Nematic–Smectic-A–Smectic-C Multicritical Point in a Single-Component System

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The first observation of the nematic–smectic-A–smectic-C multicritical point in a single-component liquid-crystal system is reported. High-resolution pressure-temperature data are presented, which support the view that the phase diagram is universal near the nematic–smectic-A–smectic-C point.

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The nematic–smectic-A–smectic-C multicritical point (NAC point) was discovered by Johnson *et al.*[1] and independently by Sigaud, Hardouin, and Achard[2] in binary liquid-crystal mixtures. This was followed by high-resolution x-ray,[3,4] calorimetry,[5,6] and light-scattering[7] studies which permitted explicit comparison with the predictions of theoretical models proposed earlier.[8–10] Brisbin *et al.*[11] have obtained high-resolution temperature-concentration (T-X) phase diagrams of four binary systems exhibiting the NAC point. They find that despite gross differences in global features, the topology of the phase diagram near the NAC point is universal. Since all these studies have been on binary systems, the need arises to observe the NAC point in a single-component liquid-crystal system in the pressure-temperature (P-T) plane to test the concept of universality near such a point, since it is unlikely that density and concentration fluctuations would produce the same topological distortions of the phase diagram. Although there have been some attempts in this direction,[12,13] the NAC point in a single-component system has so far remained elusive.

We present in this Letter results of precise high-pressure optical studies on 4-*n*-heptacylphenyl-4′-(4″-cyanobenzoyloxybenzoate), hereafter abbreviated as 7APCBB, which have led to the first observation of the NAC point in a single-component liquid-crystal system. We shall show from our high-resolution P-T diagram that the topology is indeed universal in the vicinity of the NAC point. We shall comment on another kind of multicritical point observed by us earlier in a single-component system and attempt to explain why the topology of this diagram was apparently different.

An optical high-pressure cell was used for the experiments.[14] The liquid-crystalline sample was sandwiched between two optically polished sapphire cylinders which are enclosed in a fluran tube so that the sample is isolated from the pressure-transmitting fluid (plexol). The phase transitions were detected by monitoring the intensity of laser light transmitted by the sample. The experiments were done along isobars, i.e., the transmitted temperature at any pressure was determined by scanning the temperature in the heating mode (rate of heating, 0.25 °C/min). The precision in the determination of the transition temperature is 20 mK or better. In the preliminary experiments conducted with the purpose of locating the NAC point in the P-T plane, the accuracy of the pressure measurement was ± 0.7 bar. For obtaining very precise data in the vicinity of the NAC point, pressure had to be continuously monitored electronically during the heating run. In these high-resolution experiments pressure was measured to a precision of ± 0.1 bar and was constant to within the same limits during any transition.

The complete P-T diagram of 7APCBB showing the preliminary data for the NA, AC, and NC transitions in the pressure range 1–600 bars is given in Fig. 1. Pronounced singularities are seen for all three transition lines close to the NAC point. The high-resolution data in the vicinity of the NAC point are shown in Fig. 2 on an enlarged scale. These data have been obtained from six independent sets of measurements, a fresh sample being loaded in the pressure cell each time. After every set of measurements the sample was taken out of the cell and its AN transition temperature at atmospheric pressure determined. If this did not agree exactly with the AN transition temperature of the fresh sample the data were rejected. The possible influence of chemical degradation of the sample was thus precluded. Figure 3 gives the *universal plot* of Johnson[15] wherein the phase diagrams of four binary systems are shown together after suitable normalization of the data. The striking similarity between Figs. 2 and 3 is evident.

We shall now examine quantitatively the phase boundaries close to the NAC point. We have fitted our data for the NA, NC, and AC phase boundaries individually by the following expressions which are

similar to those used by Brisbin *et al.*[11]:

$$T_{NA}-T_{NAC}=A_{NA}(P_{NAC}-P_{NA})^{\eta_{NA}}+B(P_{NAC}-P_{NA}), \quad (1a)$$

$$T_{NC}-T_{NAC}=A_{NC}(P_{NC}-P_{NAC})^{\eta_{NC}}+B(P_{NC}-P_{NAC}), \quad (1b)$$

$$T_{AC}-T_{NAC}=A_{AC}(P_{NAC}-P_{AC})^{\eta_{AC}}+B(P_{NAC}-P_{AC}). \quad (1c)$$

Following Brisbin *et al.*[11] we have carried out the computations with the universality constraint $\eta_{NA}=\eta_{NC}$, η itself being a free parameter. The results of our computations carried out with use of the high-resolution data represented in Fig. 2 are given in Table I. Interestingly, our values of η (see Table I) are, within statistical uncertainties, the *same* as those evaluated by Brisbin *et al.* (see legend of Fig. 3) although the amplitude ratio A_{NA}/A_{NC} comes out to be -3.02 ± 0.20 in our case, as compared to -5.96 ± 1.3 of Brisbin *et al.* The remarkable fact that the η values obtained by us from the P-T diagram of a single-component system agree so closely with those evaluated from the T-X diagrams of four binary mixtures is in our opinion strong evidence to support the idea that *the NAC point exhibits universal behavior.* A noteworthy feature is that the scaling axes are the *same* as the experimental axes (P and T in our case, X and T in the case of Brisbin *et al.*), rather than linear combinations of these variables. The simplicity of these results may perhaps be associated with the absence of coupling to density and concentration fluctuations.

It is relevant to recall here that we had observed earlier[16] another multicritical point, viz. the reentrant-nematic–smectic-C–smectic-A (RN-C-A) point. The topology of the P-T diagram in this case was different from the universal topology of the NAC diagram, the singularities being conspicuously absent near the RN-C-A point.[17] The RN-C transition had a zero or immeasurably small latent heat at atmospheric pressure as well as at high pressures right up to the RN-C-A point. This could be due to the RN-C transition being far away in the temperature scale (nearly 180 °C) from the nematic-isotropic transition. This would make the Brazovskii fluctuations[18] (which are believed to induce the NC transition to be first order[19]) to be extremely weak near the RN-C-A point which would explain the absence of any measurable latent heat at the RN-C transition. It would have the further effect that the bare correlation length would be very large. This in turn implies that the critical region may be too small to be experimentally approachable and could therefore account for the absence of pro-

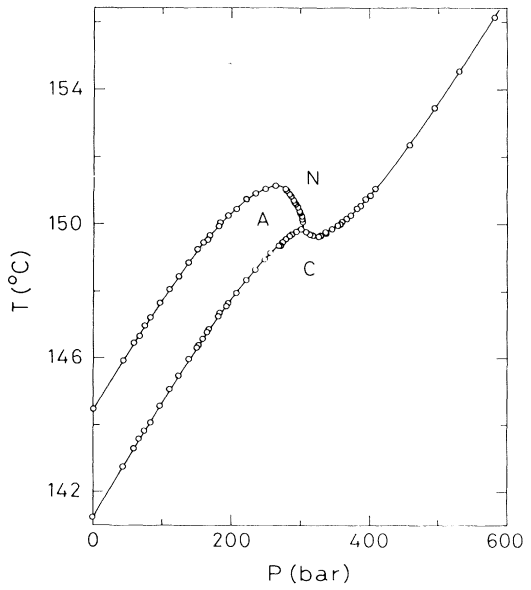

FIG. 1. Pressure-temperature (P-T) diagram of 4-*n*-heptacylphenyl-4′-(4″-cyanobenzoyloxybenzoate) (7APCBB) showing the nematic–smectic-A (NA), smectic-A–smectic-C (AC), and nematic–smectic-C (NC) transitions up to 600 bars. The NAC multicritical point occurs ~304 bars, 149.9 °C. The solid lines are guides to the eye.

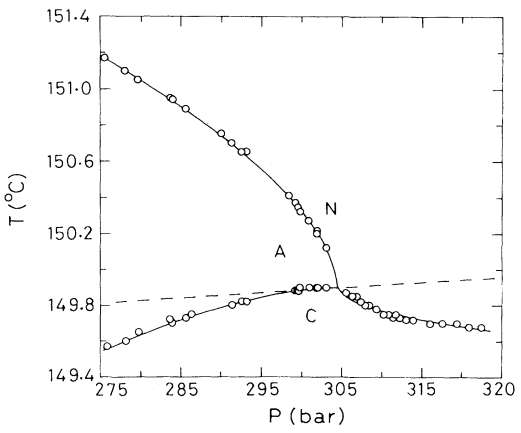

FIG. 2. High resolution P-T diagram in the vicinity of the NAC multicritical point in 7APCBB. The solid lines are computer fits of our data (see Table I) with Eqs. (1a)–(1c) representing the NA, NC, and AC phase boundaries, respectively (see text). The dashed line represents the line corresponding to the best-fit B term.

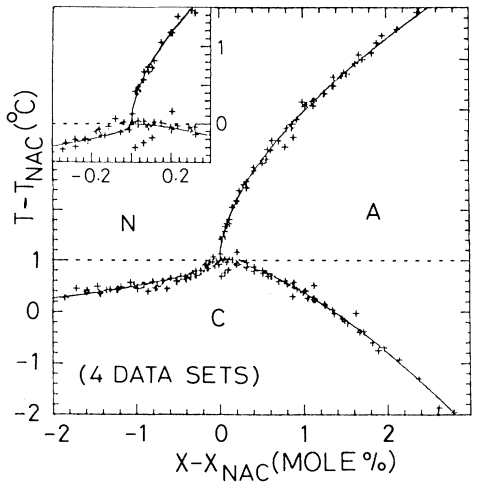

FIG. 3. The universal temperature-concentration plot of Johnson (Ref. 15) showing the data for four binary liquid-crystal systems. The best-fit η values (Ref. 11) are $\eta_{NA} = \eta_{NC} = 0.573 \pm 0.02$ and $\eta_{AC} = 1.52 \pm 0.02$.

nounced singularities near the RN-C-A point.

It must also be remarked that the early theoretical model of Chen and Lubensky[8] predicted the NAC point to be a type of Lifshitz point. The first high-resolution x-ray[3] and ac calorimetry[5] experiments yielded results which appeared to be in explicit disagreement with the Lifshitz-point model. More recent measurements of the mass density fluctuations associated with the NC transition have shown[4] that for concentrations away from the NAC point, the critical scattering at high temperature is characteristic of smectic-A fluctuations while at low temperatures there is a crossover into a regime with pretransitional smectic-C fluctuations as predicted by the Chen and Lubensky model. Nevertheless important discrepancies remain with the predictions of the model for concentrations in the immediate vicinity of the NAC point. There has also been an attempt[11] to compare the results of the NAC point with the exactly solvable magnetic Lifshitz-point model.[20] However, the relevance of such comparisons is unknown. Moreover, the theory of the liquid-crystal Lifshitz point is further complicated by the lack of long-range order in the smectic-A and smectic-C phases.[21] More recently Grinstein and Toner[22] have, by the dislocation-loop approach, applied the renormalization-group technique to the theory of the multicritical point. Although these calculations appear to represent the best theoretical treatment of the NAC problem, they do not yet bring theory and experiment into agreement—the biaxial nematic phase which is predicted by the theory to occur near the multicritical point is yet to be observed experimentally. Clearly, further studies are required for a better understanding of the NAC multicritical point.

TABLE I. Best-fit parameters and values of χ^2 for individual fits of our high-resolution data for the NA, NC, and AC phase boundaries with Eqs. (1a)–(1c) respectively. (See text for a detailed discussion.)

B	0.003 ± 0.001
T_{NAC}	149.9 ± 0.02 °C
P_{NAC}	304.5 ± 0.1 bars
$\eta_{NA} = \eta_{NC}$	0.575 ± 0.02
η_{AC}	1.523 ± 0.02
A_{NA}	0.1731 ± 0.002
A_{NC}	-0.0574 ± 0.003
A_{AC}	-0.0025 ± 0.0004
χ^2_{NA}	1.056
χ^2_{NC}	0.969
χ^2_{AC}	0.911

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