High precision density studies near the smectic A-nematic tricritical point

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High precision density studies near the smectic A–nematic tricritical point

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We have carried out very accurate density measurements (with a precision of $\pm 5 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$) near the smectic A–nematic transition in binary mixtures of 4-n-nonyl-4'-cyanobiphenyl (9CB) and 4-n-decyl-4'-cyanobiphenyl (10CB). The transition crosses over from second to first order as the temperature range of the nematic phase decreases. For mixtures with the shortest nematic range the data deviate noticeably from a single power law behaviour. Such a deviation is an indication of the first order nature of the transition. Very good fits to a single power law have been obtained for pure 9CB and the $x = 0.04$ mixture where x is the mole fraction of 10CB in 9CB. The critical exponent obtained from the power law fitting has enabled us to locate the tricritical point to be very close to $x = 0.04$, which is in agreement with the results obtained previously by high resolution calorimetric [1] and X-ray scattering studies [2].

1. Introduction

The smectic A to nematic transition in liquid crystals has been the subject of extensive experimental and theoretical studies but as yet there is no consensus in regard to the question of the universality class to which it belongs. It is well known that this transition can be either first or second order. In the molecular field model of McMillan [3] an important parameter which decides the order of the transition is the ratio $r = T_{S_A N}/T_{NI}$. The transition is second order for $r < 0.87$ and first order for $r > 0.87$; $r = 0.87$ corresponds to the tricritical point.

On the experimental side, mostly by calorimetric studies [1, 4–6], the S_A–N tricritical point has been observed in different systems. From high resolution adiabatic calorimetric investigations on the alkylcyanobiphenyl (nCB) series Thoen et al. [1] suggested that the tricritical point can occur for materials with $r = 0.99$, a number appreciably larger than the value ($r = 0.87$) predicted by McMillan. Their studies also showed that the specific heat exponent α increases as r increases on approaching the tricritical point; at this point $\alpha = 0.5$. Marynissen et al. [4] obtained the value $\alpha = 0.5$ for 9CB (for which $r = 0.994$) indicating that the S_A–N transition for this compound must be at or very close to the tricritical point. This result also suggested that in order to see a first order S_A–N transition, systems with a very narrow nematic range (i.e. $r > 0.994$) should be studied.

Very few investigations have been reported on the density changes associated with the S_A–N transition [7–11]. In particular, Dunmur and Miller [7] have carried out precise measurements of density as a function of temperature for the nCB series ($n = 5$–9). In this paper we present density studies on 4-n-nonyl-4'-cyanobiphenyl (9CB) and its mixtures with 10CB which show very narrow nematic ranges.

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2. Experimental

Experiments were conducted on 9CB and three mixtures of 9CB and 10CB with $x = 0.04$, 0.2 and 0.3. Measurements were made using an Anton Paar instrument consisting of a microcell (DMA 602H) and a processing unit (DMA 60). The principle involved in measuring the density is as follows. A hollow resonator tube made of special glass and capable of working at high temperatures was filled with the sample to be studied. The instrument, in conjunction with a digital processing unit, measures the time lapse τ for a given number of oscillations. (We measured the time interval for 10^4 oscillations.) The density ρ of the sample is related to τ by

$$\rho = A(\tau^2 - B), \tag{1}$$

where A and B are temperature dependent instrument constants which were obtained by calibration runs using dry air and distilled water. The precision in measuring the density is reckoned to be $5 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$. The temperature of the cell was measured using a bead thermistor YSI 44011 which was placed very near the sample. The cell temperature was maintained to a constancy of better than 10 mK. The liquid-crystalline sample was filled in the nematic phase and care was taken to see that there were no air bubbles.

3. Results and discussion

The partial phase diagram of the 9CB–10CB system obtained using optical microscopic observations is shown in figure 1. With the increase in 10CB concentration the nematic range decreases and finally it ceases to exist for $x > 0.35$. The density variation with temperature near the S_A–N and N–I transitions for the mixture $x = 0.04$ is shown in figure 2. With increase of temperature the density shows a slow decrease within the phase and changes abruptly at the transition. This particular feature is also in very good agreement with the results of Dunmur and Miller [7]. The value of ρ changes by 0.54 per cent across N–I but only by 0.2 per cent across S_A–N. Although, the density variation across the S_A–N transition shows a concentration dependence, it was not significant enough to locate the tricritical point accurately.

In order to achieve this we have adopted the fitting procedure used in other experiments [12–15]. The critical part of the density variation $\delta\rho$, is fitted to a function of the form

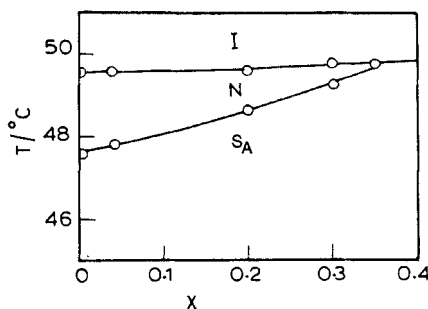$$|\delta\rho| = |\rho - \rho_0| = A_{\pm}|t|^{1-\alpha}, \tag{2}$$

Figure 1. Part of the temperature–concentration phase diagram for varying mole fraction (x) of 10CB in 9CB.
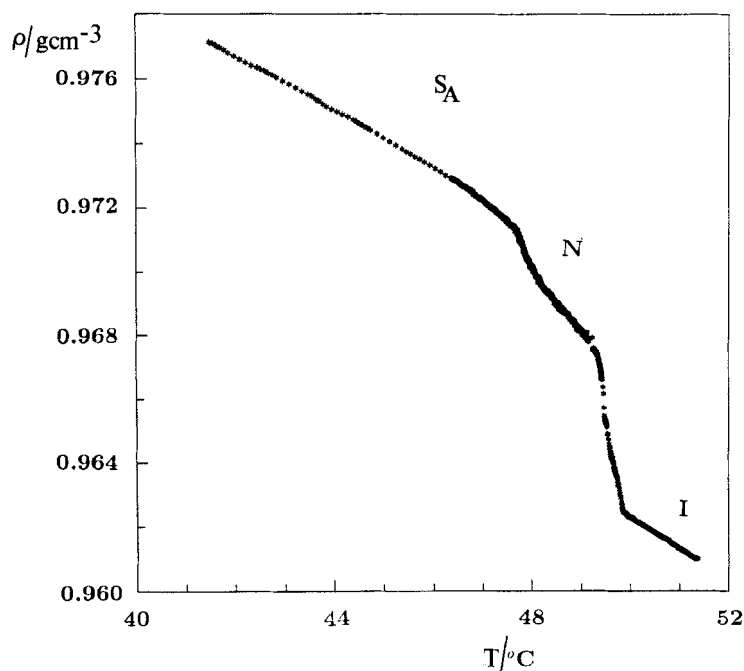
Figure 2. The temperature variation of the density in the smectic A, nematic and isotropic phases for the $x = 0.04$ mixture.

where $t = (T - T_{S_AN})/T_{S_AN}$ and ρ_0 is the value of ρ at T_{S_AN}. From equation (2) it can be seen that the slope of a $\log|\delta\rho|$ plot, which is a straight line, gives the exponent $1 - \alpha$. Such a plot for 9CB and for the three mixtures $x = 0.04, 0.2$ and 0.3 are shown in figure 3. In each case the data both above and below the transition are plotted separately. The notable features in this diagram are as follows:

(1) The data above and below the transition show the same asymptotic behaviour, i.e. they are described by the same exponent.

(2) The data for 9CB and for the $x = 0.04$ mixture do not deviate from the linear behaviour even very close to the transition ($t = 5 \times 10^{-5}$) indicating that the transition is second order in nature. In contrast, the data for $x = 0.2$ and 0.3 mixtures show a clear deviation from the linear behaviour indicating that the transition is first order [2, 16]. The values of α obtained in this way are 0.43 ± 0.01 for 9CB ($T_{NI} - T_{NS_A} = 2°C$; $r = 0.994$) and 0.5 ± 0.01 for $x = 0.04$. ($T_{NI} - T_{NS_A} = 1.7°C$; $r = 0.995$). For $x = 0.2$ the transition is clearly first order. The system therefore crosses over from second to first order S_A–N transition region through a tricritical point, which is at or very close to $x = 0.04$.

To ensure that these conclusions are reliable, we have repeated the calculation using a function of the form

$$|\delta\rho| = A_{\pm}|t|^{1-\alpha} + B|t|. \tag{3}$$

This gives $\alpha = 0.43 \pm 0.01$ for 9CB and 0.51 ± 0.01 for $x = 0.04$. Thus in the temperature range very close to T_{S_AN} the introduction of a background term linearly dependent on $|t|$ leads to the same conclusions to within the experimental limits.

Recently Thoen *et al.* [1] have measured the heat capacity for several nCB materials and mixtures using an adiabatic scanning calorimeter. The results indicated that the
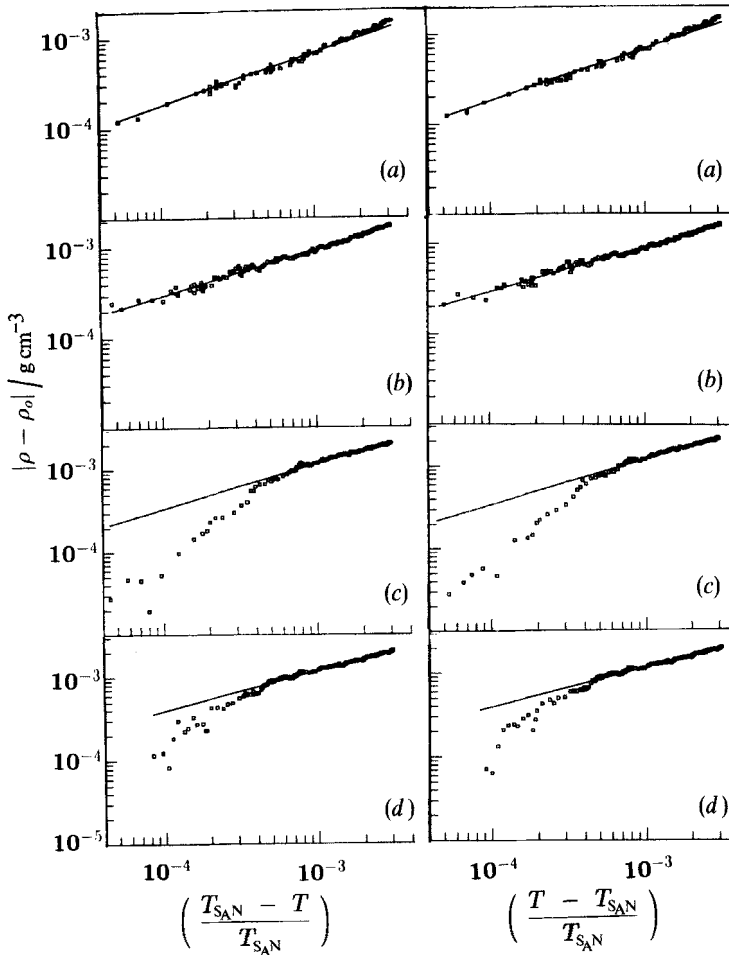
Figure 3.   Double logarithmic plot for the quantity $|\rho - \rho_0|$ of equation (2) versus t for $T < T_{S_A N}$ (left) and $T > T_{S_A N}$ (right): (a) 9CB, (b) $x = 0.04$, (c) 0.2 and (d) 0.3 mixtures. In each case the solid lines were obtained by fitting the data separately to equation (2).

S_A–N transition in 9CB is second order with $\alpha = 0.5$, implying that the transition is at or very near the tricritical point. As the nematic range is reduced by mixing 10CB with 9CB the latent heat was observed to increase steadily from zero. Ocko *et al.* [2] have carried out a detailed X-ray scattering study of the S_A–N transition in the same system. By measuring the smectic correlation length in the nematic phase, they concluded that the tricritical point lies at or very close to $x = 0.09$ if the extrapolation of the width of the co-existence region to a zero value is assumed to be linear or $x = 0$ if it is assumed to be quadratic. Thus our observations are in very good agreement with the calorimetric [1] and X-ray results [2].

   In conclusion, we have carried out the first detailed density studies near the smectic A–nematic tricritical point in 9CB–10CB mixtures. The results confirm the existence of a tricritical point for a concentration very near to a $x = 0.04$ mixture. These features are in agreement with the earlier heat capacity [1] and X-ray [2] studies.

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