

# Heat capacity anomaly near transitions between nematic and smectic phases and fluctuational nature of the $NAC$ point

M. A. Anisimov, V. P. Voronov, A. O. Kul'kov, and F. Kholmurodov  
*I. M. Gubkin Moscow Institute of the Petrochemical and Gas Industry; S. U. Umarov  
Physicotechnical Institute, Academy of Sciences of the Tadzhik SSR*

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The heat capacity has been studied near transitions between the nematic and smectic  $A$  and  $C$  phases of liquid-crystal mixture. The point at which the nematic-smectic  $C$ , nematic-smectic  $A$ , and smectic  $A$ -smectic  $C$  lines intersect is also a tricritical point. A fluctuational increment in the heat capacity has been discovered on the line of  $A$ - $C$  transitions.

1. Much interest has recently been attracted to phase transitions from the nematic phase of a liquid crystal to the smectic phases characterized by a one-dimensional density wave directed either along the director (the  $A$  phase) or at an angle from it (the  $C$  phase).<sup>1</sup> Interest has also been attracted to the transition between the smectic  $A$  and  $C$  phases. Huang and Lien recently discovered<sup>2</sup> that the point at which the lines of the  $N$ - $A$ ,  $N$ - $C$ , and  $A$ - $C$  transitions intersect (the  $NAC$  point) lies close to the tricritical point. Is the result found by Huang and Lien<sup>2</sup> a universal property of the  $NAC$  point or just a random coincidence? If the  $NAC$  point is simultaneously the tricritical point in all cases, the implication is that special requirements are imposed on the nature of the interactions among the various types of order in liquid crystals.

2. We have measured the heat capacity at constant pressure,  $C_p$ , in a mixture of two liquid crystals, 4-*n*-hexyloxyphenyl-4'-*n*'-decyloxybenzoate ( $\overline{60\ 10}$ ) and 4-*n*-hexyloxyphenyl-4'-*n*'-octyloxybenzoate ( $\overline{608}$ ).<sup>1)</sup> Both are stable and contain comparatively few impurities, as is shown by the narrowness ( $\approx 0.06$  K) of the two-phase region of the transition from the isotropic liquid to the nematic crystal. The measurements are carried out in an adiabatic microcalorimeter<sup>3</sup> holding  $\sim 0.2$  g of the substance. Far from the phase transitions the heat capacity of the sample is about half the total heat capacity of the filled calorimeter. The cell is filled in a nitrogen atmosphere. After the calorimeter is filled, it is heated to  $\sim 400$  K and shaken. The sample is held at this temperature for about a day. The heat capacity is measured by a pulsed heating method with automatic recording of the equilibrium temperature behavior; the width of the calorimetric step is reduced to 0.02 K near the transition points. The temperature and the latent heats of the phase transitions are measured simultaneously by a method of quasiequilibrium thermograms (the rate of change of the temperature is  $\sim 5 \times 10^{-6}$  K/s).

3. Figure 1 shows the phase diagram of the  $\overline{60\ 10}$  mixture near the *NAC* point. In contrast with the results predicted by the theoretical models of Refs. 4–7, the line of the *A-C* transition converts smoothly into the line of the *N-C* transition. We cannot be absolutely sure about the nature of the intersection of the *N-A* and *N-C* lines because the anomaly of the heat capacity and thus the change in the slope of the thermogram on the *N-A* line disappear as we approach the *NAC* point. At a  $\overline{60\ 10}$  concentration  $x < 0.331$  m.f., the magnitude of the heat capacity anomaly on the *N-A* line reaches a

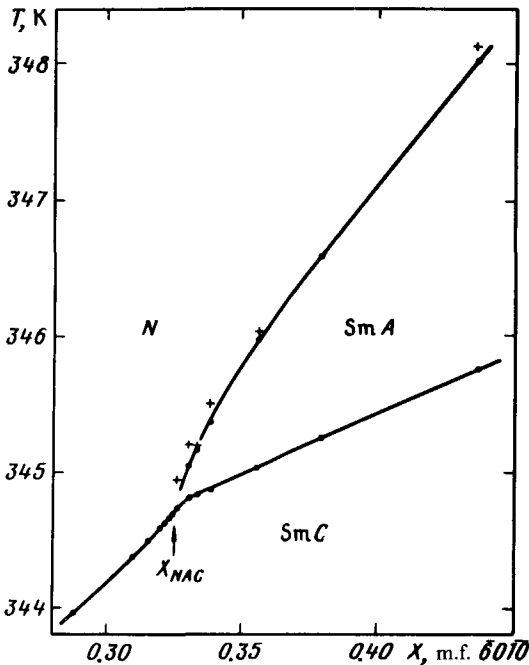


FIG. 1. Phase diagram of the  $\overline{608}$ - $\overline{60\ 10}$  mixture near the *NAC* point. The plus signs show values found for the temperature  $T_0(x)$  through an approximation of the results on  $C_p(T)$  by expression (2).

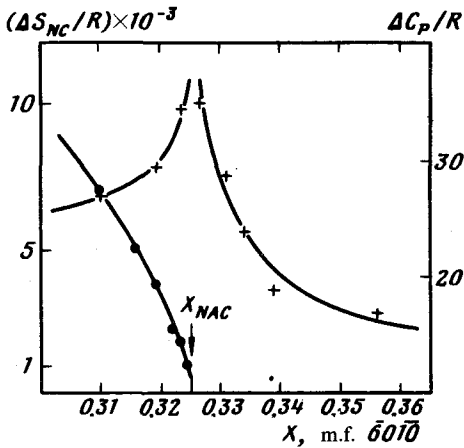


FIG. 2. + — Jump in the heat capacity at the transition to the *C* phase; ● — latent heat of the *N-C* transition near the *NAC* point.

level comparable to that of the random experimental error ( $\sim 0.1\%$ ). This result agrees with the results of a previous study of *N-A* transitions.<sup>8</sup> As we move away from the *NAC* point (as the  $\bar{60}\bar{10}$  concentration is increased), the anomaly on the *N-A* line grows. The effective critical exponent  $\alpha$ , a measure of the singularity in  $C_p$ , varies from  $\alpha \approx 0$  at 0.48 m.f.  $\bar{60}\bar{10}$  to  $\alpha \approx 0.24$  in pure  $\bar{60}\bar{10}$ , again in agreement with the results reported by other investigators.<sup>9</sup>

4. On the line of *A-C* transitions we find the opposite situation. Although the *A-C* transition is a second-order transition in all cases, the jump in the heat capacity increases as we approach the *NAC* point, seemingly becoming infinite there (Fig. 2). The jump in the heat capacity on the *N-C* line increases in a similar way. The *N-C* transitions are first-order transitions, with a latent heat of transition that vanishes at the *NAC* point (Fig. 2). On the basis of these facts, it can be asserted that, within the resolution of our experiment, the *NAC* point coincides with the tricritical point on the line of transitions to the *C* phase from the *N* and *A* phases. The coincidence of the *NAC* point with the tricritical point that was observed by Huang and Lien<sup>2</sup> is apparently not a random coincidence.

5. We have attempted to approximate the results of these measurements of the heat capacity in the *C* phase near the *A-C* transitions over the interval  $|t| = 5 \times 10^{-2} - 3 \times 10^{-5}$  by a functional dependence which follows from Landau's theory for the neighborhood of the tricritical point<sup>10</sup>:

$$C_p = A_0 (|t| + t_0)^{-1/2} + A_1 + A_2 t + A_3 t^2, \quad (1)$$

where  $t = (T - T_{AC})/T_{AC}$ ;  $t_0 = (T_0 - T_{AC})/T_{AC}$ ; and  $T_0$  is the temperature of the divergence of the heat capacity, which lies above the temperature of the *A-C* transition,  $T_{AC}$ . All the parameters in (1) are adjustable except  $T_{AC}$ , which has been determined within  $\pm 10^{-3}$  K and which was varied over this interval. It turns out that expression (1) does not give a satisfactory description of the experimental results over the entire concentration range studied. To illustrate the situation, we show in Fig. 3, along with one of the  $C_p(T)$  curves, the prediction of this expression (the dashed line). The de-

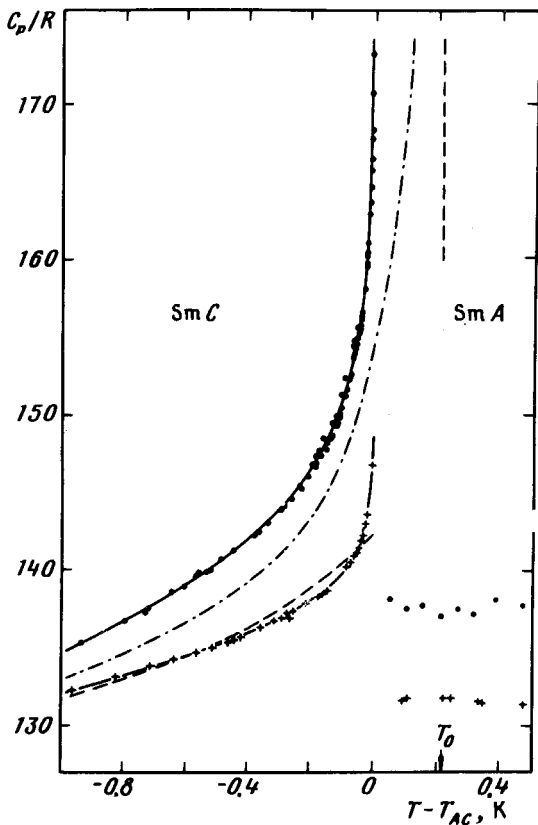


FIG. 3. Heat capacity near the  $A$ - $C$  transition.  $+ - x = 0.481$ ;  $\bullet - x = 0.3266$  m.f.  $\bar{60} \bar{10}$ . The value of  $T_0$  is shown for  $x = 0.3266$ .

scription of the experimental results by the power law  $C_p \sim t^{-\alpha}$  with a single effective exponent becomes more satisfactory as  $x \rightarrow x_{NAC}$ . For  $x = 0.3266$  at  $|t| = 3 \times 10^{-3} - 3 \times 10^{-5}$ , we find  $\alpha = 0.10 \pm 0.03$ .

A satisfactory description of  $C_p(T)$  over the entire temperature range,  $|t| = 5 \times 10^{-2} - 3 \times 10^{-5}$ , and for all concentrations, is given by the expression

$$C_p = A_0(|t| + t_0)^{-1/2} + \tilde{A}_0 |t|^{-\alpha} + A_1 + A_2 t + A_3 t^2 \quad (2)$$

(the solid lines in Fig. 3).

Consequently, in addition to the "classical" square-root dependence, associated with the proximity to the tricritical point, with a divergence temperature  $T_0$  (the dot-dashed line in Fig. 3), there is an increment  $\tilde{A}_0 |t|^{-\alpha}$  in the heat capacity which diverges at the point of the  $A$ - $C$  transition and which apparently stems from fluctuations in the angular positions of the molecules in the  $C$  phase. The optimum value of  $\alpha$  for the various concentration ranges from 0.3 to 0.6. In view of the error in the determination of this quantity, we conclude that, at the very worst, this value does not contradict the value  $\alpha = 0.5$  corresponding to the Ornstein-Zernike approximation.<sup>10</sup> At the fixed value  $\alpha = 0.5$ , the amplitude  $A_0$  shows a tendency to increase toward the

*NAC* point. Unfortunately, the increased scatter of the points in the *A* phase near the *NAC* point prevents us from determining the nature of the corresponding increment in the heat capacity above the temperature of the *A-C* transition. There is a corresponding increment in the behavior of  $C_p(T)$  near the line of *N-C* transitions, but the divergence temperature in this case lies above  $T_c$ , since the transition becomes a first-order transition.

As Swift has shown,<sup>11</sup> the *N-C* transition is of first order because of fluctuations in the angular positions of the molecules in the smectic layer. The latent heat of the transition disappears at the *NAC* point. In the models that have been offered,<sup>4-7</sup> the *NAC* point can be a tricritical point only for the *N-C* and *N-A* lines. The complete suppression of the heat capacity anomaly on the *N-A* line as  $x \rightarrow x_{NAC}$  contradicts that assertion. We note that again in this case the model of Gorodetskiĭ and Podnek<sup>7</sup> nevertheless predicts an increase in the jump in the heat capacity on the *A-C* line as the *NAC* point is approached.

We have observed yet another feature of the *NAC* point, which should be of considerable importance for reaching an understanding of this point. The divergence temperature of the tricritical square-root dependence of the heat capacity,  $T_0^*(x)$ , agrees, within the error of the determination of this parameter, with the temperature of the *N-A* transitions<sup>2)</sup> (Fig. 1). This fact implies that there are additional restrictions on the nature of the interactions among the order parameters of the nematic and smectic phases.

<sup>1)</sup>Also known as HOPDOP and HOPOOP.

<sup>2)</sup>The error in the values of  $T_0$ , which ranges from 0.1 to 0.4 K, is determined primarily by the interval over which the experimental data are approximated.

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Translated by Dave Parsons