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New alternative for the smectic-A_1–reentrant nematic–smectic-A_d bicritical point

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A high-resolution temperature-concentration diagram and detailed differential scanning calorimetry data near an expected smectic-A_1–reentrant nematic–smectic-A_d bicritical point in a binary liquid-crystal system are presented. These results show that the bicritical point has split into a critical end point and a tricritical point, a situation which has not been predicted by any of the theories so far.

Smectic-A polymorphism has been successfully explained in terms of a phenomenological model.[1-4] Recently this model has been used in the framework of mean-field theory to evaluate different types of phase diagrams.[5] One of the predictions of the theory is the occurrence of a bicritical point where the second-order nematic–smectic-A_1 (N-A_1) and nematic–smectic-A_d (N-A_d) phase boundaries meet a first-order smectic-A_d–smectic-A_1 (A_d-A_1) line. However, when the effect of fluctuations are considered in the theory, the existence of such a bicritical point becomes questionable. It has been argued[5] that since both A_d and A_1 phases have the same symmetry, the N-A_d and N-A_1 transitions should both belong to the same universality class, i.e., the inverted xy universality class.[6] Renormalization-group calculations show[7] that under such a circumstance the resulting multicritical point should be a tetracritical point and not a bicritical point. It has also been predicted[8] that an offshoot of this situation would be an incommensurate A phase with both A_d- and A_1-like modulations. On the experimental side the A_1-$N_{\rm re}$-A_d point has been observed in the temperature-concentration (T-X) diagram of binary liquid-critical systems[9,10] and it has been pointed out[4] that the shape of the phase diagram near this point is similar to the typical topology of a magnetic bicritical point.[11,12] (Here $N_{\rm re}$ refers to the reentrant-nematic phase.) However, a high-resolution study of the topology of the phase diagram near the A_1-$N_{\rm re}$-A_d point has not been carried out so far. Since it is well known from the studies on the nematic–smectic-A–smectic-C (NAC) multicritical point[13-15] that the true topology of the phase diagram can be brought out only by the data in the immediate vicinity of the NAC point, the need arises to map out accurately the phase boundaries close to the A_1-$N_{\rm re}$-A_d point.

In this Rapid Communication we present the high-resolution T-X diagram for a binary system exhibiting the A_1-$N_{\rm re}$-A_d point which clearly shows that the topology of the phase diagram does not conform to a typical bicritical topology. We also present detailed differential scanning calorimetry (DSC) studies on the A_1-$N_{\rm re}$ and $N_{\rm re}$-A_d transitions which show that the bicritical point has split into a critical end point and a tricritical point. This novel alternative for a bicritical point has not been suggested so far by any of the existing theories on liquid crystals.

The complete phase diagram for the binary system of 4-n-octyloxyphenyl-4′-(4″-nitrobenzolyloxy) benzoate or DB.$\bar{8}$.NO$_2$ and 4-n-decyloxyphenyl-4′ (4″-nitrobenzoyloxy) benzoate[16] or DB.$\overline{10}$.NO$_2$ exhibiting A_1-$N_{\rm re}$-A_d point is given in Fig. 1. The high-resolution data obtained with a precision of ±0.05 mol% in X and ±20 mK in T, in the immediate vicinity of the A_1-$N_{\rm re}$-A_d point which

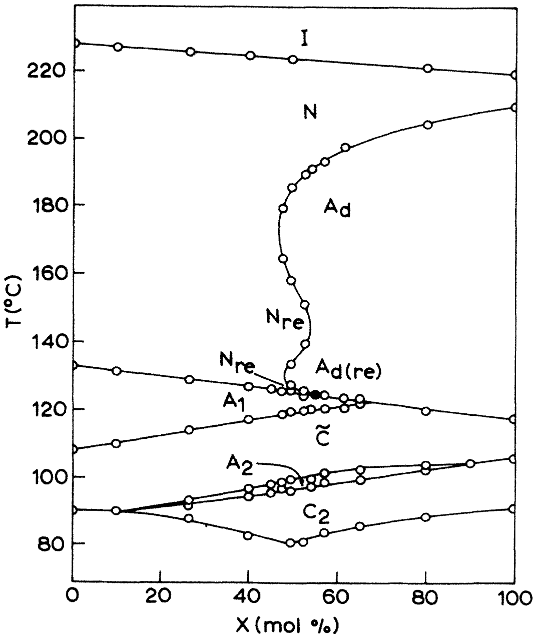

FIG. 1. Complete temperature-concentration (T-X) diagram for binary mixtures of 4-n-octyloxyphenyl-4′-(4″-nitrobenzoyloxy) benzoate or DB.$\bar{8}$.NO$_2$ and 4-n-decyloxyphenyl-4′-(4″-nitrobenzoyloxy) benzoate or DB.$\overline{10}$.NO$_2$ X is the mol% of DB.$\overline{10}$.NO$_2$ in the mixture. The solid lines are guides to the eye. The A_1-$N_{\rm re}$-A_d point which occurs at $X=55.0$ is denoted by a closed circle. The size of this circle constitutes the entire region of T and X for which the high-resolution data are shown in Fig. 2. (For an explanation of the various phases see Ref. 10.)

occurs at $X = 55.0$ (X being the mol% of DB.$\overline{10}$.$\mathrm{NO_2}$ in the mixture) are shown in Fig. 2. It is clear that although the global phase diagram (Fig. 1) near the A_1-N_{re}-A_d point does resemble the topology of the magnetic bicritical point,[12] the high-resolution diagram (Fig. 2) shows that this is not really the case. Since the latent heat of the A_1-A_d transition should vanish at the bicritical point,[3] we undertook a detailed DSC study [using the Perkin Elmer DSC-4 system in conjunction with the thermal analysis data station (TADS)] of the A_1-A_d transition in the vicinity of the A_1-N_{re}-A_d. We also studied the A_1-N_{re} transition whose signature was seen in the DSC runs while the A_d-N_{re} transition was not detectable. In all eight mixtures ($X = 55.13$, 55.37, 55.72, 56.02, 56.97, 57.83, 58.91, and 60.79) exhibiting the A_1-A_d transition and seven mixtures ($X = 49.99$, 51.95, 53.52, 53.92, 54.39, 54.73, and 54.92) showing the A_1-N_{re} transition were studied. For each concentration DSC runs were taken at ten different rates, ranging from 1.0 °C/min. to 0.1 °C/min., the lowest rate possible with the DSC set up. The total area under the endothermic peak was calculated using the computerized TADS system and the corresponding enthalpy (ΔH), which includes both the latent heat and the specific-heat contributions, was evaluated for each heating rate. The value of ΔH obtained in this manner is shown as a function of heating rate for a few representative concentrations in Fig. 3. These data in fact constitute the average of at least two different heating runs taken for each heating rate. A least-squares fit of the ΔH data to a straight line was carried out which gave $(\Delta H)_0$ the enthalpy at zero heating rate. Although, in principle, DSC cannot differentiate between rapidly varying entropy and the true latent heat of transition, we believe that the value of $(\Delta H)_0$ evaluated in this manner should be very close to the latent heat of transition. [The efficacy of this technique has already been ascertained[17] by studying the A-N and nematic-isotropic (N-I) transitions of 4-*n*-octyloxy-4′-cyanobiphenyl or 8OCB for which adiabatic calorimetry data are available.]

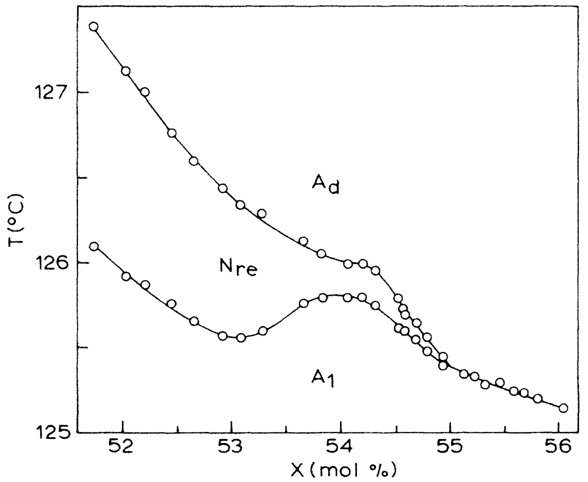

FIG. 2. High resolution T-X diagram in the vicinity of the A_1-N_{re}-A_d point. The solid lines are guides to the eye.

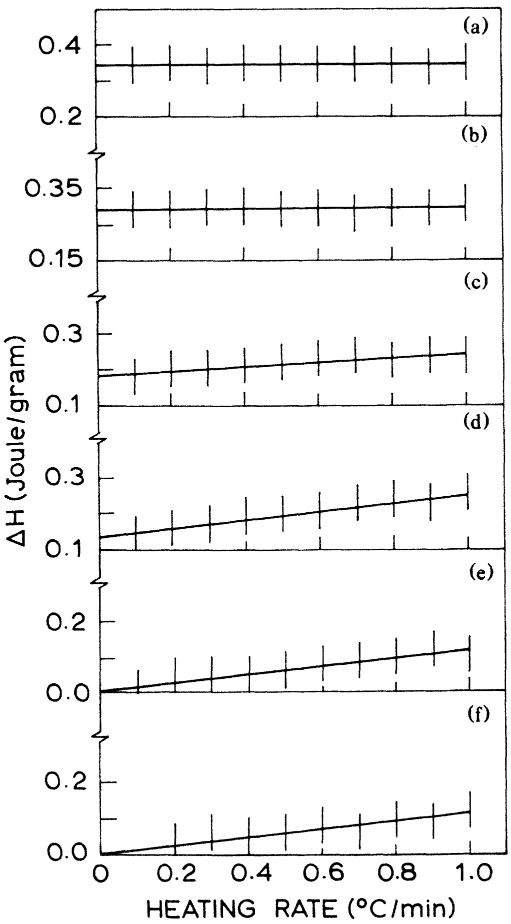

FIG. 3. Plots of enthalpy (ΔH) vs heating rate for the A_1-A_d [(a),(b)] and A_1-N_{re} transitions [(c)–(f)] as obtained by DSC runs for different concentrations. The values of X are (a) 56.02, (b) 55.13, (c) 54.92, (d) 54.73, (e) 51.95, and (f) 49.99. Each data point is shown as a vertical line whose height represents the error bar in the determination of ΔH. The solid line is a least squares-fit of the data to a straight line. The same fit also gives $(\Delta H)_0$ the enthalpy extrapolated to zero heating rate which can be equated to the latent heat of transition (see text).

We shall now examine the plots of ΔH versus heating rate for different concentrations (Fig. 3). For the A_1-A_d transition [Figs. 3(a) and 3(b)] the value of ΔH is seen to be independent of the heating rate, a feature that is generally expected for first-order transitions with little or no pretransitional effects.[18] In the case of the A_1-N_{re} transition, ΔH is strongly dependent on the heating rate. For some concentrations [Figs. 3(c) and 3(d)], $(\Delta H)_0$ is seen to be nonzero implying that the transition is weakly first order with large pretransitional effects. On the other hand, for some concentrations [Figs. 3(e) and 3(f)], $\Delta H_0 \approx 0$ signifying that the A_1-N_{re} transition for these concentrations is second order.

The complete data of $(\Delta H)_0$ for all the concentrations are plotted against the concentration (X) in Fig. 4. The following important features are clear from the diagram. First, though $(\Delta H)_0$ for the A_1-A_d transition decreases initially with decreasing X, it does not go to zero at

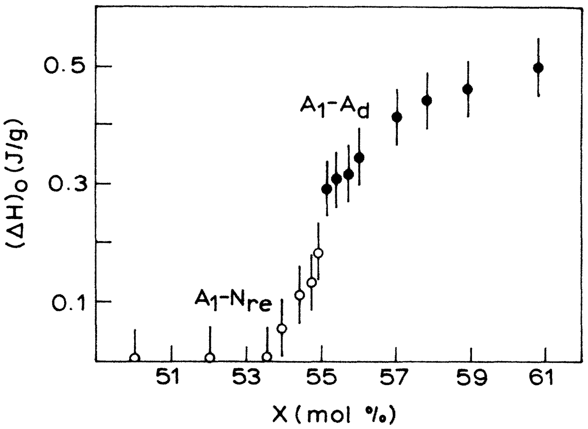

FIG. 4. Plot of latent heat $(\Delta H)_0$ associated with A_1-A_d (●) and A_1-N_{re} (○) transitions in the neighborhood of the A_1-N_{re}-A_d point.

$X = 55.0$, the concentration at which the A_1-N_{re}-A_d point occurs. We, therefore, infer that the A_1-N_{re}-A_d point is *not a bicritical point.* Second, the A_1-N_{re} boundary is seen to be second order at low concentrations but becomes first order on approaching the A_1-N_{re}-A_d point and, hence, there should be a tricritical point on the A_1-N_{re} line. It should also be mentioned that our x-ray and optical studies (not described here) near the A_1-N_{re}-A_d point have failed to reveal an incommensurate phase and thereby a tetracritical point for this system can be ruled out. Therefore, we postulate that the *bicritical point has split into a critical end point (CEP) and a tricritical point (TCP).* Such a situation has indeed been predicted theoretically in magnetic systems,[19,20] but has not yet been envisaged by the theory of frustrated smectics.[1-5] It should also be mentioned that the accuracy in the determination of $(\Delta H)_0$ which is ± 0.05 J/g, is not sufficient for us to exactly locate the concentration at which the TCP occurs on the A_1-N_{re} line. The possibility that the TCP may lie extremely close to or at the CEP itself cannot be completely ruled out either. In the case of the latter, the A_1-N_{re}-A_d point would be a new kind of multicritical point which has again been considered theoretically in anisotropic ferromagnets.[20] It should also be mentioned that recently a dislocation loop theory[21] of the A-N transition has predicted that a first-order A_1-A_d phase boundary can terminate either at a critical point or as a nematic island,[22] which exists in a sea of smectic A separated from another nematic phase nearby. Under certain conditions this nematic island can join the other nematic leading to an unusual phase diagram. Some of its topological features appear to be qualitatively similar to our phase diagram (Fig. 2). Clearly, further studies, experimental as well as theoretical, are needed before we can generalize the situation concerning the existence of a bicritical point.

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