier data by Żywociński et al.[16] using the fitting equation for molar volume and parameters given in ref 16, Table 5, fits 11 and 12. Linear background $\rho_{bg} = a + bT$ with the same constant $b = -7.00 \times 10^{-4}$ (same slope) was subtracted for both curves, but they were shifted by a constant for clarity: for the Paar data $a = 1.2361$ and for the dilatometric data $a = 1.2363$; this difference corresponds to 0.0002 g cm^{-3} of direct density difference. An arrow shows the SmA$_d$-N phase transition temperature in pure 8OCB.

results obtained by Bouchet and Cladis[3] from the Paar instrument, so independent experiments have been carried out with the aid of the instrument of the same type with the newly prepared sample and the results are presented below.

B. Density Measurements with the Paar Instrument. The sample of composition 28.02 wt % 6OCB (mole fraction x_{6OCB} = 0.2999), which is slightly different from that in refs 3 and 10, was studied here with the aid of the Paar Density Meter, Model DMA 602 HT. This instrument does not allow us to maintain the sample truly isolated from an atmosphere, nor can the temperature stability be improved beyond ±5 mK. Before the run with the liquid crystal sample, the Paar instrument was calibrated[27] with air and deionized water through the whole investigated temperature range with temperature increments of 5 deg. The constants of the instrument are temperature dependent, so the density measured at various temperatures was calculated by means of these constants interpolated to the desired temperature. Results of the density vs temperature are shown in Figure 5 as the direct data and are compared with the data from the dilatometer (same as in Figure 4). The dilatometric data were fitted with a linear equation to depict that without a subtraction of a steep background the extremely small changes in a behavior of $\rho(T)$ for different phases cannot be visible. On the other hand, the departure of the density data for the smectic-A$_d$ phase obtained with the aid of the densimeter from the dilatometric data is undoubted. The plot of data from the Paar instrument is basically the same as that in Figure 5 of ref 3. Even though the graph[3] displays a temperature dependence of T^2, i.e., a squared multiple period of vibrations measured directly by the Paar densimeter, its similarity to the density changes is obvious, because T^2 can be converted to density by linear transformation using necessary calibration constants[27] treated as the temperature functions.

Schematic dependencies of the density, $\rho(T)$, and the corresponding thermal expansion, $\alpha_p(T)$, as deduced from the Paar data are illustrated in Figure 3 as curves a and b, respectively. For comparison, curves c and d display what, with exaggeration, the hypothetical case with two peaks of $\alpha_p(T)$ for both transitions would mean. Disagreement of the effect at the SmA$_d$-N$_r$ is

obvious. Since density data from the dilatometer are the results of direct measurements, obviously measurements of "apparent density" obtained with the aid of a Paar instrument cannot be trusted in this case. To make sure that the above effect is not connected with the system under study, the same measurements were performed for pure 8OCB and results were compared with the earlier volumetric data by Żywociński et al.[17] converted to density. They are presented in Figure 6, after subtraction of a linear background, $\rho_{bg} = a + bT$, with the same slope (same constant "b"), but shifted by a constant for clarity (different constants "a"). A continuous SmA$_d$-N phase transition in 8OCB was already proved with no doubts, but the "apparent density" shows a big jump, suggesting a first-order transition. Such behavior can be explained by the large viscosity changes at the N—SmA$_d$ and SmA$_d$—N$_r$ transitions, and a discussion of that effect is given below.

Recently, Barbosa and Palangana[28] studied densities of the nematic and isotropic phases in a thermotropic liquid crystal, and also isotropic and hexagonal phases in a lyotropic liquid crystal. They also found a difference between the results obtained from the dilatometer and from the Paar densimeter for the hexagonal phase, but they found no difference for the nematic and isotropic phases. Authors[28] assigned this difference to the structural changes in hexagonal phase caused by vibrations of the oscillator in the Paar densimeter, but in our opinion those results also support the assumption about viscosity influence, as the hexagonal phase is extremely viscous as compared to nematic and isotropic phases.

The viscosities of the nematic, smectic A$_d$, and reentrant nematic phases have been measured by Bhattacharya and Letcher.[29] Three Miêsowicz geometries were studied, showing that the nematic and the reentrant nematic phases are identical from the standpoint of hydrodynamics and that the smectic-A phase has "an average" kinematic viscosity a few orders of

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magnitude higher than the nematic and the reentrant nematic. The kinematic viscosity for the geometry $\vec{v} \parallel \vec{n}$ and $\nabla\vec{v} \perp \vec{n}$ (where $\vec{v}$ is the flow velocity and $\vec{n}$ is the nematic director), marked as η_b, measured in circular capillary exhibits a divergence[29] in the smectic-A phase, which means that the flow was blocked. This geometry is similar to that used in a Paar densimeter, provided that liquid crystal molecules are oriented perpendicularly to the wall of the vibrating U-shaped tube. It is obvious that vibrations of the mechanical oscillator filled with a viscous liquid must be damped. However, the situation is different and more complicated than that for the oscillator vibrating in a viscous environment, and it is out of the scope of the present work to derive the dependence of the damping coefficient, k, on the kinematic viscosity, η, especially in geometry η_b.[29] Anyway, for damped vibrations an angular frequency is, in general, related to the viscosity by the relation $\omega^2 = \omega_o^2 - k^2(\eta)$, where $\omega = 2\pi/T$, T is the period of vibrations the and ω_o corresponds to undamped vibrations. Then, the quantity T^2 measured by the Paar instrument, which is the multiple vibration period, increases and results in a greater "apparent density" when the viscosity of the sample suddenly increases at the onset of the phase transition.

It has to be noted that the error of the Paar instrument described above is less than approximately 0.1% and comes from the differences in the viscosities of standards used for calibration and the viscosity of a sample. If there is no such difference, the instrument is perfect and allows for measurements of high resolution and precision. Using this instrument, one has to be careful dealing with substances of viscosity a few orders of magnitude higher than the standards, which are usually air and water, or one should use the standards of similar viscosity.

III. Discussion and Conclusions

The $p-T$ phase diagram for pure 8OCB from ref 2 (sketched out here in Figure 2) contains two characteristic points, $(dp/dT)_{crit} = \infty$ and $(dp/dT)_{crit} = 0$, with a region of $(dp/dT)_{crit} \leq 0$ in between. This behavior has been analyzed by Clark[15] with an assumption of the first-order transitions and with the Clapeyron equation. His considerations should be revised in the context of the continuous smectic-A_d to nematic and to reentrant nematic phase transitions. It has been proved by our earlier volumetric measurements[16] at atmospheric pressure and by high-resolution ac-calorimetry[7,8] at atmospheric and elevated pressures that the SmA$_d$-N transition in pure 8OCB is a second-order transition of the critical fluctuation type. Series of calorimetric data measured along the isobars[8] in the range 1−2000 bar revealed a diminishing peak of heat capacity and did not show any singularity for the isobars at $p =$1500 bar, as well as at $p = 2000$ bar, where the reentrant nematic should be observed. Same authors investigated the 8OCB + 6OCB mixture with the same calorimetric technique[7,9] and also observed the diminishing C_p peak with increasing concentration of 6OCB. For concentration 27 wt % 6OCB, no transitions (except nematic−isotropic) were detected, although the existence of the reentrant nematic phase at this concentration was confirmed by optical observations,[9] birefringence studies,[10] density measurements,[3] and volumetric studies of the present work. The reason no C_p peaks were observed at the transitions has been explained by Kortan et al.[12] The authors found from the X-ray measurements the very large size of the correlation volume $(\xi_\parallel\xi_\perp^2)$ in 27 wt % 6OCB + 8OCB when compared to that in pure 8OCB or mixtures with relatively smaller amounts of 6OCB. As is well-known from the two-scale universality for anisotropic smectic liquid crystals $\delta C_p(\xi_\parallel\xi_\perp^2)t^2 = $ constant and the value

of this constant is known theoretically and experimentally, Kortan et al.[12] predicted that the maximum $\delta C_p = C_p - C_p(normal)$ for this mixture should be only 0.4% of $C_p(normal)$ and thus undetectable.

Also, as can be seen from the $T-x$ phase diagram in Figure 1, the ratio T_{AN}/T_{NI}, called the McMillan parameter,[30] decreases with increasing concentration of 6OCB, so the transition must be continuous through the concentration range and becomes even weaker with increasing pressure or concentration of 6OCB.

Results obtained for pure 8OCB at high pressures can be related to the results for the 8OCB + 6OCB mixture measured at atmospheric pressure. Phase boundaries in the $p-T$ plane for different compositions, given by Cladis et al.,[4] in conjunction with the $T-x$ phase diagram[3,4] (see also Figures 1 and 2) allow us to imagine the shape of a $p-T-x$ surface. The locus of $p_{max}(p,T,x)$ points forms a ridge line on this surface. The p_{max} points represent the local maxima on each $p-T$ plane for a given x, where $(dp/dT)_{crit} = 0$, and they correspond to the points of x_{max} on each $T-x$ plane for a given p, where $(dT/dx)_{crit} = \infty$ (p_{max} decreases from $p_{max} = 2100$ bar for pure 8OCB to $p_{max} = 1$ bar for $x = x_{max} \cong 28.5$ wt %). On the other hand, it can be seen from Figure 7a in ref 4 that $(dp/dT)_{crit}$ changes sign at atmospheric pressure for the concentration between 12.0 and 19.7 wt %. Thus, $(dp/dT)_{crit}$ is negative on the upper branch of the boundary line in Figure 1 for the concentrations higher than approximately 20 wt % and changes sign again to positive at x_{max}.

For critical fluctuation second-order transitions $(dp/dT)_{crit}$ is related to other second derivatives of the Gibbs free energy by the Pippard equations:[26]

$$\frac{C_p}{T} = (dp/dT)_{crit}V\alpha_p + \text{constant} \tag{1}$$

$$\alpha_p = (dp/dT)_{crit}\beta_T + \text{constant} \tag{2}$$

where $\alpha_p = -(1/\rho)(d\rho/dT)_p$ is the isobaric thermal expansion coefficient and $\beta_T = (1/\rho)(d\rho dp)_T$ is the isothermal compressibility coefficient.

The above equations give the relations between thermodynamic properties of a single phase, but it is obvious from eq 1 or 2 that if, for example, C_p/T or β_T is an increasing function of temperature for $T < T_c$ and $(dp/dT)_{crit}$ is negative, then α_p must be a decreasing function of temperature, and oposite for $T > T_c$. The excess heat capacity δC_p is always positive due to the intrinsic energy/enthalpy fluctuation nature of heat capacity, so $\delta\alpha_p \leq 0$ (a dip in α_p) is expected when $(dp/dT)_{crit} < 0$. This case is shown schematically as curves e and f in Figure 3.

The above analysis of the $p-T-x$ surface proved that $(dp/dT)_{crit}$ is negative on the upper part of the boundary line N−SmA$_d$ in the $T-x$ phase diagram for the composition range $\sim$0.2 $< x < x_{max}$ with the limiting values: $(dp/dT)_{crit} \rightarrow \pm\infty$ when $x \rightarrow \sim$0.2 from the left-hand side (lhs) and right-hand side (rhs), respectively, $(dp/dT)_{crit} = 0$ at x_{max}, and $(dp/dT)_{crit} > 0$ on the lower part (SmA$_d$−N$_r$) of the curve. The volumetric measurements performed with a high-resolution dilatometer for 26.97 wt % 6OCB revealed the well-established peak of $\alpha_p(T)$ at the SmA$_d$−N$_r$ transition and lack of an undoubted peak at the SmA$_d$-N transition. It is hard to say from the present data whether the change of α_p between the SmA$_d$ phase and the nematic phase is smooth or through the dip in $\alpha_p(T)$, as expected from above discussion. Anyway, we believe that this case is similar to that shown with exaggeration as curves e and f in Figure 3.

The derivation of the Pippard equations is based on a "cylindrical" approximation for the $S(p,T)$ and $V(p,T)$ surfaces. A validity of this assumption was confirmed by Buckingham and Fairbank[26] for the λ transition in helium and by Garland[26] for the $\alpha-\beta$ transition in quartz. It is a challenge for future experimental work to confirm the validity of the approximation in the Pippard equations near the phase transitions in liquid crystals for which $(dp/dT)_{crit}$ is negative.

In summary, it has to be mentioned that changes in molecular ordering at the phase transitions studied here are less important for thermodynamic properties of the phases in the region of nematic *reentrance* than specific dipolar interactions. A singularity in the thermodynamic properties can be visible also at the nematic-to-isotropic phase transition as a minimum (a dip) in $(dT/dp)_{NI}$ found by Shashidhar,[5] and it appears at the concentration of 6OCB about 18 wt %, approximately the same as the concentration at which $(dp/dT)_{AN}$ changes sign.

The consequences of a negative $(dp/dT)_{crit}$ value are hardly visible in thermodynamic properties of the system studied. The thermal expansion of the smectic-A_d phase is smaller than the thermal expansion of both nematic phases. It allows for both transitions, of which one (SmA$_d$–N$_r$) exhibits clear pretransitional effects of the critical fluctuation type and the other is to date undetectable in C_p and α_p measurements, without affecting *a continuity* of the nematic phase. Discrepancies between analysis of the phase diagram[15] and "apparent" density measurements[3] were straightened out and explained as coming from huge viscosity changes at the transitions, which affects the results and makes them, at least, misleading. Work presented here is, to the best of the author's knowledge, the first pointing out the anomalies in density and thermal expansion near the nematic to smectic-A_d and smectic-A_d to reentrant nematic phase transitions.

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(27) Density, ρ, is related to vibration period, T, by $\rho = A^{-1}(T^2 - B)$, where constants A and B are temperature dependent and they can be found from calibration against two standards, usually air and water; then, having $A(T)$ and $B(T)$, one can calculate the dependence of $\rho(T)$.

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