

Calorimetric investigation of a reentrant-nematic liquid-crystal mixture

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An ac calorimetric study of binary mixtures of octyloxycyanobiphenyl (8OCB) and hexyloxycyanobiphenyl (6OCB) reveals that the magnitude of the C_p peak associated with the nematic-smectic-*A* (N-SmA) transition decreases strongly with increasing concentration of 6OCB. These data are consistent with a second-order N-SmA transition for which the entropy vanishes with increasing 6OCB concentration. A reentrant mixture containing 27 wt. % 6OCB did not exhibit any critical heat capacity at either the N-SmA transition or the SmA-reentrant-nematic transition, both of which were observed visually.

I. INTRODUCTION

The extreme sensitivity of liquid-crystal mesophase stability to small changes in molecular structure is well known.¹⁻³ Mesophase changes may also be achieved in a continuous fashion by varying the composition of a binary mixture of liquid crystals at constant pressure³⁻⁶ or by varying the pressure on a pure liquid crystal or a mixture with fixed composition.^{1,7-10} Both pressure and composition have a strong effect on the molecular interactions leading to mesophase formation.

The subtle nature of these interactions and the close analogy between the effects of pressure and composition variables is especially clear in connection with the nematic (N)-smectic-*A* (SmA)-reentrant-nematic (RN) phase sequence shown by certain bilayer smectics. The low-temperature RN phase has been termed reentrant to distinguish it from the high-temperature nematic phase, although optically the two phases appear to be identical.⁵ The reentrant-nematic phase has been observed both in pure materials at high pressure¹ and in binary mixtures at 1 atm.^{5,11}

Reentrant behavior in liquid crystals may be described phenomenologically by a simple Landau theory which incorporates a free-energy term coupling density and composition to the smectic order parameter ψ .¹² Despite the ability of this theory to replicate the observed phase boundary, there remains some uncertainty as to the nature of the RN phase and the character of the SmA-RN transition. Cladis *et al.*¹ found a large (1-3 K) scatter in the SmA-RN and N-SmA transition temperatures in *p*-cyanobenzilidene-*n*-octyloxylaniline (CBOOA), a bilayer smectic which has a reentrant-nematic phase at high pressures. They interpreted this behavior as evidence for hysteresis, implying first-order character at both transitions. Binary mixtures of octyloxycyanobiphenyl

(8OCB) with its shorter-chain homolog 6OCB were studied at 1 atm,⁵ and the optical observation of stable microcrystallites coexisting with the RN phase was reported.

We have previously carried out a high-pressure calorimetric study of the N-SmA transition in 8OCB,^{8,9} which has a reentrant-nematic phase above ~ 1.2 kbar. However, we were unable to study the reentrant portion of the 8OCB phase diagram due to spontaneous crystallization of the supercooled SmA phase. (The SmA-RN transition is 15-25 K below the equilibrium melting point of the crystalline phase at 1600 bar.) In this paper we report the results of a 1-atm calorimetric study of the N-SmA and SmA-RN transitions in 8OCB-6OCB mixtures. 6OCB has a nematic range (57.0-75.5°C) comparable to that of 8OCB, but has no stable SmA phase. Our measurements show no indication of first-order behavior at either the N-SmA transition or the SmA-RN transition, but rather support the concept of a vanishing N-SmA transition enthalpy with increasing concentration of 6OCB.

II. EXPERIMENTAL RESULTS

The heat capacities of four different 8OCB-6OCB mixtures were measured with an ac technique described previously.⁹ The pure liquid crystals were obtained from BDH Chemicals, Ltd., and the compositions of the mixtures were determined to better than ± 1 wt. %. The observed N-I (isotropic) and N-SmA transition temperatures are shown in Fig. 1 together with the phase lines reported in Ref. 5. A mixture containing 37 wt. % 6OCB exhibited no smectic phase and gave a N-I heat-capacity peak that was completely typical of such transitions. Data for this sample will not be shown. The data obtained on the other three mixtures are shown in Fig. 2, togeth-

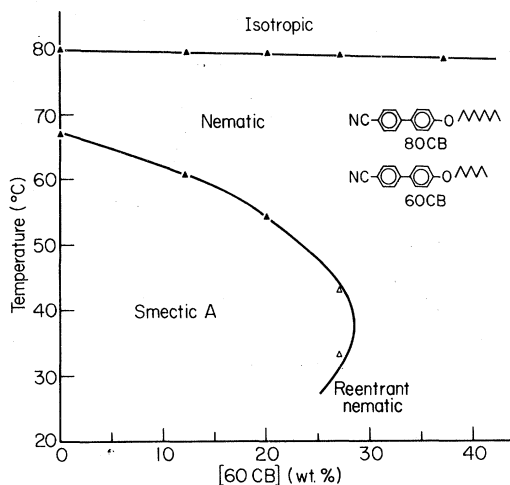


FIG. 1. Phase diagram for binary mixtures of 8OCB and 6OCB. The solid triangles indicate transitions observed calorimetrically, and the open triangles indicate transitions observed visually. The solid phase lines are from Ref. 5.

er with data on pure 8OCB from Refs. 8 and 9. Differences in the absolute C_p values of 5–10% between various runs, common when using the ac technique,⁹ have been removed by normalizing the data in the isotropic phase. The data are reported in the dimensionless units \tilde{C}_p/R where \tilde{C}_p is a molar heat capacity and the effective molecular weight M_{eff} is taken to be an average of 8OCB ($M = 307.44$) and 6OCB ($M = 279.41$) based on the molar composition of the mixture. The normalization was carried out by assuming that the heat capacity *per gram* for each mixture at 90°C was identical to that of pure 8OCB. Thus $\tilde{C}_p(\text{mix})/\tilde{C}_p(8\text{OCB}) = M_{\text{eff}}/307.44$ at 90°C.

The trends in the heat-capacity data are strikingly similar to those observed in pure 8OCB as a function of pressure.^{8,9} The C_p peak at the N-I transition is insensitive to the composition (or pressure), while the N-SmA peak changes dramatically. A detailed view of the region around the N-SmA transition in each mixture is presented in Fig. 3. If the background curves shown in this figure¹³ are used to compute $\Delta\tilde{C}_p = \tilde{C}_p(\text{tot}) - \tilde{C}_p(\text{bkgd})$, then the transition enthalpies $\delta H_{N_A} = \int \Delta\tilde{C}_p dT$ are 100, 42, and 14 J mole⁻¹ for the 0-, 12-, and 20-wt. % mixtures, respectively. The behavior of the corresponding transition entropies $\delta\tilde{S}_{N_A} = \int (\Delta\tilde{C}_p/T) dT$ as a function of the transition temperature difference $T_{N_I} - T_{N_A}$ is completely consistent with that reported earlier⁸ for pure 8OCB and for the related material octylcyanobiphenyl (8CB) at various pressures.

In the 27 wt. % 6OCB sample, the only C_p peak is associated with the N-I transition. The existence of both a SmA phase and a reentrant N phase was, however, confirmed optically¹⁴ *before and after* the

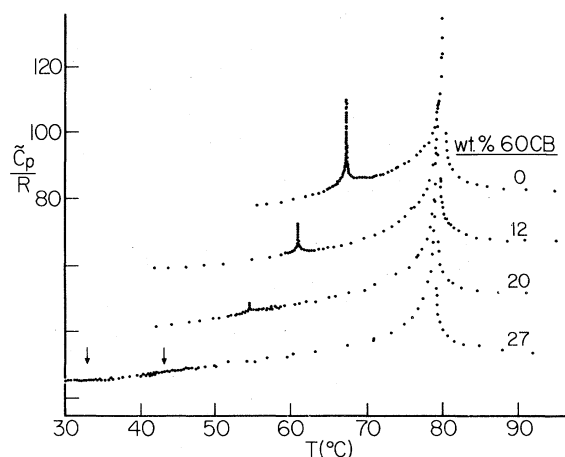


FIG. 2. Heat capacity of 8OCB-6OCB mixtures at 1 atm. Data for the 12-, 20-, and 27-wt. % mixtures have been shifted downward by 15, 30, and 45 units, respectively. The arrows indicate the N-SmA and SmA-RN transition temperatures observed visually in the 27-wt. % sample.

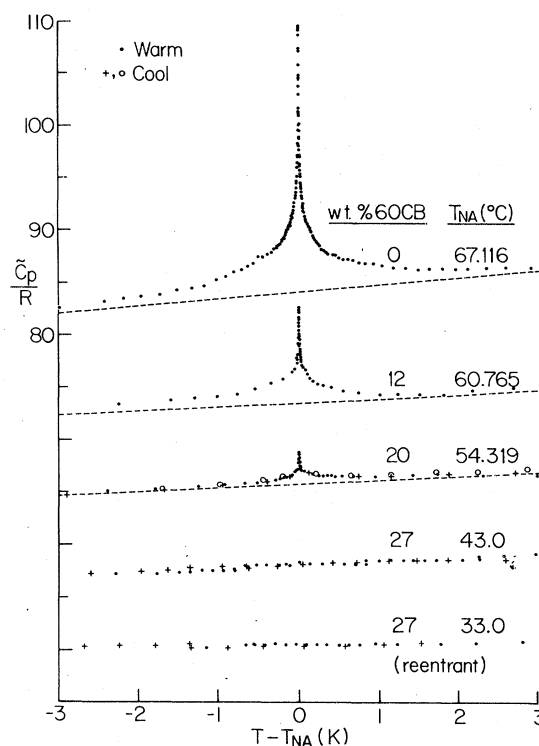


FIG. 3. Heat capacity in the vicinity of the N-SmA and SmA-RN transitions in 8OCB-6OCB mixtures. The dashed curves indicate the background used to obtain ΔC_p and the transition enthalpy $\delta H_{N_A} = \int \Delta C_p dT$. For pure 8OCB, there was no hysteresis in T_{N_A} and no discernible difference between \tilde{C}_p values obtained on warming and cooling. (See Ref. 9 for details.)

calorimetric measurements. The absence of any peaks in the vicinity of the N-SmA or the SmA-RN transition in this sample indicates that the second-order C_p effects associated with these transitions are either below our experimental resolution or are spread over such a broad temperature range that they are indistinguishable from the background C_p values. Furthermore, the absence of any hysteresis, step discontinuities in C_p , or anomalous phase shifts in the T_{ac} signal¹⁵ suggests that any first-order latent heat at these transitions is small. Since small latent heats ΔH (as opposed to the continuous enthalpy variation given by $\delta H = \int \Delta \tilde{C}_p dT$) could be missed by the ac method, we decided to compare our result for δH_{NA} with the total enthalpy ($\Delta H + \delta H$) given by a conventional differential scanning calorimeter (Perkin-Elmer DSC II). With a scanning rate of 5 K min^{-1} , which considerably smeared the very sharp N-SmA peaks, the total enthalpy obtained from DSC was 60 J mole^{-1} for pure 8OCB and 20 J mole^{-1} for 12 wt. % 6OCB in 8OCB. No N-SmA peaks could be observed for DSC runs on samples with 6OCB concentrations larger than 12 wt. %. We conclude that DSC is not capable of providing truly quantitative information about such liquid-crystal transitions. However, the DSC results do indicate that any latent heat contributions must be very small. Since a small latent heat does not necessarily imply a small volume discontinuity,¹⁶ it would seem worthwhile to make precise volumetric measurements near this transition as a test for first-order character.

III. DISCUSSION

The N-I and N-SmA transition temperature for our mixtures agree well with the values reported by Guillon *et al.*⁵ It should be noted that the concentration variable used in Ref. 5 is $100W_{6OCB}/W_{8OCB}$; these units have been converted to weight percent to obtain the lines shown in Fig. 1. In the case of the 27-wt. % sample our transition temperatures as determined from visual observations, are only accurate to ± 1 K.¹⁴

Although the $\Delta \tilde{C}_p$ peaks for the N-SmA transition in the 12- and 20-wt. % 6OCB mixtures are very small, they are generally consistent with the conclusion based on studies of 8OCB (Ref. 9) and 8CB (Ref. 10) that the shape of the peak is independent of the T_{NA}/T_{NI} ratio. The only data on the mixtures which are of sufficient quality for meaningful least-squares estimation of the critical exponent α are those in the N phase of the 12-wt. % sample. Power-law fits of these data with

$$\Delta \tilde{C}_p/R = At^{-\alpha} + B \quad (1)$$

have been made over several reduced temperature

ranges between $t = (T - T_{NA})/T_{NA} = 1 \times 10^{-5}$ and $t = 1 \times 10^{-2}$. Such fits yield exponents in the range $\alpha = 0.17-0.24$ and are quite consistent with $T_{NA} = T_m$, the temperature of the C_p maximum. These results agree reasonably well with the value $\alpha = \alpha' = 0.25 \pm 0.05$ obtained for pure 8OCB.⁹

Another way to test whether the C_p peaks have the same shape for all compositions is to multiply the $\Delta \tilde{C}_p$ values for each mixture by an appropriate normalization factor Z and overlay the resulting points on the well-characterized peak for the pure 8OCB sample. The results of such a comparison (see Fig. 4) are consistent with the hypothesis that a single shape will describe the excess heat capacity at all compositions. The largest discrepancy occurs in the SmA phase of the 12-wt. % sample, where the data points far from T_{NA} are clearly high.¹⁷

We can interpret the calorimetric results near the N-SmA transition in three cyanobiphenyl liquid-crystal systems—8OCB, 8CB, and 8OCB-6OCB mixtures—as being characterized by a single effective critical exponent $\alpha = \alpha' \approx 0.25$. Although it is theoretically attractive to satisfy scaling and universality, it must be admitted that there are trends in the data^{9,10} suggesting that $\alpha > \alpha'$ for this transition and that both exponent values decrease slightly with increasing $T_{NI} - T_{NA}$ (i.e., decreasing T_{NA}/T_{NI}). There is a strong indication that the critical enthalpy δH_{NA} is largely due to fluctuations in the nematic order parameter S , and that the apparent departures from

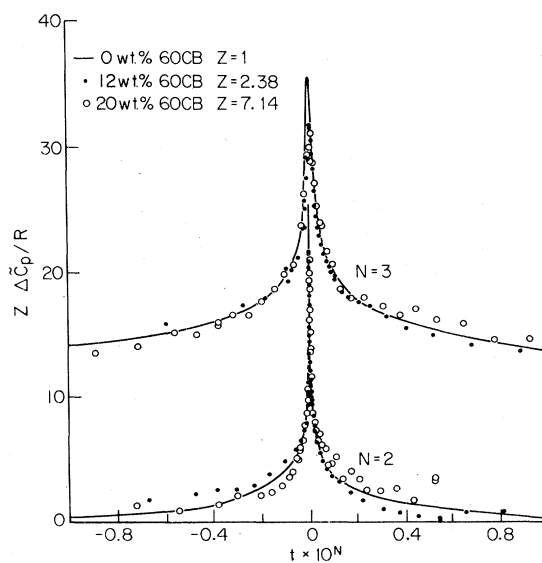


FIG. 4. Superposition of excess heat-capacity peaks associated with the N-SmA transition. The normalization factor Z was chosen to produce the best agreement between the data for 12- and 20-wt. % mixtures and the line representing $\Delta \tilde{C}_p/R$ variation in pure 8OCB ($Z = 1$).

scaling behavior diminish as these fluctuations (and T_{NA}/T_{NI}) decrease. Although the possibility of a very weak first-order transition¹⁸ or a very gradual crossover from tricritical¹⁹ or anisotropic-critical²⁰ to asymptotic XY behavior cannot be completely ruled out, it has been clearly demonstrated that XY behavior²¹ is not dominant in the experimentally accessible temperature range in these materials.

ACKNOWLEDGMENTS

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- ¹³The backgrounds in Fig. 3 correspond to quadratic fits to data points for which $3 < |T - T_{NA}| < 10$ K.
- ¹⁴The phases were identified under a polarizing microscope

by their characteristic defect structures. Due to lack of a suitable microscope hot stage, however, the N-SmA and SmA-RN transition temperatures were determined by direct visual observation of the sample in a capillary melting-point apparatus. The transitions were difficult to detect by the latter technique, so that the transition temperatures reported for the 27-wt. % sample are only accurate to ± 1 K.

- ¹⁵Large phase shifts associated with the coexistence of two phases have been observed in 8OCB and several other materials. For details see Ref. 9 and K. J. Lushington, G. B. Kasting, and C. W. Garland, *J. Phys. (Paris) Lett.* (in press).
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