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Reentrant nematic transitions in cyano-octyloxybiphenyl (8OCB)

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Owing to the large dipole associated with its nitrile bond, 8OCB (cyano-octyloxybiphenyl) tends to associate as antiparallel pairs. The number of pairs, N, increases with increasing mole fraction, x_{6OCB}, of a shorter homolog, 6OCB (cyanohexyloxybiphenyl). The stability of the nematic and smectic-A phase depends upon N: increasing N favors the nematic and decreasing N, the smectic-A phase. When N saturates, the smectic-A phase no longer exists and the nematic reenters. Experimental results which support the above are presented. (1) Density measurements of the 8OCB-6OCB system yield two main results. (a) The density ρ is not linear in temperature at high temperatures but becomes so at low temperatures. (b) $(1/\rho) \propto x_{6OCB}$. The first indicates saturation in the number of associations at low temperatures. The second implies that the volume of the mixture is simply the sum of the volumes of the two components. An investigation of the temperature dependence of (1b) indicates that the saturation effect of (1a) is associated with the reentrant nematic phase. (2) Using the results of (1b), we estimate N from lattice-spacing measurements of the smectic-A phase of the mixtures. Even though N is large in 8OCB ($\sim$95% of the molecules are paired at any one time) it increases with the addition of 6OCB. All the molecules are paired when $x_{6OCB} \sim 37\%$. (3) In the pressure-temperature phase diagram, the maximum pressure at which the smectic-A phase is stable, P_M, decreases as N increases. Since pressure tends to stabilize the nematic at the expense of the smectic-A phase, this is consistent with an increase in N with pressure. P_M is found to decrease linearly in the 6OCB-8OCB scavenging parameter, $x_2 = 2x_{6OCB}x_{8OCB} - (x_{6OCB})^2$. x_2 is proportional to the difference between the number of 6OCB-8OCB and 6OCB-6OCB pairs. These results, as well as others, are discussed in terms of a Landau theory which assumes that the nematic and smectic-A order parameters are coupled, and that the coupling depends upon N, temperature, and pressure.

I. INTRODUCTION

Normally in phase transitions, the higher-temperature phase is less well ordered (more symmetric) than the lower-temperature phase.[1] This is not a law of thermodynamics,[2] however, and although counterintuitive, the reentrant nematic phase[3] is one more example of a more-symmetric phase reoccurring at a lower temperature than the less-symmetric smectic-A phase, S_A.[4] Other examples of this phenomenon in condensed-matter physics are superconducting materials doped with magnetic impurities,[5] rare-earth superconducting materials which order magnetically at a temperature below the superconducting transition temperature,[6] and the solid-liquid ^{3}He transition exploited in the Pomeranchuk cryostat.[7]

In the case of liquid crystals, the nematic–smectic-A–reentrant-nematic phenomenon has been found to occur in certain cyano compounds which form antiparallel molecular association,[8-11] perhaps even in the isotropic liquid phase, due to the very large dipole associated with the nitrile bond (~4.5 D). The number of associations (and their lifetime) increases as the temperature decreases and results in a smectic-A layering which is not commensurate with a molecular length[12] (as is the usual case) but rather the length of an associated pair, for example.[13] Sufficiently long lived at lower temperatures, such pairing is postulated to neutralize the long-range attractive electrostatic forces necessary to stabilize layering so that only the shorter-range, repulsive interactions remain. These latter stabilize the nematic phase at the expense of the smectic-A phase which requires an attractive interaction to localize the molecules in layers.

The reentrant nematic is believed to be composed of relatively long-lived associated molecular pairs packed into a tight but mobile configuration. A further decrease in temperature so that the pairs have longer lifetimes can sometimes result in the nucleation of a "solid" phase which has as a characteristic spacing, a length compatible with a close packing of pairs, and which coexists with the supercooled reentrant nematic.[14] In other materials, it leads to a destruction in pairing and a restoration of attractive interactions so that the smectic-A phase reappears this time with a layer spacing commensurate with the molecular length.[15] *And so, it emerges: pairing favors the nematic phase, depairing the smectic-A phase.*[16]

In the next section, we present the results of our measurements and observations on the reentrant-nematic phenomena in 8OCB (cyano-octyloxybiphenyl) and mixtures of 8OCB with 6OCB (cyanohexyloxybiphenyl), the shorter homolog.

First, it will be shown that the density of these mixtures exhibits a saturation effect in the vicinity

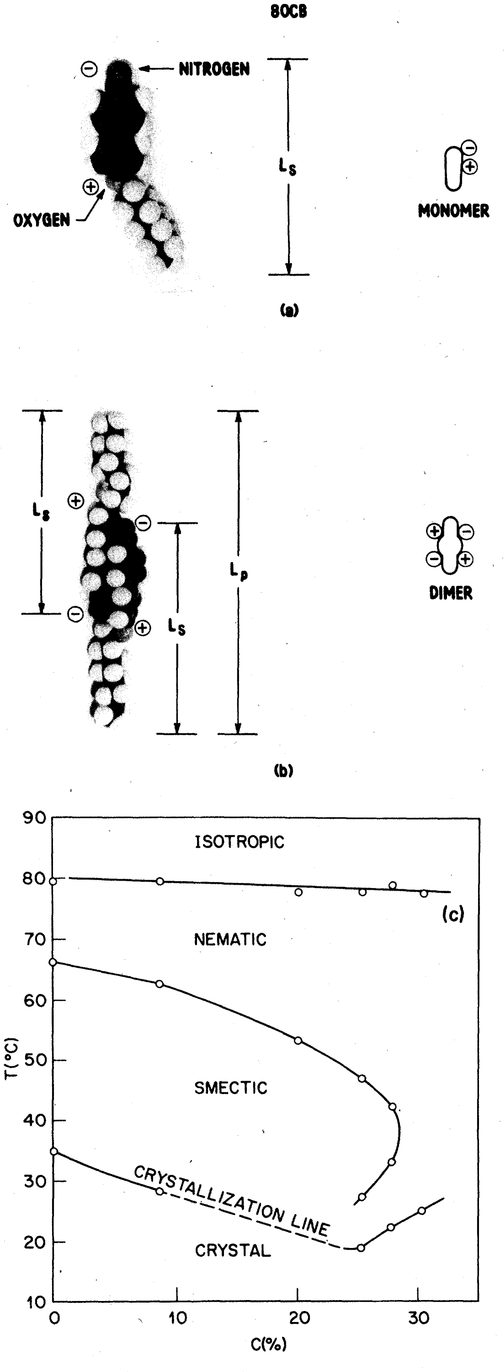

FIG. 1. (a) Molecular model of 8OCB. To the right is a schematic of a cross-sectional view of this molecule in the nematic or smectic-A phase. L_s indicates its molecular length. (b) The model for the dimer. The rationale for the dimerization is that it cancels the longitudinal dipoles, thus decreasing the electrostatic energy of the ensemble. The dimer length is L_p. It is very close to the observed smectic-A layer spacing indicating that about 95 wt.% of the 8OCB is dimerized (Ref. 16). (c) The one-atmosphere phase diagram of 8OCB and 8OCB 8OCB-6OCB mixtures. C is the mass percent 6OCB.

of the reentrant transition and that the volume of the mixture is a simple sum of the volumes of each component. This result provides a basis for a straightforward analysis of the x-ray data presented next.

Figure 1(a) shows the 8OCB monomer and Fig. 1(b) the previously proposed dimer.[13] The monomer is of length L_s; the dimer of length L_p. The partial negative charge in the vicinity of the nitrogen atom is due to the nitrile bond withdrawing electrons from the benzene rings. On the other hand, oxygen donates electrons to the cloud of unlocalized electrons associated with the benzene rings leading to a partial positive charge near it, thus a net longitudinal dipole as shown. When two monomers overlap in the fashion in Fig. 1(b), this longitudinal dipole is annihilated.[13]

The breadth of a benzene ring is about 6.5 Å and its depth 2 Å. In the nematic and smectic-A phases, these molecules rotate freely about their long axis so that the monomer volume is approximated by a cylindrical volume; 3 Å radius and 24 Å long. Our combined x-ray results on the smectic-A layer spacing and the density measurements of pure 8OCB indicate that the equivalent volume for a dimer is very close to 3 Å in radius, also, and 32.3 Å in length.

Consequently, if smectic-A layers are to be

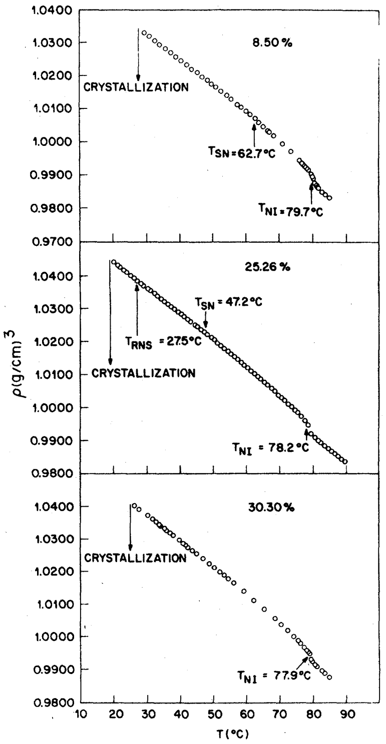

FIG. 2. The density ρ as a function of temperature for various concentrations of 6OCB.

constructed from M single molecules of length L_s as well as N much longer[13] associated molecules of length L_p, then the neighboring layers must intercalate in such a way that the net layer spacing d observed in an x-ray diffraction experiment is simply

$$d=(ML_s+NL_p)/(M+N)\,. \qquad (1)$$

These measurements indicate that N increases and is very nearly saturated at the reentrant-nematic–smectic-A transition. Pressure-temperature phase diagrams provide additional evidence that the smectic-A layer spacing is inversely related to the number of pairs.

In the third section we outline a Landau-type description, and we discuss these experimental results as well as others, in this context, in the fourth section.

II. EXPERIMENTS AND OBSERVATIONS

Figure 1(c) shows the one-atmosphere phase diagram of the 8OCB-6OCB mixtures.[14] For concentration of 6OCB $\gtrsim 20$ wt.%, but less than 30 wt.%, the following sequence of transitions is observed with decreasing temperature: isotropic, nematic, smectic-A, and reentrant nematic. For concentrations less than 20 wt.%, the reentrant-nematic phase is preempted by crystallization. When the concentration exceeds 30 wt.%, there is no longer a smectic-A phase.

A. Density

The density of representative mixtures from Fig. 1 was determined using a commercially available instrument (PAAR). The details of these measurements can be found elsewhere.[17] Their precision is 2×10^{-4} g/cm^3. The two results we wish to highlight here are the gradual onset of linearity in ρ as a function of temperature, shown in Fig. 2, and the linear relation between $1/\rho$ and the concentration C at fixed temperature, shown in Fig. 3. The slopes and intercepts of Fig. 3 are shown in Fig. 4. The slope $b(T)$ is the difference between the inverse density of 6OCB and 8OCB. After an initial rise in the smectic-A phase, $b(T)$ saturates as the reentrant-nematic temperature range is approached. This reinforces the notion of saturation suggested by Fig. 2.

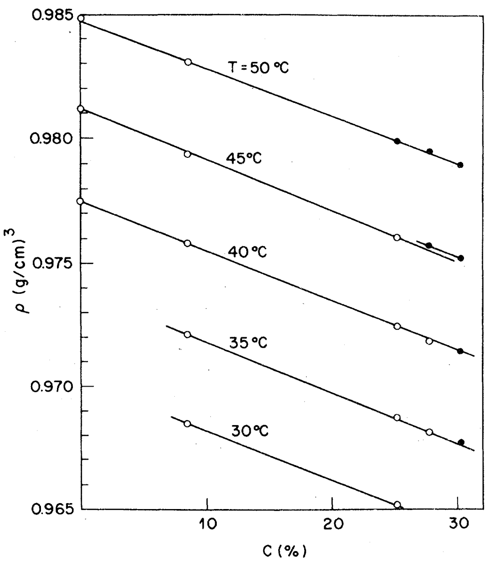

FIG. 3. The inverse of the density as a function of concentration for fixed temperature. Open circles indicate smectic-A phase; closed circles, nematic.

Another important conclusion to be drawn from Fig. 3 is that the volume of the mixture is simply the sum of the volumes of the two components. This presents no problems for a nematic phase where there is no translational ordering. In the smectic-A phase, however, the problem is to pack quantities of dissimilar lengths into layers. The implication of Fig. 3 is that this is done without leaving gaps around the shorter molecules so that the layer spacing is not the longest length but some average determined by the relative amounts of the various molecular species to be packed. We use this to analyze the x-ray results.

B. Layer spacing measurements

1. Measurements

Representative mixtures from Fig. 1 were loaded into thin quartz capillaries and their diffraction observed using a 6-W rotating anode and a linear detector.[14,18] The temperature, monitored by a thermocouple, was controlled to better

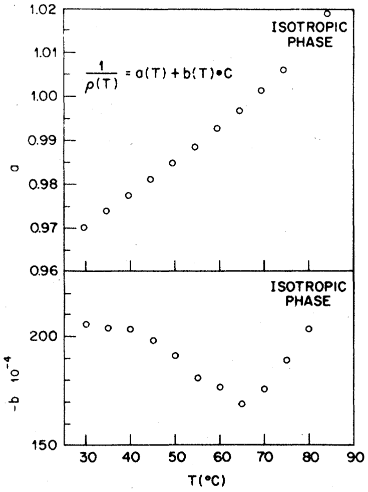

FIG. 4. The slopes $b(T)$ and intercepts $a(T)$ of Fig. 3 as a function of temperature.

than 0.1 °C using a YSI controller.

In the smectic-A phase, only a single, resolution-limited peak was observed characterizing the layer spacing. This spacing decreased at the rate of ~0.1 Å per 10 °C decrease in temperature. In the solid phase, however, at $T \sim 26$ °C, many peaks were observed as a general rule. The solid diffraction of the mixtures is unusual and an example is shown in Fig. 5. The background intensity rises sharply at about 14 Å, levels off, and is constant into the very small angle region. Depending upon the sample, peaks are observed at 32.3, 30.3, 28.28, 24, and 21.9 Å. These lengths correspond to an 8OCB-8OCB pair,[13] an 8OCB-6OCB pair, a 6OCB-6OCB pair, a single 8OCB, and a single 6OCB molecule, respectively. The solid phase of pure 8OCB shows only a single sharp peak at 18 Å which has been interpreted as being due to the close packing of 8OCB pairs.[13,14]

2. *Analysis of x-ray measurements*

We have seen that the density of 8OCB is about 1.00, e.g., at 40 °C it is 1.023 g/cm^3. The molecular weight of 8OCB is 307.4346. Let r_s and r_p be the radius of the right cylindrical volume occupied by the monomer (s) and dimer (p), respectively. Other experiments indicate that 95 wt.% of 8OCB is dimerized.[16] Above we have found $L_s = 24$ Å and $L_p = 32.3$ Å. Taking r_s to be 3 Å,[17] we compute r_p from these data:

$$0.95(\tfrac{1}{2})r_p^2 L_p + 0.05 r_s^2 L_s = 307.4346/[(1.023\pi)(6.02\times10^{23})] ,$$

where 6.02×10^{23} is Avogadro's number per mole; thus $r_p = 3.11$ Å only slightly larger than the monomer.

In what follows, therefore, we consider the dimer and the monomer as distinguishable units. [See Fig. 1(a) and 1(b)]. Each occupies nearly the *same* molecular area. They differ in length [see Fig. 1(a) and 1(b)]. Since 8OCB and 6OCB are homologs of each other, their molecular areas are the same.

To relate the number of pairs of biphenyls in the smectic-A phase to the observed layer spacing d, let N^{ij} be the number of (i,j) pairs and M^i the number of single molecules of species i. The species are 6OCB (6) and 8OCB (8). Then, for x mole fraction 6OCB,

$$d = \frac{N^{88}L_p^8 + N^{68}L_p^{68} + N^{66}L_p^6 + M^8L_s^8 + M^6L_s^6}{(N^{88} + N^{68} + N^{66} + M^8 + M^6)} , \qquad (2)$$

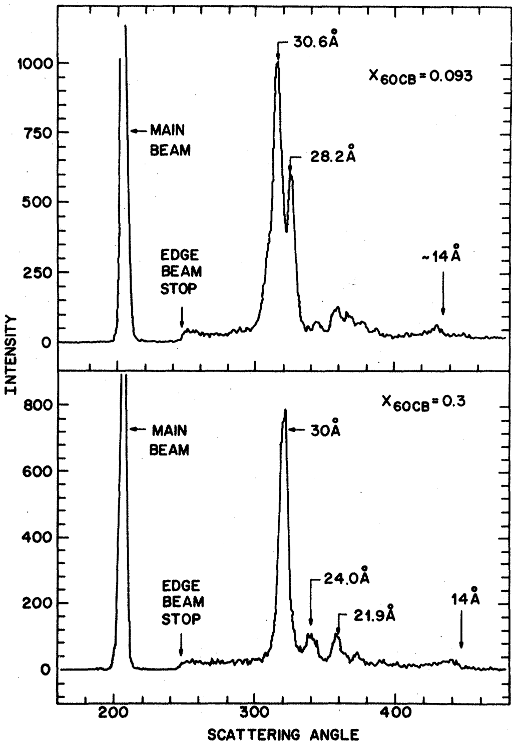

FIG. 5. An x-ray diffraction pattern of the solid phase of $x_{6OCB} = 0.093$ and 0.3 showing several peaks.

where the L's are the lengths of the appropriate units. Let N/T be the ratio of the total number of pairs to the total number of molecules at any given concentration, then

$$\frac{N}{T} = \frac{N^{88} + N^{68} + N^{66}}{T} , \qquad (3)$$

where

$$\frac{N^{88}}{T} = (1-x)^2\frac{N}{T}; \quad \frac{N^{68}}{T} = 2x(1-x)\frac{N}{T}, \quad \frac{N^{66}}{T} = x^2\frac{N}{T} \qquad (4)$$

and

$$\frac{M^6}{T} = x\left(1 - \frac{2N}{T}\right) \frac{M^8}{T} = (1-x)\left(1 - \frac{2N}{T}\right). \qquad (5)$$

The total number of pairs may vary with concentration of 6OCB but for any given N, the distribution of pair types will be statistically determined by (4). Thus,

$$\frac{N}{T} = \frac{(1-x)L_s^8 + xL_s^6 - d}{2[(1-x)L_s^8 + xL_s^6] - d - (1-x)^2L_p^8 - 2x(1-x)L_p^{68} - x^2L_p^6} . \qquad (6)$$

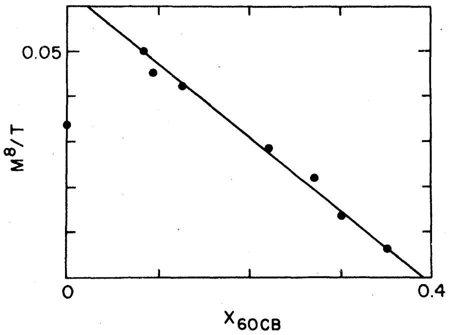

FIG. 6. The number of unpaired 8OCB molecules as a function of $x_{6\mathrm{OCB}}$.

In Fig. 6, M^8/T, deduced from the smectic-A layer spacing observed 5–10 °C below T_{NS} for each mixture, is seen to drop monotonically for $0.08 < x_{6\mathrm{OCB}} < 0.39$.

The initial rise in M^8/T at dilute concentrations of 6OCB is partly spurious depending upon how well we can rely upon our determination of all the L's in Eq. (2). It is also partly due to the somewhat greater pairing efficiency of 6OCB which could displace paired 8OCB molecules.

Estimating how pairs change with temperature from these measurements requires knowing how L_s and L_p change with temperature. In order to estimate this, we assume that the length of the dimer has the same temperature dependence as the monomer; i.e.,

$$L(T)=L(T_0)\left(1-\frac{\beta}{3\rho(T)}(T-T_0)\right), \tag{7}$$

where $\beta_s=7.7\times10^{-4}$ g/cm^3/°C is the iaobaric compressibility found for the smectic-A phase of this system.[18] Modifying L_s and L_p according to this rule, then recalculating N/T now as a function of temperature, $\Delta(N/T)/\Delta t$(°C) is found in the 30-50 °C range of temperature to be $(-2\pm1)\times10^{-4}$ pairs/total number of molecules/°C; the number of pairs increases very slowly with decreasing temperature.

C. Pressure-temperature phase diagram

As might be expected from the foregoing and from similar results in other systems,[10,13] the maximum pressure at which the smectic-A phase is stable, P_M, decreases with increasing concentration of 6OCB [Fig. 7(a) and 7(b)].

Figure 8 shows the linear dependence of P_M on x_2, where x_2 is proportional to the number of additional pairs formed by 8OCB for $x_{6\mathrm{OCB}}>0$; i.e.,

$$x_2=2x_{8\mathrm{OCB}}x_{6\mathrm{OCB}}-(x_{6\mathrm{OCB}})^2, \tag{8}$$

where $x_{8\mathrm{OCB}}$ is the mole fraction of 8OCB, and the squared term recognizes that 6OCB also pairs with itself. $P_M=0$ when $x_{6\mathrm{OCB}}=0.33$. As we have seen in the previous section, in the pure state, 95 wt.% of pure 8OCB is paired. 6OCB scavenges the unpaired biphenyls so that the 37 wt.% mixture is completely dimerized. Figure 1(c) shows the system is no longer polar enough to support a smectic-A phase when the concentration of 6OCB exceeds 30 wt.%.

III. LANDAU DESCRIPTION

A phenomenological description which accounts for these results as well as many others,[16] has already been given. It's main hypothesis is that there is an isotropic, quadratic coupling between the nematic and smectic-A order parameters and that the coupling constant can be either positive or negative and depends on the molecular composition, temperature, and pressure. For the nematic order parameter, Q and the smectic-A order parameter, ψ, the free-energy function $\Delta F=F-F_I$, where F_I is the free energy of the isotropic liquid is

$$\Delta F=\frac{\alpha}{2}Q^2+\frac{\beta}{4}Q^4+\frac{a}{2}\psi^2+\frac{b}{4}\psi^4+\frac{\eta}{2}Q^2\psi^2, \tag{9}$$

where $\alpha=\alpha_0(T-T^0_{NI})$, $a=a_0(T-T^0_{NS})$, and β, b are both positive constants, then

$$Q^2=-(\alpha+\eta\psi^2)/\beta \tag{10}$$

and

$$\Delta F=[-\alpha^2+2\psi^2(\beta a-\eta\alpha)+\psi^4(\beta b-\eta^2)] \tag{11}$$

and

$$\psi^2=-(\beta a-\alpha\eta)/(\beta b-\eta^2). \tag{12}$$

In particular, when the coupling constant $\eta>0$ grew faster with decreasing temperature than ψ, it was shown that the nematic phase could reenter.

IV. DISCUSSION

A. McMillan's theory

In 1971, with a specific microscopic interaction, McMillan[20] was the first to demonstrate that given the nematic–smectic-A transition was of second order, then it could be driven first order due to the coupling between the smectic-A order parameter and some external agency such as the nematic order parameter. To date, no coupling is known which drives this transition second order. We have demonstrated[16] for a second-order transition that for $\eta>0$, the reentrant nematic could occur before a first-order transition. The

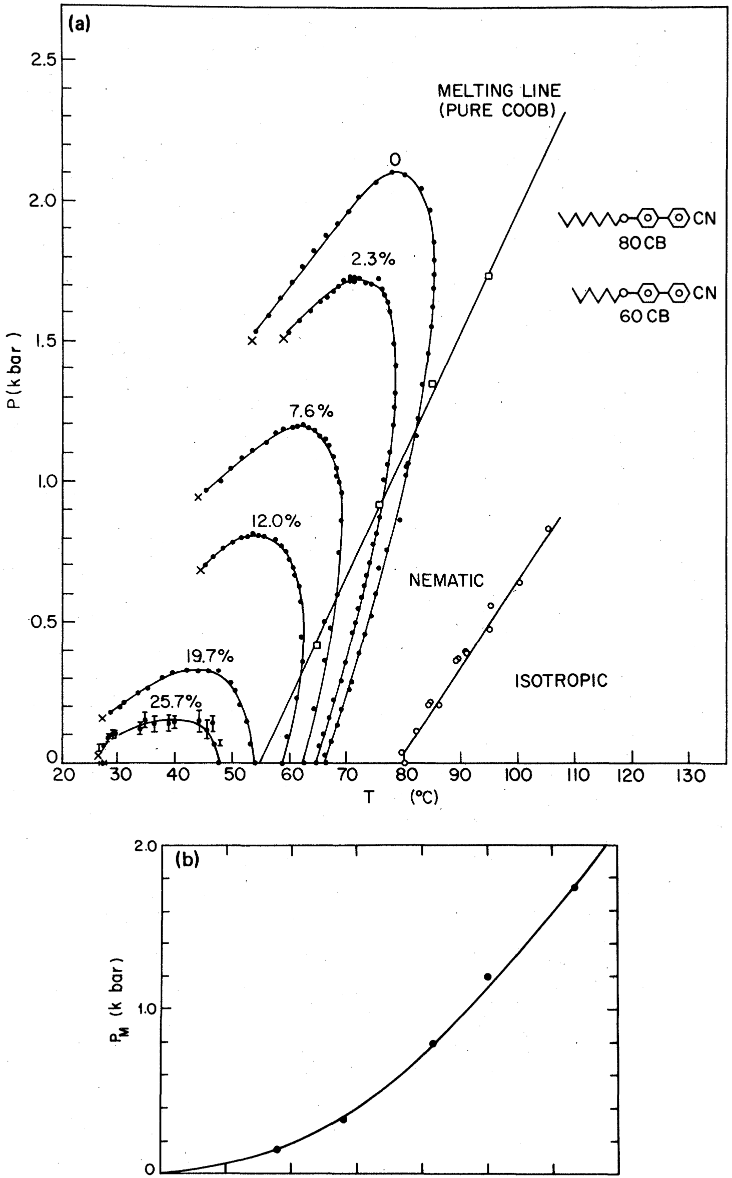

FIG. 7. (a) Pressure-temperature phase diagram for 8OCB and mixtures of 8OCB and 6OCB. The numbers parametrizing the curves is mass percent 6OCB. (b) Correlation between stability of the smectic-A phase as measured by P_m versus the number of unpaired 8OCB molecules determined from the measured layer spacing (Fig. 6).

requirement that the transition remain second order is

$$\beta b > \eta^2 . \qquad (13)$$

If η_0 = maximum value of $\eta = a_0\beta/\alpha_0$ then (13) implies[1]

$$\frac{(\Delta C_p)_{NS}}{(\Delta C_p)_{NI}} < \frac{T^0_{NS}}{T^0_{NI}} = M . \qquad (14)$$

Strictly speaking we cannot apply this criteria to the 8OCB-6OCB system since it seems that first or second order may be too simple to describe these transitions. There is no jump at the nematic–smectic-A transition and only a very small one at the nematic-isotropic transition.[21] The transition entropies of pure 8OCB and of the 8OCB-6OCB mixtures have been measured,[22] and in terms of the integrated enthalpy, the nematic-isotropic transition is about an order of magnitude larger than the nematic–smectic-A transition in 8OCB. If one assumes that this reasonably ap-

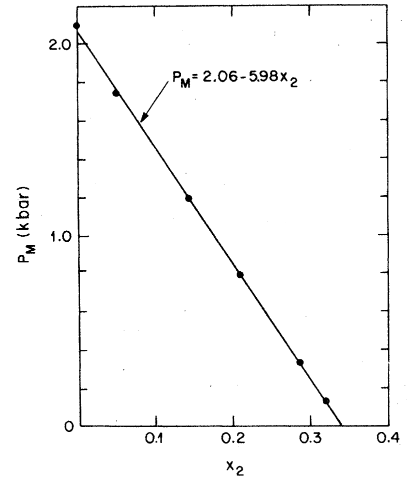

FIG. 8. P_M, the maximum pressure at which the smectic-*A* phase is stable, from Fig. 7, $x_2 = 2x_{8OCB}x_{6OCB} - (x_{6OCB})^2$.

proximates an estimate for ΔC_p, then (14) appears to be satisfied.

Figure 9 shows M, the McMillan number, for both the reentrant transition at one atmosphere and under pressure. It is seen that for $M \sim 0.88$, rather than become first order (or second order), the smectic-*A* phase disappears. In other words, the nematic ordering increases at the *expense* of the smectic-*A* phase as predicted by the isotropic quadratic coupling between the two order parameters [Eq. (9)].[16] This is a different result from McMillan's, where an increase in nematic ordering results in a second-order smectic-*A* transition. Klug and Whalley[2] and independently Clark[2] have shown that a first-order reentrant transition is not particularly unusual and violates no laws of thermodynamics.

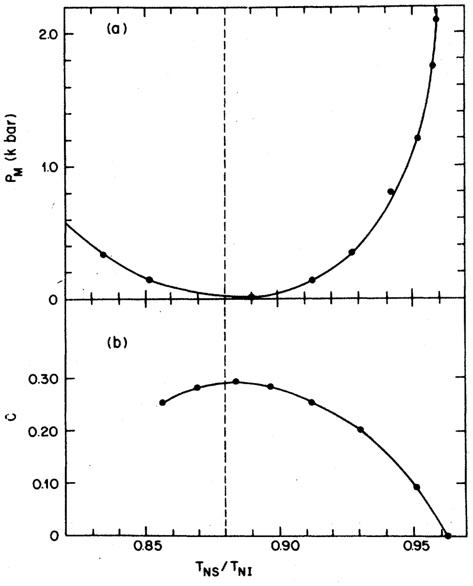

FIG. 9. The nematic-smectic-*A* transition of (a) Fig. 7 and (b) Fig. 1 as a function of reduced temperature $T_{NS}/T_{NI} = M$ at one atmosphere.

B. Layer spacing measurement under pressure

Using a diamond anvil, Chandrasekhar *et al.*[23] monitored the smectic-*A* layer spacing of 8OCB under pressure. They observed an increase in layer spacing just before the reentrant transition. This increase in layer spacing can be interpreted as an increase in the number of pairs with increasing pressure. However, in order to demonstrate this we need to know how L_s^8 and L_p^8 change with pressure. Since the compressibility of most liquids ~0.05 kbar^{-1}, then to estimate N/T from Eqs. (2)–(6) as a function of pressure we put

$$L_s^8(P) = L_s^8(0)\left(1 - \frac{0.05}{3}P\right), \tag{15a}$$

$$L_p^8(P) = L_p^8(0)\left(1 - \frac{0.05}{3}P\right), \tag{15b}$$

where P is pressure in kilobars. Doing this, we find that $N/T \to 0.5$ as $P \to P_M$; that is, the number of pairs saturates and consequently the smectic-*A* phase is no longer stable and the nematic phase reenters.

C. Dielectric measurements

Ratna, Shashidhar, and Rao[9] have measured $\epsilon_\parallel$ and $\epsilon_\perp$, the dielectric constants parallel and perpendicular to the long molecular axis. The argument is that this is a sensitive probe for the pairing hypothesis since if there are such antiparallel correlations, then $(\epsilon_\parallel + 2\epsilon_\perp)/3$ will be less than an extrapolated isotropic value because $\epsilon_\parallel$ is less than one would expect. What they find is that $\epsilon_\parallel$ continues to increase even in the reentrant-nematic phase (which could be due to the continued increase in density with decreasing temperature) but that $(\epsilon_\parallel + 2\epsilon_\perp)/3$ becomes identical to (not less than) a value extrapolated from the isotropic phase. As Dunmur[24] points out, this could be due to the fact that the temperature dependence of the pairing has ceased to be anomalous because the pairs are saturated just prior to the appearance of the reentrant-nematic phase.

V. CONCLUSIONS

Here we have presented our measurements and observations on the 8OCB and 8OCB-6OCB mixtures which exhibit the reentrant-nematic phase. We draw the following conclusions.

(1) Reentrant behavior is linked to the relative polarness of the system. As the number of pairs N saturates, the smectic-A phase is destabilized and the nematic phase reenters.

(2) As N increases, the maximum pressure at which the smectic-A phase is stable, P_M, decreases. This would be consistent with steric exigencies which tend to homogenize the ensemble by increasing the pairing with pressure. P_M is found to decrease linearly as the probability that 6OCB pairs with 8OCB rather than another 6OCB molecule.

(3) A Landau description in which the nematic and smectic-A order parameters are coupled suggests that, in the presence of this coupling, before a second-order nematic–smectic-A transition becomes first order, the nematic phase will reenter. In particular it accounts for the *disappearance* of the smectic-A phase where the uncoupled theory predicts a tricritical point.

(4) It is suggested that the saturation in pairing deduced from our density measurements is consistent with the dielectric results of Ratna, Shashidhar, and Rao.

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