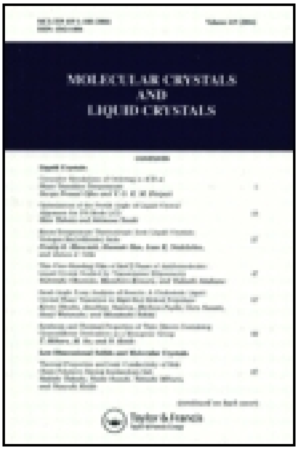

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Experimental Evidence for a Nematic to Smectic A Tricritical Point in Alkylcyanobiphenyl Mixtures†

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An adiabatic scanning calorimeter has been used to investigate the temperature dependence of the enthalpy and the heat capacity near the smectic A (A) to nematic (N) phase transition in mixtures of alkylcyanobiphenyl (nCB) liquid crystals. Mixtures of 8CB + 10CB with small N-ranges undergo first-order transitions, but mixtures with large N-ranges exhibit continuous ones. A tricritical point could be located for the 10CB mole fraction of 0.3135. For a nearly tricritical mixture, a critical exponent $\alpha = 0.50 \pm 0.02$ has been observed. For mixtures with continuous AN transitions it is seen that this specific heat exponent α decreases with the width of the nematic range.

INTRODUCTION

Many liquid crystalline materials exhibit a rich variety of phases intermediate between normal isotropic liquids and crystalline solids. The different types of phase transitions between several of these mesophases have become increasingly important in testing general ideas about phase transitions.[1] The transition between the nematic (N) and the smectic-A (A) phase in particular has been investigated intensively both experimentally and theoretically. In spite of numerous efforts, the first- or second-order nature of this transition has been a matter of controversy until very recently and there is still no consensus about the universality class of the transition. As will be-

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come clear later, much of the difficulty of the interpretation of experimental data is probably due to the fact that near the AN transition, critical and tricritical behavior is mixed in different unknown proportions for different systems.

In two previous publications[2,3] we reported detailed calorimetric investigations near phase transitions in several pure compounds of the alkylcyanobiphenyl (nCB) homologous series. The measurements were carried out by means of an adiabatic scanning calorimeter, which allowed us to obtain simultaneously, high-resolution data for the heat capacity and the enthalpy (including possible latent heats at a phase transition). It was shown that within the experimental resolution, the AN transition in 8CB and 9CB is continuous. For 8CB as an upper limit a possible latent heat a value of 0.4 J/mol was obtained. For 9CB an upper limit of about 5 J/mol was derived from the data.[3] Both systems showed large pretransitional effects in the heat capacity C_p. The critical exponents associated with the C_p anomalies are, however, appreciably different: $\alpha = 0.31$ for 8CB ($T_{NI} - T_{AN} = 7.0$ K) and $\alpha = 0.50$ for 9CB ($T_{NI} - T_{AN} = 1.9$ K).

In order to investigate further the relation between the nature of the AN transition and the width of the nematic range, new calorimetric measurements have been carried out for several mixtures of nCB compounds. In 9CB + 10CB mixtures (with small N-ranges) the AN transition has a first-order character, with a latent heat which became vanishingly small on approaching pure 9CB, suggesting the presence of a tricritical point at that location. In 7CB + 8CB mixtures the heat capacity exponent α and the amplitude of the anomaly decrease with increasing width of the nematic range. The results for the 9CB + 10CB mixtures and for two 7CB + 8CB mixtures have been recently reported elsewhere.[4] In this paper we present new data on a series of mixtures of 8CB + 10CB. In this system mixtures with small N-ranges also have a first-order AN transition, but mixtures with sufficiently large N-range are clearly second-order. A comparison with the 9CB + 10CB mixtures will be made. Special emphasis will also be placed on the relation between the value of the exponent α for the continuous AN transitions and the width of the nematic range.

All the cyanobiphenyl liquid crystals used in these studies were obtained from BDH Chemicals Ltd (Poole, Dorset, U.K.). The same adiabatic scanning calorimeter was used for all the systems. The calorimeter and its possible modes of operation are described in detail elsewhere.[5] Typical sample sizes were between 5 and 10 g. The scanning rate for the temperature $\dot{T}$ was of the order of 0.05 K/h or less.

RESULTS AND DISCUSSION

In the phase diagram for 8CB + 10CB in Figure 1, the vertical dashed lines indicate the systems which have been measured. The mole fractions of eleven mixtures (labeled 1 to 11 in Figure 1), which were investigated are given in Table I. The mixtures 1 and 2 as well as pure 8CB itself[2] have continuous AN transitions. Mixture 3 is, within our actual experimental resolution, actually at the tricritical point, where the continuous AN transition line (solid line in Figure 1) changes into a first-order AN transition (dashed line in Figure 1). Mixtures 4 → 10 show a latent heat jump at T_{AN} in the enthalpy versus temperature curve. Mixture 11 did not have a nematic phase but had a direct smectic A to isotropic phase transition. The enthalpy curves near T_{AN} for the mixtures 3 → 10 are given in Figure 2. From these results, in particular for the largest 10CB mole fraction (X_{10}), it is clear that we are dealing with first-order transitions. The latent heats,

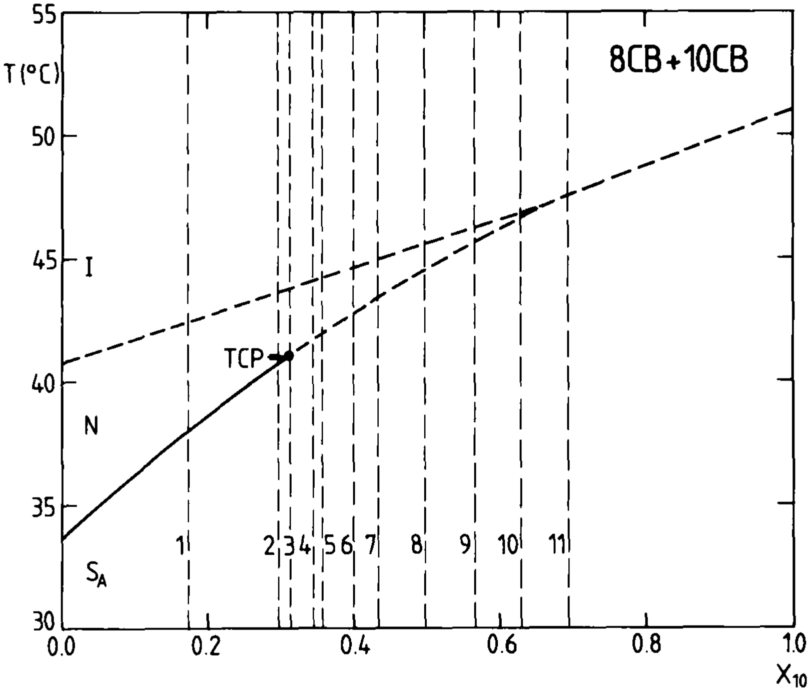

FIGURE 1 Phase diagram of 8CB + 10CB mixtures. Heavy solid and dashed lines are, respectively, second- and first-order transitions. TCP is the AN tricritical point. Vertical dashed lines indicate the measured mixtures. The mole fractions for these mixtures are given in Table I.

TABLE I

The composition of the different mixtures investigated. X_n is the mole fraction of nCB in a given mixture.

8CB + 10CB		9CB + 10CB	
No[a]	X_{10}	No[b]	X_{10}
1	0.1769	1	0.0000
2	0.2978	2	0.0494
3	0.3127	3	0.0814
4	0.3433	4	0.1116
5	0.3583	5	0.1348
6	0.4006	6	0.1735
7	0.4344	7	0.2535
8	0.4986	8	0.2914
9	0.5671	9	0.3348
10	0.6261		
11	0.6920		

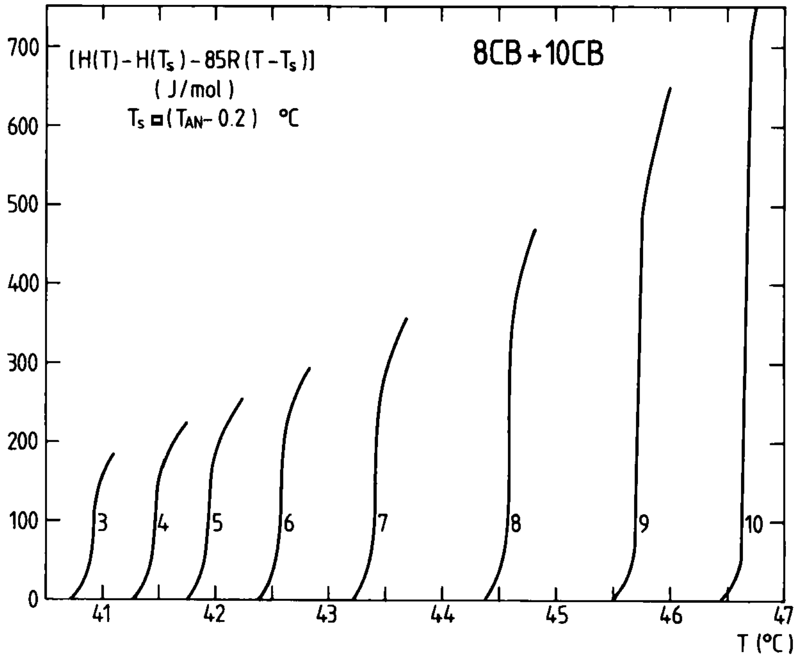

FIGURE 2 Enthalpy *vs* temperature near T_{AN} for the tricritical mixture (No 3) and seven mixtures of 8CB + 10CB with a first-order AN transition. A regular part $85R(T - T_s)$ is subtracted for display reasons (R is the gas constant).

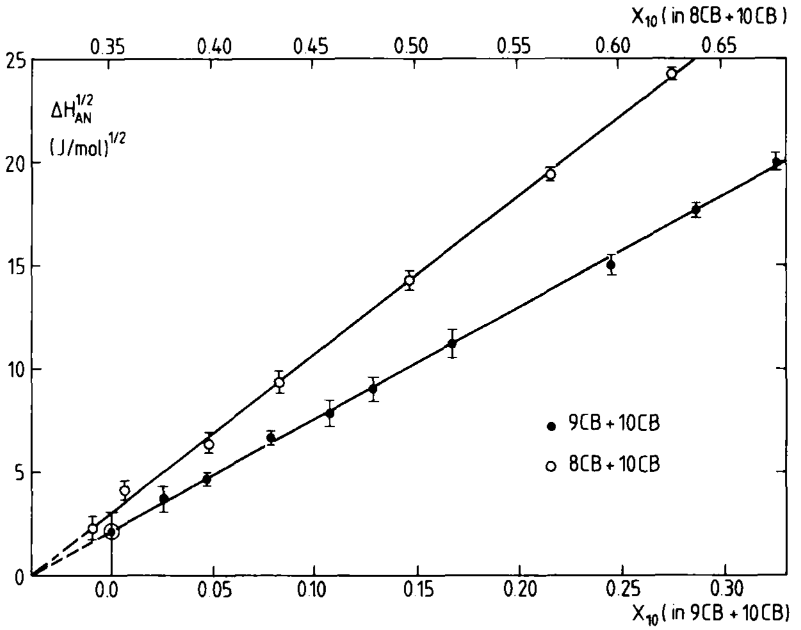

FIGURE 3 The simple relationship between the square root of the A → N latent heat ΔH_{AN} and the mole fraction of X_{10} in the mixtures of 9CB + 10CB and of 8CB + 10CB.

ΔH_{AN}, however, decrease drastically with X_{10} (or with increasing N-range; see Figure 1). By looking at higher order derivatives also one can extract reasonably accurate values for ΔH_{AN}. Full details on the derivation of ΔH_{AN} from H(T) will be given elsewhere.[6]

In Figure 3 the concentration dependence of ΔH_{AN} is illustrated. The square root of ΔH_{AN} is plotted as a function of X_{10} for the mixtures of 8CB + 10CB (open symbols) and also of 9CB + 10CB (solid symbols). It is apparent that for both types of mixtures (within the experimental accuracy) a linear relationship is obtained. The linear fits to the $\Delta H_{AN}^{1/2}$ data (the solid lines in Figure 3) give a simple way of extrapolating to the mole fraction X_{10} (TCP) of the tricritical point, where ΔH_{AN} becomes zero. From the 8CB + 10CB mixtures a value X_{10} (TCP) = 0.3135 was obtained. The mole fraction of the mixture 3 in Figures 1 and 2 was chosen very close to this value. From the extrapolation of the straight line through the $\Delta H_{AN}^{1/2}$ results for the mixtures of 9CB + 10CB a value X_{10} (TCP) = −0.0390 is obtained. This is, of course, a physically non-realizable mole fraction. It indicates that the AN transition in 9CB itself must still be very slightly first-order. In our results for 9CB, previously reported,[3] we had observed a very narrow 0.5 mK range where the enthalpy and especially the heat capacity data, showed a rounding-off effect. This could be interpreted[3] in terms of a narrow two-phase region corresponding to a very weakly first-order transition with a latent heat of about 5 J/mol. This interpretation seems to be consistent with the other data for 9CB + 10CB mixtures. This means that by changing temperature at atmospheric pressure, 9CB undergoes an AN transition, which has an extremely low latent heat and is consequently very nearly tricritical. We infer that a true TCP could occur in mixtures of 9CB with shorter homologues.

In 1970 and 1971 Kobayashi[7] and McMillan[8] predicted, on the basis of mean-field calculations, that the AN transition should be first-order unless $T_{AN}/T_{NI} < 0.87$. Above this value the transition is first-order and a tricritical point is thus predicted for $T_{AN}/T_{NI} = 0.87$. The same qualitative features are present in the de Gennes[9] model, where the order of the transition depends on the strength of the coupling between the nematic orientational order parameter and the order parameter for the one-dimensional layered structure of the A phase. Alben[10] has explicitly predicted that a He^3-H_e^4-like tricritical point may occur in binary liquid crystal mixtures for the smectic A to nematic transition.

In Figure 4 the latent heats ΔH_{AN} for 8CB + 10CB and for 9CB + 10CB are given as a function of the McMillan ratio T_{AN}/T_{NI}. Here we have plotted ΔH_{AN} itself and not its square root and because of the shape of the phase diagrams (see Figure 1 and Figure 1 in Ref. 4) the simple relationship with X_{10} is not observed anymore. We clearly see that for both sets of data, a different tricritical T_{AN}/T_{NI} ratio applies. For the 9CB + 10CB systems the extrapolated $(T_{AN}/T_{NI})_{TCP}$ value will, in view of the above discussion, fall a little below the 9CB ratio of 0.994. We estimate it now to be at 0.9935. For the 8CB + 10CB set of data $(T_{AN}/T_{NI})_{TCP}$ is lower than 0.992. On the basis of the T_{AN} and T_{NI} values for mixture 3 (in Figure 1) with $X_{10} = 0.3127$ we obtain $(T_{AN}/T_{NI})_{TCP} = 0.9909 \pm 0.0001$. Qualitatively one may state that the results are consistent with the McMillan and de Gennes phase diagram predictions. It is indeed the case that systems with very small N-ranges have first-order AN transitions and a change over into second-order occurs when the nematic range becomes sufficiently wide. The theoretically predicted TCP ratio, $T_{AN}/T_{NI} = 0.87$ is, however, much smaller than the experimentally observed value. Moreover, the experimentally observed TCP ratio for T_{AN}/T_{NI} is not universal, because it is different for 8CB + 10CB and for 9CB + 10CB. An even greater difference was found from X-

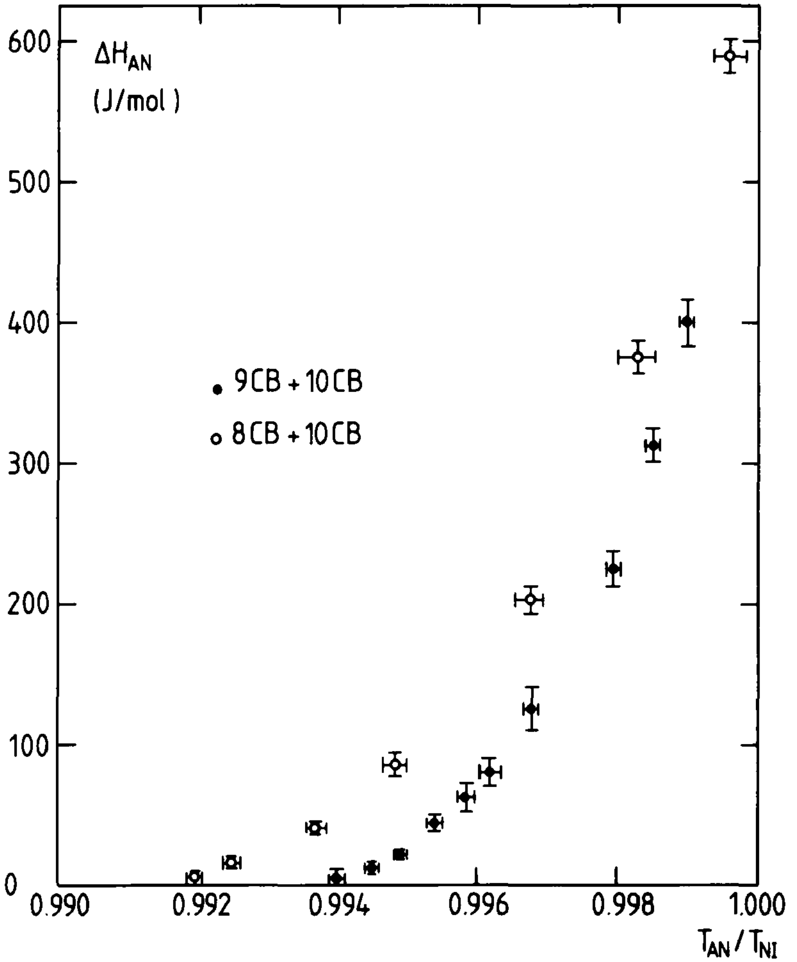

FIGURE 4 The A → N latent heat ΔH_{AN} as a function of T_{AN}/T_{NI} for 9CB + 10CB and the 8CB + 10CB mixtures.

ray[11] and ac-calorimetric[12] investigations in the 4-n-pentylphenylthiol-4′-n-alkyloxybenzoate ($\bar{n}$S5) homologous series, where a TCP was located close to $\overline{10}$S5, which has $T_{AN}/T_{NI} = 0.984$.

As far as the critical exponent α for the heat capacity anomaly is concerned, one would in general expect[13,14] a theoretical XY value[15] ≃ −0.02 along the continuous AN phase transition line and a tricritical value 1/2 at the TCP,[16] where the continuous AN phase transition line changes into a first-order line. From our measurements in

9CB + 10CB and 7CB + 8CB, reported in Ref. 4, and also from exponent α values for other systems[12,17] it has been observed that only for systems with very large nematic ranges (small T_{AN}/T_{NI} ratios) an XY value for α is obtained. For T_{AN}/T_{NI} values approaching $(T_{AN}/T_{NI})_{TCP}$ effective α's, between α_{XY} and α_{TCP}, depending on T_{AN}/T_{NI}, are obtained experimentally.

In Figure 5 the gradual increase, of the heat capacity anomaly on approaching $(T_{AN}/T_{NI})_{TCP}$, is illustrated. On the left side a 7CB + 8CB mixture m_a with a large N-range has an anomaly close to the XY behaviour, while the mixture m3 is a nearly tricritical mixture of 8CB + 10CB. It should also be noted that, in addition to drastic changes in the effective exponent values, the amplitudes decrease with decreasing T_{AN}/T_{NI}. From a preliminary analysis of our very recent 8CB + 10CB results we obtain a complete confirmation of the trend in α pointed out in Ref. 4. For mixture 1 and 2 of Figure 1, respectively, with $T_{AN}/T_{NI} = 0.9858 \pm 0.0001$ and $T_{AN}/T_{NI} = 0.9904 \pm 0.0001$, we have $\alpha = 0.36 \pm 0.02$ and $\alpha = 0.47 \pm 0.02$.

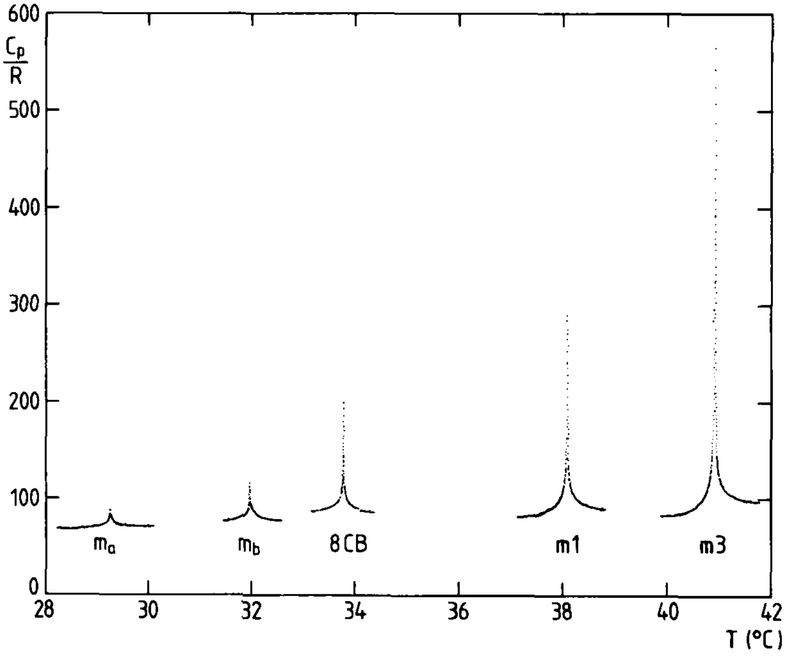

FIGURE 5 The reduced heat capacity per mol near continuous AN transitions in alkylcyanobiphenyl systems. m_1 and m_3 are the mixtures 1 and 3 of 8CB + 10CB in Figure 1 and Table I. m_a (indicated as m_{11} in Ref. 4) is a mixture of 7CB + 8CB with $x_8 = 0.6940$. m_b is also a 7CB + 8CB mixture with $x_8 = 0.8558$.

For the almost tricritical mixture 3, we obtain $\alpha = 0.50 \pm 0.02$. Full account of the analysis and fitting procedures will be presented elsewhere.[6] On the basis of the calorimetric results alone, one would be inclined to consider the T_{AN}/T_{NI} dependence of the α values as caused by crossover between XY critical and tricritical behaviour. There are, however, other experimental results which do not seem to be compatible with a simple crossover picture. The exponent values for susceptibility (γ) and correlation length (υ) for large nematic ranges are for example, not in agreement with the XY values. Values for γ and $\upsilon_{//}$ more than 10% too large are found.[17] This remains an important problem, which seems to persist[11] at the tricritical point near 9CB and $\overline{10}$S5.

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