Nematic–Smectic-*A* Tricritical Point in Alkylcyanobiphenyl Liquid Crystals

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From adiabatic-scanning calorimetric results it is demonstrated that in mixtures of 9CB and 10CB, two compounds of the alkylcyanobiphenyl (*n*CB) series, the nematic (*N*) to smectic-*A* (*A*) transition becomes first order for narrow *N* ranges. From the latent heats a tricritical point is located in the phase diagram. Measurements for 7CB + 8CB mixtures show that the specific-heat exponent α depends on the width of the *N* range for continuous *AN* transitions.

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In spite of numerous experimental and theoretical efforts, the transition between the nematic (*N*) and the smectic-*A* (*A*) phases in liquid crystals remains a major problem in the field of phase transitions and critical phenomena. The first- or second-order nature of the transitions has been a matter of controversy, and there is not yet a theoretical or experimental consensus about the universality class of the transitions.

In the early 1970's Kobayashi[1] and McMillan[2] predicted on the basis of mean-field calculations for a molecular model that the transitions should be first order unless $T_{AN}/T_{NI} < 0.87$, with T_{AN} the $A \rightarrow N$ transition temperature and T_{NI} the nematic (*N*) to isotropic (*I*) transition temperature. For $T_{AN}/T_{NI} = 0.87$ a tricritical point (TCP) is thus predicted. The same qualitative features are present in the de Gennes[3] 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. Lubensky[4] recently summarized the predictions of the de Gennes model concerning the universality class and the critical exponents for the second-order *AN* transitions. According to this account there seem to be two asymptotic possibilities: an isotropic critical point described by an inverted *XY* model[5-7] or an anisotropic critical point. For the isotropic case the critical exponents for the heat capacity, the susceptibility, and the correlation length are $\alpha \simeq -0.02$, $\gamma \simeq 1.32$, and $\nu_{\parallel} = \nu_{\perp} \simeq 0.67$, respectively. The exponents for the anisotropic case are not yet established, but it is predicted that $\nu_{\parallel} = 2\nu_{\perp}$ in this class.[8] In comparing theory with experiments a complication arises because some theories[6,7] predict the *XY* behavior for an unphysical order parameter. Transformation to the physical frame should not affect the exponents for thermodynamic quantities like the heat capacity or the nematic elastic constants. Correlation lengths obtained from x rays may, however, show a different behavior with asymptotically different $\nu_{\parallel}$ and $\nu_{\perp}$ values.[6,7]

In early calorimetric measurements the sharp enthalpy increase at the transition was interpreted as a proof of the first-order character. Later on high-resolution x-ray and light scattering and ac calorimetry gave for nearly all cases indirect indications of the second-order nature of the transition: There was no two-phase region detected and the critical temperature occurring in the power-law fits of the data above and below the transition did coincide.[9,10] This was also the case for the high-resolution calorimetric work[9] done by ac calorimetry, which does not allow the measurement of latent heats. With adiabatic-scanning calorimetry it is possible, however, to obtain directly the temperature dependence of the enthalpy including a possible latent heat at a phase transition. Recently we reported on high-resolution measurements by this method for liquid crystals of the 4-cyano-4′-*n*-alkylbiphenyl (*n*CB) series.[10,11] Within experimental resolution the *AN* transition for 8CB was continuous.[10] An upper limit for the latent heat was 1.4×10^{-3} J/g. Also for 9CB we found no experimental evidence for a first-order transition.[11] Combined with the results on other systems,[9] this suggests continuous *AN* transitions for all T_{AN}/T_{NI} values < 0.99, which is appreciably larger than the value of 0.87 from the mean-field theory of McMillan.[2] The experimental values for the critical exponent α of the heat capacity near T_{AN} deviate substantially from the *XY* value for most systems.[9,10] Usually a much larger value is obtained. Only for 4-*n*-pentylphenylthiol-4′-*n*-octyloxybenzoate ($\overline{8}$S5) and 4-*n*-butyloxybenzylidene-4′-*n*-heptylaniline ($\underset{\sim}{4}$O.7) have α's consistent with α_{XY} been reported.[9,12] Both systems have large *N* ranges with $T_{AN}/T_{NI} \simeq 0.93$. On the other hand for 4-*n*-pentylphenylthiol-4′-*n*-decyloxybenzoate ($\overline{10}$S5) ($T_{AN}/T_{NI} = 0.984$) and 9CB ($T_{AN}/T_{NI} = 0.994$), α's close to 0.5 have been reported.[11,12] From a survey[9,10] one can observe an increasing α with increasing T_{AN}/T_{NI}. α values for small T_{AN}/T_{NI} are close to the tricritical value of 0.5. The fact that for our 9CB data[11] an α of 0.5 was obtained, but also that the transition was still continuous, indicated that it must be very close to a TCP. It also suggested that in order to see a first-order *AN* transition, systems with very narrow nematic ranges with $T_{AN}/T_{NI} > 0.994$, the value for 9CB, should be investigated.

In this paper we present new results demonstrating that in mixtures of 9CB and 10CB, with very narrow *N* ranges, the *AN* transition is indeed first order. The associated latent heats have been measured, and the location of the TCP in the phase diagram is determined. Measurements in mixtures of 7CB+8CB, with large *N* ranges, further substantiate the T_{AN}/T_{NI} dependence of the α value for the second-order *AN* transitions.

The measurements have been carried out with the same adiabatic-scanning calorimeter as described earlier.[10,11] With a constant heating power *P* applied to the measuring cell the experimental curve of temperature versus time, $T(t)$, directly results in the enthalpy of the sample[10]:

$$H(T) = H(T_s) - P(t - t_s), \tag{1}$$

where the index *s* refers to the starting conditions of the run. The heat capacity $C_p(T)$ is given by $C_p = P/\dot{T}$. By numerical differentiation $\dot{T}$ (typically 10 mK/h) can be obtained from the $T(t)$ data. If a first-order transition occurs at T_1 between T_s and T, the temperature will be essentially constant for a time interval $\Delta t = \Delta H(T_1)/P$ with ΔH the latent heat.

In the phase diagram of Fig. 1 the vertical dashed lines indicate the systems which have been measured. The results for the pure 8CB, 9CB, and 10CB have already been published.[10,11] Nine mixtures (labeled 1 to 9 in the inset of Fig. 1) have been investigated for 9CB+10CB. The enthalpy curves near T_{AN} for the nine mixtures and also for 9CB are given in Fig. 2. From these results, in particular for the largest 10CB mole fractions ($x_{10\mathrm{CB}}$), it is clear that we have to do with first-order transitions. ΔH, however, decreases drastically with $x_{10\mathrm{CB}}$ (or with increasing *N* range; see Fig. 1). In Fig. 3 the ΔH values are displayed as a function of T_{AN}/T_{NI}. Full details on the derivation of ΔH from $H(T)$ will be given elsewhere.[13] From an extrapolation to zero ΔH in Fig. 3 we find that the transition point from first to second order, which can be identified as a tricritical point, is located very close (within ± 0.01 in $x_{10\mathrm{CB}}$) to pure 9CB with $T_{AN}/T_{NI} = 0.994$. For *N* ranges larger than for 9CB the *AN* curve is second order, as we did observe[10] for 8CB and confirmed[13] for the two mixtures 10 and 11 of 7CB+8CB (see Fig. 1).

As already pointed out the exponents α and α' in the power law[14]

$$C_p = A\epsilon^{-\alpha} + B, \tag{2}$$

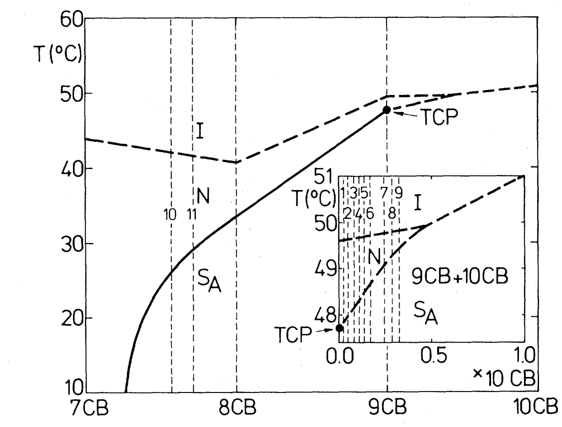

FIG. 1. Phase diagram of *n*CB mixtures. Vertical dashed lines indicate the measured systems. Heavy solid and dashed lines are, respectively, second- and first-order transitions. TCP is the tricritical point.

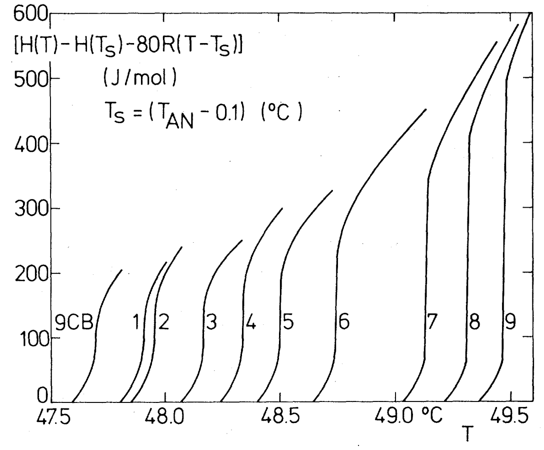

FIG. 2. Enthalpy vs temperature near T_{AN} for 9CB and the nine mixtures of 9CB + 10CB. A regular part $80R(T - T_s)$ is subtracted for display reasons (*R* is the gas constant).

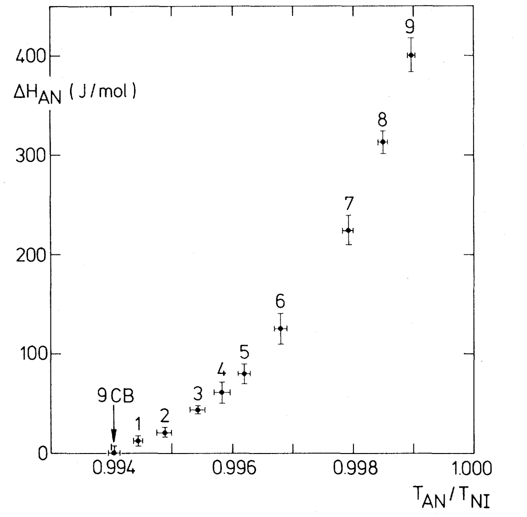

FIG. 3. The $A \rightarrow N$ latent heat ΔH_{AN} as a function of T_{AN}/T_{NI} for the 9CB + 10CB mixtures.

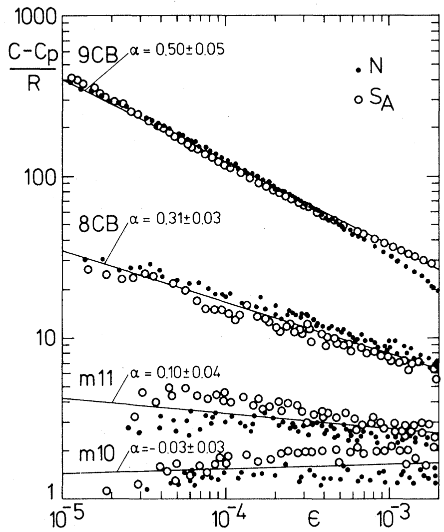

FIG. 4. Doubly logarithmic plot for the quantity $C - C_p$ (in units of R) of Eq. (4) vs $|\epsilon|$ for systems with continuous AN transitions. m10 and m11 are the mixtures 10 and 11 of 7CB + 8CB indicated in Fig. 1.

with $\epsilon \equiv (T - T_{AN})/T_{AN}$ for $T > T_{AN}$, and a similar one with primed symbols for $T < T_{AN}$, seem to depend on T_{AN}/T_{NI} along the second-order line.[9,10] In order to investigate this further we have measured two 7CB + 8CB mixtures with large N ranges. From our $H(T)$ results α's can be extracted in different ways. C_p can be obtained by numerical differentiation and fitted with Eq. (2). Also an enthalpy expression, derived from Eq. (2), can be used to fit the $H(T)$ data directly.[10] Both procedures require nonlinear least-squares fitting. However, α can also be obtained in a quite simple way by introducing the following quantity:

$$C(T) \equiv \frac{H(T) - H(T_{AN})}{T - T_{AN}} = \frac{P(t - t_{AN})}{T - T_{AN}}. \tag{3}$$

It is easily verified[10] that C diverges with the same α as C_p, but with an amplitude modified by a factor of $(1-\alpha)^{-1}$. It then also follows that

$$C - C_p = \alpha A \epsilon^{-\alpha}(1-\alpha)^{-1}. \tag{4}$$

Thus in a double logarithmic plot a linear relationship, with slope $-\alpha$, is found between $C - C_p$ and ϵ. In Fig. 4 we have displayed in this way $C - C_p$ vs ϵ for the two 7CB + 8CB mixtures, and for comparison purposes also our previous[10,11] results for 8CB and 9CB. We clearly observe a decreasing α with increasing N range (see also Fig. 1). $\alpha \simeq -0.03 \pm 0.03$ for mixture 10 is in good agreement with α_{XY}.

These calorimetric data for alkylcyanobiphenyls give evidence for a first-order AN transition line going over, at a tricritical point, into a second-order AN line. Along this second-order line the critical exponent α, describing the heat-capacity anomaly, is observed to change drastically with T_{AN}/T_{NI} from the tricritical value $\alpha = 0.5$ for 9CB (with a narrow N range of 1.9°C) to an α consistent with α_{XY} for our mixture 10 (with an N range of 15 °C) of 7CB + 8CB. 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 tricritical and XY critical behavior. This could, in principle at least, be verified by fitting all the data by a crossover scaling form with two scaling fields related to the temperature difference from the tricritical temperature and to another field h connected with differences in material properties between the tricritical system (supposedly 9CB) and the other ones. Identification of h with differences in effective chain length, in the concentration, or in the T_{AN}/T_{NI} ratio did not lead to a unified picture for all the available data. It is, however, not excluded that another choice for h might do a better job. Nevertheless there are other results which do not seem to fit in a simple crossover picture. The numerical values for the exponents γ, $\nu_\parallel$, and $\nu_\perp$ for large nematic ranges are not in agreement with the XY values. In particular γ and $\nu_\parallel$ values more than 10% too large are found.[9] As pointed out by Ocko *et al.*,[15] this discrepancy between theory and experiment persists at the tricritical point in 9CB and $\overline{10}$S5.

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