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Phase diagram exhibiting a smectic-*A* –smectic-*C* –smectic-*F* meeting point

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We report an observation of a smectic-*A*-smectic-*C*-smectic-*F* (*A*-*C*-*F*) meeting point in a binary liquid-crystalline system. Detailed high-precision x-ray measurements enabled us to characterize the meeting point as a *triple point*, a point at which the three phases coexist. A direct consequence of this result is the existence of a *tricritical point* (TCP) on the *A*-*C* boundary. Contrary to the known results, the TCP appears despite a large temperature range for the *A* phase and the occurrence of a nematic phase at a higher temperature. Bearing in mind that *F* is a tilted hexatic phase, it is suggested that a possible reason for this behavior is the molecular-tilt field arising from the coupling between the tilt and the bond-orientational-order parameters.

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Smectic-*A* (*A*) and smectic-*C* (*C*) liquid crystals are characterized as orientationally ordered fluids with a one-dimensional mass-density wave. In the former the wave vector of this wave is along the director, while in the latter it is tilted. Experimentally, the *A*-*C* transition is generally found to be second order. As the transition is governed by a two-component order parameter it was proposed initially that the transition might exhibit heliumlike critical behavior [1]. However, subsequent studies [2–7] showed that, owing to a large bare correlation length [8], the transition is almost always mean-field-like with a relatively large sixth-order term in the Landau free-energy expansion. Based on heat-capacity results Lien and Huang [9] postulated that this transition can be driven in a first-order manner by fluctuations seen as a consequence of the nearby isotropic-to-*A* phase transition. Recent experiments [10] have shown that the temperature range of the *A* phase has a pronounced effect on the order of the *A*-*C* phase transition.

Extension of the two-dimensional melting theory to liquid crystals led to the prediction [11] and subsequent experimental observation [12] of bulk phases of matter referred to as *hexatic* phases which exhibit long-range bond orientational order (BOO) as in a solid but a short-range positional order like in a fluid. The tilted versions of this phase, viz. smectic *F* (*F*) and smectic *I* (*I*) are described by two order parameters, namely, sixfold-BOO and the molecular-tilt order parameter. Studies on these have been made all the more interesting since in the *C* phase the existence of finite molecular tilt gives rise to an induced BOO [13] although of a very small amplitude. Thus both *C* and *F* phases have the same symmetry. Consequently *C* phase transforms into *F* phase either through a first-order transition or evolves continuously without a transition. There are many theoretical studies [13,14] to map out different phase diagrams involving hexatic phases. However, no phase diagram with *A*, *C*, and the tilted hexatic phases has been studied so far. In this Rapid Communication we present phase diagram and x-ray diffraction studies on a binary liquid-crystal system of terephthal-bis-butylaniline (TBBA) and *n*-(4-*n*-nonyloxy benzylidene)-4-*n*-butylaniline (9O.4) which shows an *A*-*C*-*F* meeting point. High-precision layer-spacing measurements performed on either side of the meeting point enabled us to characterize it as a triple point, at which all the three phases coexist. An interesting offshoot of these studies is the observation of a tricritical point on the *A*-*C* boundary (and the concomitant first-order-transition line). A notable feature is that for all the mixtures exhibiting the *A*-*C* transition, the *A* phase has a relatively large temperature range and in addition is followed by a nematic phase. This is puzzling since the *A*-*C* transition is expected [10] to become first order, in the absence of a strong lateral dipole moment of the molecule, only when the temperature range of the *A* phase is quite small.

The partial temperature-concentration (*T*-*X*) phase diagram, obtained by optical microscopy and x-ray diffraction studies, is shown in Fig. 1. It can be seen that for $X < 0.28$ (where X is the weight fraction of 9O.4 in TBBA) *C* phase goes to smectic-*G* (*G*) phase directly and for $X > 0.28$ the *F* phase intervenes between the *C* and *G* phases and with increasing X the range of the *F* phase grows at the expense of the *C* phase. Finally, for $X > 0.585$ the *C* phase ceases to exist resulting in an *A*-*C*-*F* meeting point.

The x-ray experiments have been conducted on aligned samples obtained by slowly cooling the sample from the nematic phase in the presence of a 2.4-T magnetic field. The setup is essentially identical to the one described earlier [15]. The precision in the determination of the wave vector is 2×10^{-4} Å^{-1} while the resolution in the equatorial direction is 1×10^{-3} Å^{-1} half-width at half maximum. The temperature was maintained to a constancy of better than 10 mK during each measurement. The temperature variation of the layer spacing for $X = 0.45$ in the neighborhood of the *A*-*C* transition is shown in Fig. 2. The most striking feature of this diagram is the existence of the two-phase coexistence region wherein the modulations corresponding to both the phases are present clearly signifying the first-order *A*-*C* transition. This feature is exactly as expected and indeed observed earlier for a first order *A*-*C* transition [10]. Figure 3 shows the tilt angle (Φ) variation for different concentrations in the temperature range very close to *A*-*C* transition. [Φ was evaluated

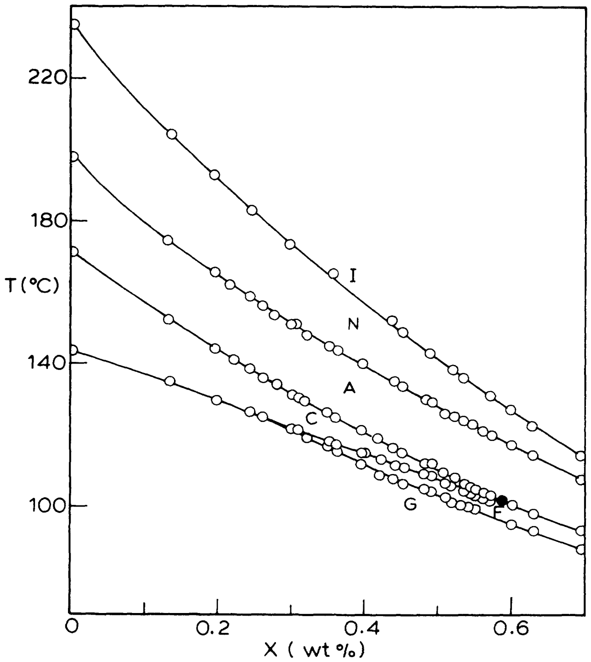

FIG. 1. Partial temperature-concentration phase diagram for varying weight fraction (X) of n-(4-n-nonyloxy benzylidene)-4-n-butylaniline (9O.4) in terephthal-bis-butylaniline (TBBA). The solid lines are guides to the eye. The A-C-F point is denoted by the solid circle.

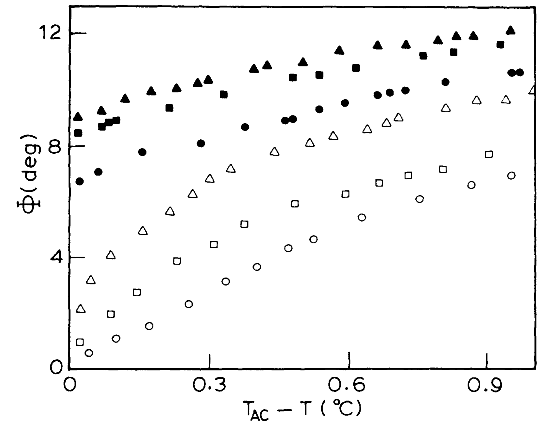

FIG. 3. Smectic-C tilt-angle variation vs the reduced temperature for $X=0.54$ (▲), 0.51 (■), 0.45 (●), 0.4 (△), 0.36 (□), and 0.32 (○).

by using the expression $\Phi=\cos^{-1}(d_c/d_A)$ where d_c and d_A being the layer spacing corresponding to the C and A phases, respectively.] It is observed that for $X \geq 0.45$, the tilt angle jumps abruptly to zero indicating a first-order transition while for $X \leq 0.40$ it goes continuously to zero as for a second-order transition. Evidently there is a tricritical point in the concentration range $0.4 \leq X \leq 0.45$.

The temperature variation of layer spacing near the C-F transition is shown in Fig. 4. The abrupt jump in the layer spacing and the presence of the two-phase region unambiguously show that this transition is first order for all the concentrations studied. The inset shows the jump in layer spacing across C-F transition for four different mixtures. The jump in the layer spacing is observed to increase with the increase in the temperature range of the F phase. It may be noted that a similar feature [16] was observed for the transition between C and I phases. Beyond the triple point the A phase directly goes to the F phase. The temperature variation of the layer spacing across the A-F transition for $X=0.6$, a concentration which lies very close to the A-C-F meeting point is shown in Fig. 5. Clearly, the transition is first order in nature.

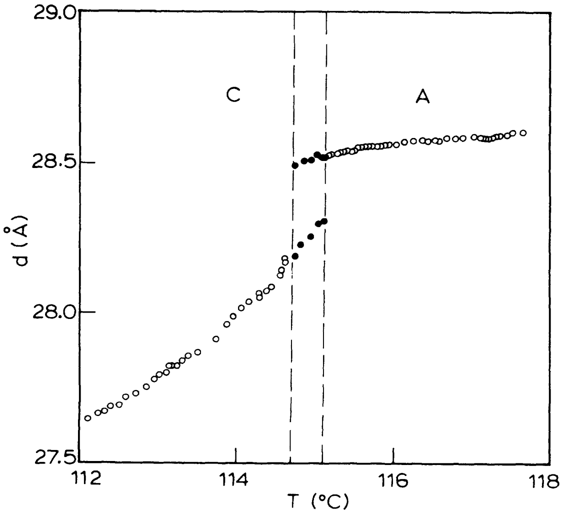

FIG. 2. Temperature variation of the smectic-layer spacing (d) in the vicinity of the A-C transition for $X=0.45$. The vertical dashed lines indicate the two-phase region where the data are represented by the solid circles.

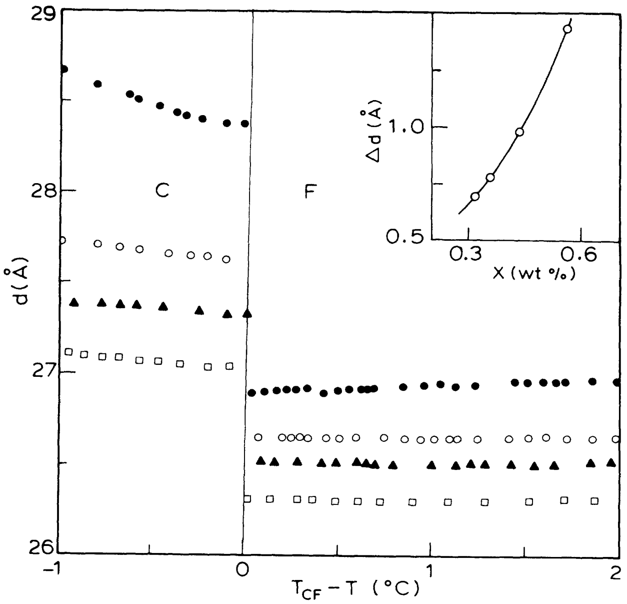

FIG. 4. Variation of the smectic-layer spacing (d) as a function of the reduced temperature in the vicinity of the C-F transition for $x=0.56$ (●), 0.44 (○), 0.36 (▲), and 0.32 (□). For the sake of clarity, the data in the two-phase region corresponding to the C phase are not shown. The jump in the layer spacing across the C-F transition for these mixtures is shown in the inset.

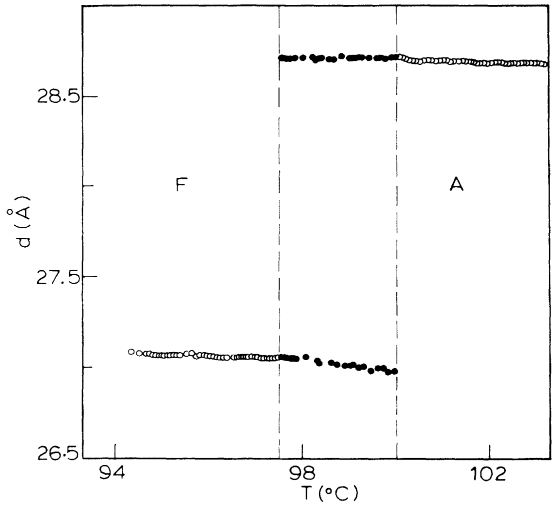

FIG. 5. Temperature variation of the smectic-layer spacing (d) in the vicinity of the A-F transition for $X = 0.60$. The solid circles stand for the data in the two-phase region which is marked by the vertical dashed lines.

These results lead us to infer that A-C-F meeting point is a meeting point of three first-order phase boundaries and hence is a triple point. To our knowledge this kind of a phase diagram has not been envisaged by theory so far. Furthermore, as mentioned earlier, in the vicinity of the triple-point concentration, the A-C transition changes from second order to first order even though the A-phase range is quite large. This is contrary to the known experimental results that the A-C transition becomes a first-order one only when the strength of the transverse dipole moment of the constituent molecules is large [17] and/or the temperature range [10] of the A phase is very small. But in the present system neither of these two conditions is met and still the transition becomes a first-order one. One possible cause for this behavior is the molecular-tilt arising due to the coupling between the BOO and the molecular-tilt order parameter. Such a possibility still remains to be investigated theoretically.

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