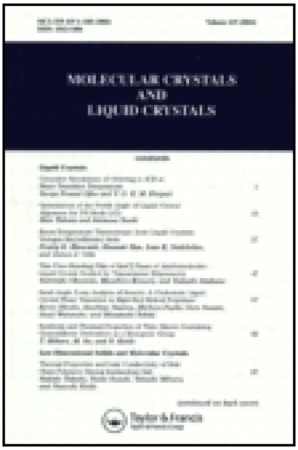

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DENSITY MEASUREMENTS OF ALLOYS EXHIBITING THE RE-ENTRANT NEMATIC PHASE

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ABSTRACT

Measurements of the density, ρ, of mixtures of 6OCB (cyanohexyloxybiphenyl) and 8OCB (cyanooctyloxybiphenyl) are presented as a function of temperature and composition. In a certain range of temperature, T, and composition, C, these mixtures exhibit the re-entrant nematic phase. $\rho(T)$ is not linear but exhibits an approach to linearity at lower temperatures. Consequently the isobaric compressibility is evaluated only in the vicinity of the smectic A phase and is found to be $\beta_S = 7.71 \pm 0.06 \times 10^{-4}$ $g/cc/^\circ C$ for the smectic A phase and $\beta_N = 8.03 \pm 0.15 \times 10^{-4}$ $gms/cc/^\circ C$ for the nematic and re-entrant nematic phases. $1/\rho$ is found to depend linearly on C implying the partial intercalation of molecules in neighboring layers of the smectic A phase to ensure that, when alloyed, 6OCB and 8OCB occupy no more than their volume in pure compounds. Finally, very precise measurements in the vicinity of the smectic A re-entrant nematic transition show an anomalously large pretransitional increase in the density of the smectic A phase.

I. INTRODUCTION

The nematic-smectic A-re-entrant nematic phenomenon[1-8] has been found to occur in several cyano compounds which form antiparallel molecular pairs[2,8-12] (perhaps even in the isotropic phase) due to the very large dipole associated with the nitrile bond (~ 4.5 debye). With decreasing temperature, the number of these associations and their lifetime increases resulting in a smectic A layering which is (most often) closer to the length of an associated pair of molecules rather than a single molecular length.[2,7,10-13] It is postulated[8] that such pairing neutralizes the long range electrostatic interactions necessary to stabilize the layers leading to the appearance of a lower temperature nematic phase, called the re-entrant nematic.

Here we present the results of measurements of the density of several mixtures of 8OCB (cyano-octyloxybiphenyl) and 6OCB (cyano-hexyloxybiphenyl) (Fig. 1). In the figure, it is seen that for mixtures with more than ~ 22% but less than 30% 6OCB the following transitions are observed with decreasing temperature: isotropic, nematic, smectic (A), (re-entrant) nematic, solid. We have

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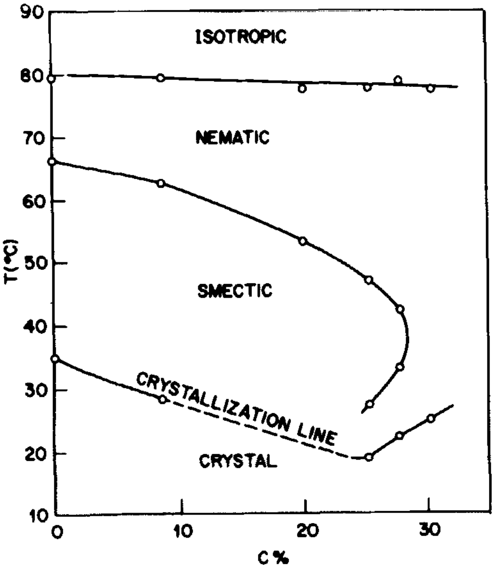

Fig. 1. Phase Diagram of mixture of 6OCB in 8OCB.

found the temperature dependence of the density of these mixtures to be more linear at lower temperatures than higher temperatures suggesting a saturation in the number and lifetimes of the associations at lower temperatures. This we note may be relevant to the appearance of the re-entrant nematic. As a function of composition, we have found that if $a(T)$ and $b(T)$ are two temperature sensitive coefficients, then the density, $\rho(T)$, for a mixture of composition C% of 60CB is simply:

$$\rho(T) = [a(T) + b(T) \times C]^{-1} \qquad (1)$$

This implies that the volume of the mixtures is the sum of the volumes of 60CB and 80CB. Consequently, even though the smectic A layers of these mixtures are composed of molecules of different lengths, the molecules in neighboring layers are intercalated so that there are no more empty spaces in the mixtures than in the pure materials.

II. EXPERIMENT

Measurements were performed using a commercially available instrument (PAAR) which counts the resonance frequency of a hollow oscillator filled with the material to be studied. The value read is the time lapse, t, for a given number, N, of oscillations. t is directly related to the density by

$$\rho = A(t^2 - B) \qquad (2)$$

where A and B are temperature dependent constants of the instrument. The variation of $A(t)$ and $B(T)$ for $20°C \leq T \leq 80°C$ were obtained using dry air and distilled water as a standard. The data were fit to a second degree polynomial so that the total error introduced by the calibration is $\pm 1 \times 10^{-4}$ *gms/cc*. Temperatures were controlled by a circulating bath to $\pm$ 0.02°C. This was measured using a quartz thermometer. Thus, the total precision of the measurement was $2 \times 10^{-4}\, g/cm^3$. The samples for these experiments had been prepared by weighing the ingredients and leaving in a vacuum oven at 100°C overnight.

The second experiment was conducted on a PAAR DMA 02, working on the same principle but counting the time lapse during 10^4 periods. We did not make an absolute calibration on this machine but the relative precision is ± 0.001%. The temperature was controlled to $\pm\ 0.002^{\circ}C$ by means of a large capacity circulating bath and measured with a quartz thermometer. The sample was prepared and degassed 24 hours in advance by heating to $110^{\circ}C$ in a vacuum oven, then cooling to room temperature under vacuum. All the transition temperatures were checked visually using the Mettler microscope hot stage whose precision is $\pm\ 0.02^{\circ}C$.

III. RESULTS AND DISCUSSION

A. Temperature Dependence

Fig. 2 shows the non-linear dependence of ρ vs T for three of the mixtures. When $T \lesssim 50^{\circ}C$, ρ seems to be more linear than for $T > 50^{\circ}C$. If the enhanced curvature at higher temperatures is due to changes in the number of molecular associations (specifically of the anti-parallel pairing variety[2,8–10]) then the more pronounced linearity of $\rho(T)$ at lower temperatures points to a saturation in the associations.

The results of fitting only those portions of the curves which do not deviate too much from a straight line to an expression of form

$$\rho = \rho_0 - \beta T \tag{3}$$

where $\rho_0 = \rho(T = 0^{\circ}C)$ and β is the isobaric thermal expansion coefficient, are summarized in Table I. In Table I we see, independent of composition, that for the smectic A phase, $\beta_S = 7.71 \pm 0.06 \times 10^{-4}\ gms/cc/^{\circ}C$ and for the nematic phase (both high temperature and re-entrant) $\beta_N = 8.03 \pm 0.15 \times 10^{-4}\ gms/cc/^{\circ}C$. Although our data do not permit a precise evaluation of β in the isotropic phase, the jump in density at the nematic isotropic transitions of the mixtures is $\dfrac{\Delta\rho}{\rho} = 3 \pm 1 \times 10^{-3}$.

B. Concentration Dependence

Fig. 3 shows that the inverse of the density varies linearly in the mass percentage C of 60CB to the total mass of the mixture. The slopes $(b(T))$ and intercepts $(a(T))$ of these lines depend upon temperature and can be calculated from the data. In Fig. 4 we show the temperature variation found for these quantities fitting Eq. (1).

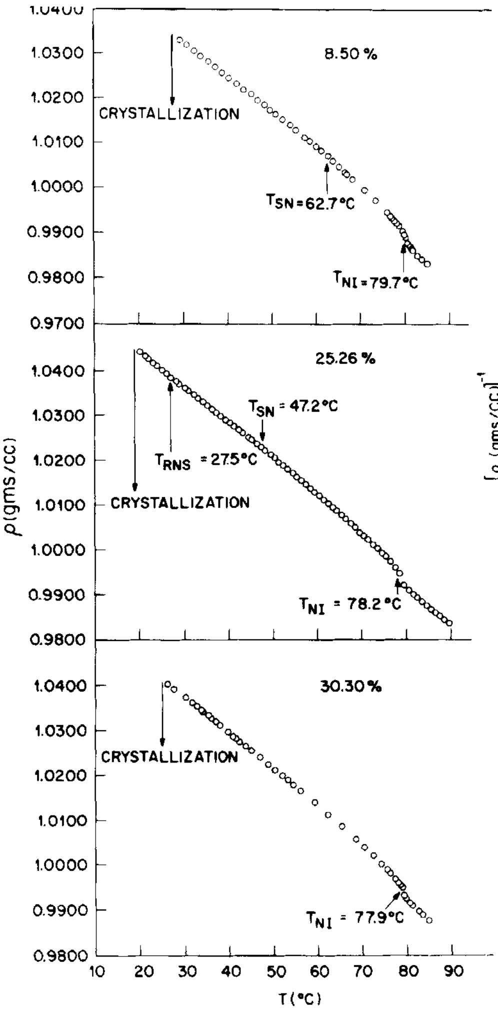

Fig. 2. ρ vs T for various concentrations of 6OCB.

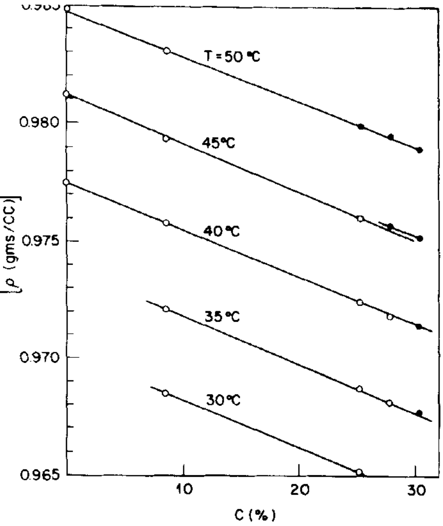

Fig. 3. The inverse of the density vs concentration for various temperatures.

One could further fit $a(T)$ and $b(T)$ to polynomials in $T(^\circ C)$ but this only gives ρ for $25^\circ C \leq T \leq 85^\circ C$ to a precision of 1×10^{-2} assuming C can be measured with no error.

Table I. The thermal expansion coefficient for the smectic A phase (β_S) and for the nematic phase (β_N) of $C = 27.76\%$ for $T > 65°$ and the re-entrant nematic phase for the same composition for $T < 65°$. For comparison β_N for $T < 65°C$ is shown for the 30.30% solution.

T	C%	$\beta_S \times 10^{-4}$ *gms/cc/°C*	$\beta_N \times 10^{-4}$ *gms/cc/°C*	$\beta_{RN} \times 10^{-4}$ *gms/cc/°C*
	0	7.68		
	8.5	7.64		
	25.20	7.74		
	27.76	7.78	8.2	7.9
$T < 65°C$	30.30		8.0 ± 0.2	

The inverse relation between ρ and C follows from the assumption that the volume of 60CB and 80CB are the same in the alloys as in the pure state. In particular, in the smectic A phase, molecules of different lengths must now be arranged in planes. In order to avoid the gaps that result for perfectly planar layers the layers must buckle and the ends of the aliphatic chains of the longer molecules (most probably) now partly intercalate into the neighboring layer in the vicinity of the shorter molecules.

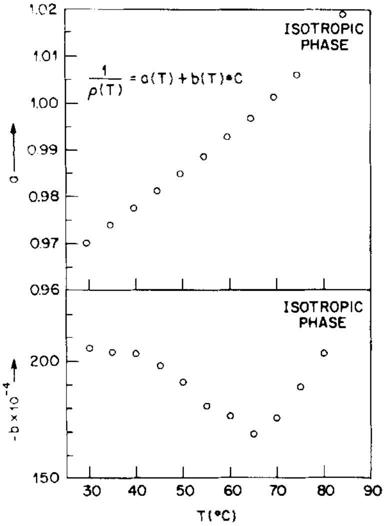

Fig. 4. The temperature dependence of the coefficients of Eq. 1 deduced from the data.

We note the interesting temperature dependence of $b(T)$ [Fig. 4] which is equal to the difference in the inverse of the density of 60CB and 80CB. The absolute value of $b(T)$ is a minimum in the vicinity of T_{NI}, increases throughout the nematic and smectic phases to finally level off in the vicinity of the re-entrant nematic.

We conjecture that this is additional support for the saturation of pairing in the vicinity of T_{RN}, the re-entrant nematic transition temperature and additional evidence that the "associations" in the re-entrant nematic phase are different from the nematic phase.[14]

C. High Precision Measurement in the Vicinity of the Re-entrant Nematic Phase

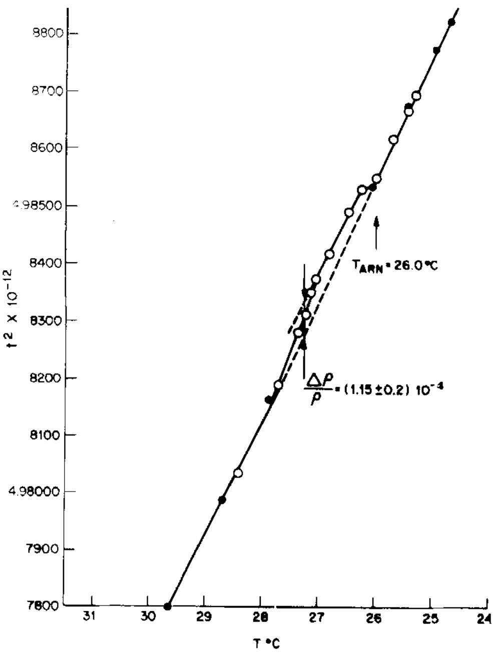

Fig. 5. High precision density measurements vs temperature.

Fig. 5 displays the square of the time for 10^4 oscillations vs temperature as one approaches the re-entrant nematic state. The data shown represent two sets of measurements but both taken with decreasing temperature. The sample was heated to the isotropic phase between two series of measurements. Using the results of section 2, one can give an estimate of the magnitude of this pretransition effect: $\Delta\rho/\rho \sim 1.15 \pm 0.2 \times 10^{-4}$.

This is surely very unusual behavior and indicates an enhancement of the density in the smectic A phase. Coupled with the observation that in these systems the smectic A layer spacing is insensitive to temperature[11] or even very slightly increases[13] in the vicinity of the re-entrant nematic, the largest change in the molecular volume is associated with the molecular area.

IV. CONCLUSION

The density of various mixtures of 6OCB and 8OCB shows that:

1. ρ vs T is not linear. We attribute this to the continuous change in the structure of the liquid from one in which there are only a few associations at high temperature to one in which there are only a few single molecules at low temperatures.

2. In the vicinity of the smectic A phase and independent of composition, the isobaric compressibility is $\beta_S = 7.71 \pm 0.06 \times 10^{-4}$ gm/cc/°c for the smectic A phase and $\beta_N = 8.03 \pm 0.15 \times 10^{-4}$ gms/cc/°c for the nematic and re-entrant nematic phases, for $C < 30\%$.

3. ρ varies inversely with concentration. The temperature dependent parameters which control this behavior have been deduced from the data (Fig.

4). The implication of this is that in the smectic A phase, molecules in adjacent layers must partially interpenetrate.

4. Despite the anomalous increase in the density in the vicinity of the smectic A-re-entrant nematic transition, the re-entrant nematic is more dense

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