Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

High-Resolution Adiabatic Calorimetry Measurements in the Vicinity of the Liquid Crystal Phase Transitions

M. A. Anisimov [a], V. P. Voronov [a], A. O. Kulkov [a], V. N. Petukhov [a] & F. Kholmurodov [a b]

[a] Moscow Oil and Gas Institute, Moscow, B-296, USSR

[b] Physico-Technical Institute of Tadzhik, Academy of Sciences, Dushanbe, Tadzhik, SSR, USSR

Version of record first published: 13 Dec 2006.

To cite this article: M. A. Anisimov , V. P. Voronov , A. O. Kulkov , V. N. Petukhov & F. Kholmurodov (1987): High-Resolution Adiabatic Calorimetry Measurements in the Vicinity of the Liquid Crystal Phase Transitions, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 150:1, 399-418

To link to this article: http://dx.doi.org/10.1080/00268948708074812

Mol. Cryst. Liq. Cryst., 1987, Vol. 150b, pp. 399–418
Photocopying permitted by license only

Printed in the United States of America

High-Resolution Adiabatic Calorimetry Measurements in the Vicinity of the Liquid Crystal Phase Transitions†

M. A. ANISIMOV, V. P. VORONOV, A. O. KULKOV, V. N. PETUKHOV† and F. KHOLMURODOV‡

Moscow Oil and Gas Institute, Moscow B-296, USSR

(*Received July 5, 1986; in final form February 26, 1987*)

High-resolution adiabatic calorimetry has been used for the study of the liquid crystal phase transitions in mixtures of 4-n-hexyloxyphenyl-4′-n-octyloxybenzoate ($\bar{6}0\bar{8}$), 4-n-hexyloxy-phenyl-4′-n-decyloxybenzoate ($\bar{6}0\bar{1}0$) and 4-n-hexyloxyphenyl-4′-n-dodexyl-oxybenzoate ($\bar{6}0\bar{1}2$) with emphasis on the vicinity of the NAC (nematic-smectic A–smectic C) multicritical point and the tricritical point along the NA (nematic–smectic A) line. Our results demonstrate the fluctuation nature of both these multi-critical points.

Keywords: phase transitions, adiabatic calorimetry, multicritical points

I. INTRODUCTION

Many liquid crystals have a variety of phases between an isotropic liquid and a crystalline solid. Some of the phase transitions are the first order ones while the others have the second order character. As a rule various phases influence one another, transition lines cross and multicritical points can appear on phase diagrams.

Many efforts both of the experimentalists[1–9] and theorists[10–15] were made during the last years for understanding the nature of the AC (smectic A–smectic C) transition and the NAC (nematic-smectic A–

†Paper presented at the 11th International Liquid Crystal Conference, Berkeley, June 30–July 4, 1986.

‡Physico-Technical Institute of Tadzhik, Academy of Sciences, Dushanbe, Tadzhik SSR, USSR.

smectic C) multicritical point (point of intersection of the NA, AC and NC lines on the phase diagram). The description of the NAC point as a Lifshitz point[9] implies the first order character of the NC transition as a result of the tilt fluctuations while the AC and NA transitions remain second order.

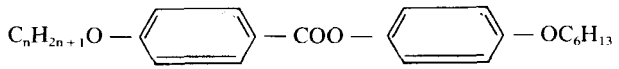
What is the character of the heat capacity behaviour in the vicinity of the NAC point? Excluding qualitative measurements[1] such data are lacking. Many works deal with the study of the AC transition heat capacity behaviour.[4,5,16,17] The main question which the researches are trying to answer is whether the mean-field quasitricritical behaviour or crossover from the mean-field behaviour to the critical one takes place. No unique answer exists. Tilt measurement data in the C-phase are well described both by quasitricritical[3] and pure meanfield[18] as well as by scaling approach.[19] On the other hand the C-phase heat capacity data in many cases[4,5,16] are well described in the frame of the Landau expansion up to the sixth-order term (quasitricritical behaviour). An elaborate analysis of tilt, susceptibility and heat capacity measurements has been carried out for the liquid crystal AMC-II.[8] Preference is given to the crossover from the mean-field behaviour to scaling, the crossover temperature being $t_G \approx 3 \cdot 10^{-3}$.

The next disputable problem is the nature of the NA (nematic-smectic A) transition and the tricritical point (TCP) on the NA line. Conventional interpretation of the evolution of the heat capacity anomalies along the NA line is a crossover between meanfield tricritical behaviour near the TCP and helium-like one far from it. However the character of the tricritical anomaly in 9CB and 8CB-10/CB mixture observed by Thoen and Seynhaeve[17] is so unusual that one can consider it to be a challenge to theorists.

II. EXPERIMENTAL PROCEDURE

With the help of the precision adiabatic calorimetry method[22] we have carried out the heat capacity and enthalpy measurements on the two mixtures ($\bar{6}0\bar{8}$-$\bar{6}0\bar{1}\bar{0}$ and $\bar{6}0\bar{1}0$-$\bar{6}0\bar{1}\bar{2}$)‡. The sample (0.2 gram

‡$\bar{6}0\bar{8}$, $\bar{6}0\bar{1}\bar{0}$ and $\bar{6}0\bar{1}\bar{2}$ are 4-n-hexyloxyphenyl-4′-n-alkyl (octyl-, decyl-, dodecyl-) oxybenzoates. The structural formula is



(n = 8,10,12)

The liquid crystals were made and kindly given to us by D. Demus ($\bar{6}0\bar{1}\bar{0}$) and B. M. Bolotin ($\bar{6}0\bar{8}$, $\bar{6}0\bar{1}\bar{2}$).

approximately) was contained into a titanium alloy calorimetric cell. The calorimetric cell was surrounded with two thermal screens. This system was placed in a vacuum bulb and water thermostat. A thermocouple battery with a sensitivity of 200 μV/K was used for measuring the temperature difference between the cell and the internal screen as well as between the internal and external screens. A platinum resistor thermometer was placed on the internal screen. Far from the phase transition points the heat capacity of the empty calorimeter was about half of the total heat capacity. We carried out measurements in the impulse-heat regime (the minimum step was 0,01K, the error in the temperature measurements was about 10^{-4}K) and in the adiabatic scanning regime. The rate of heating could be changed from $2 \cdot 10^{-3}$K/h to 20 K/h. The impulse-heat regime was used for the heat capacity measurements, the scanning regime—for determining the temperatures and enthalpies of the phase transitions. The samples were chemically stable and rather pure (the two-phase region for the isotropic-nematic phase transitions (N-I) was less than 0,06K). The calorimetric cell was being filled by the sample, which was degased in vacuum at $T > T_{NI}$ (T_{NI} is the temperature of the nematic-isotropic phase transition) and the free cell volume was filled by dry nitrogen. So Filled and then germitized cell was subjected to heating up to the temperatures $T \approx T_{NI} + 20$K, then carefully shaken up and placed in the adiabatic calorimeter, not allowing the sample crystallization. During the whole measurement cycle (up to 40 days) the sample was not cooled below the melting temperature. Such a procedure of filling was necessary in order to exclude the nonhomogeneity of the sample composition.

III. RESULTS AND DISCUSSION

Phase diagram

Pure samples were purposedly chosen having such sequences of phase transitions which provide the possibility of existence of multicritical points on a phase diagram. Three samples of the same homological series were chosen and synthesized having the following sequences of phase transitions: in $\bar{6}0\bar{8}$ K (crystal)-C-N-I, in $\bar{6}0\bar{1}0$ K-C-A-N-I and in $\bar{6}0\bar{1}2$ K-C-A-I. On the T-x phase diagram (see Figure 1) of the mixture of these substances ($\bar{6}0\bar{8}$ – $\bar{6}0\bar{1}0$ and $\bar{6}0\bar{1}0$-$\bar{6}0\bar{1}2$) there exist three singular points: multicritical NAC point (x_{NAC} = 0,326 mol. fr. $\bar{6}0\bar{1}0$), tricritical point on the line of the NA transitions (x_{TCP} =

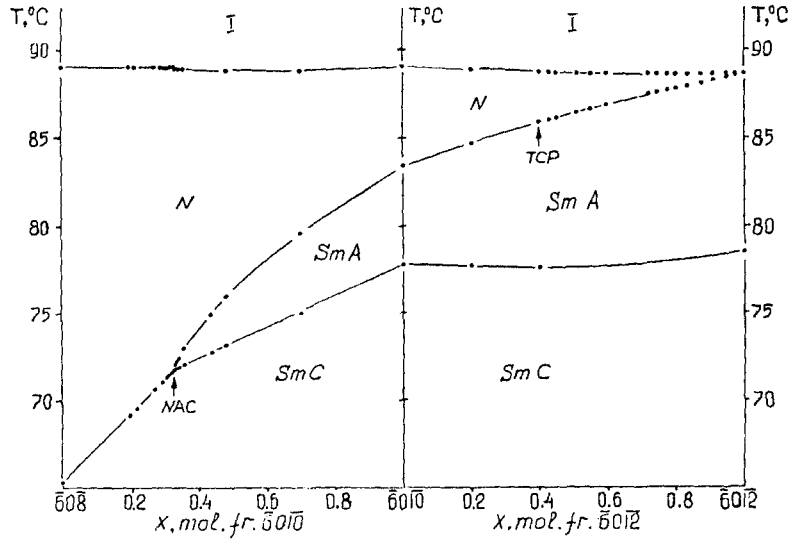


FIGURE 1 Phase diagram of $\bar{6}0\bar{8}$-$\bar{6}0\bar{1}0$ and $\bar{6}0\bar{1}0$-$\bar{6}0\bar{1}2$ mixtures.

0,400 mol. fr. $\bar{6}0\bar{1}\bar{2}$) and triple NAI point, which has coincided with the concentration of a pure sample $\bar{6}0\bar{1}\bar{2}$. So we have got an opportunity to trace the evolution of the heat capacity along the different lines of phase transitions depending on the proximity of these singular points and also the behaviour of latent heats of the transitions along the first order parts of the NC and AN lines. The topology of the NAC point obtained by us qualitatively supports its universality[6,7] and by its character is very similar to the topology of the NAC point in the $\bar{7}S5 - \bar{8}S5$ mixtures.[1b] In completely different systems such as mixtures investigated in the work by Brisbin *et al.*[6] and pure substance, where the NAC point was obtained under the pressure,[7] AN, NC and AC lines can be described with the help of one and the same formula:

$$T_{\mathrm{NAC}} - T_{tr} = A(x_{\mathrm{NAC}} - x)^{\eta} + B(x_{\mathrm{NAC}} - x) \qquad (1)$$

where T_{tr} and x are transition temperatures and corresponding concentrations of the AN, NC and AC lines. The exponents along the AN and NC lines are the same: $\eta = 0{,}57 + 0{,}02$. This result confirms the theoretical conclusion[13] which predicts the continuous junction of the two AN and NC "paraboles" in the NAC point. We could not fit our phase diagram in the vicinity of the NAC point with the help

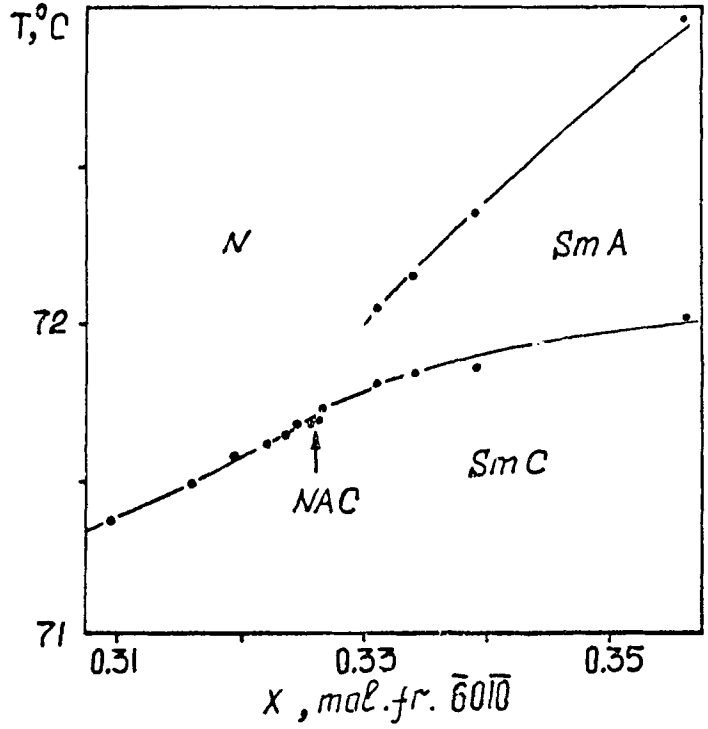


FIGURE 2 Phase diagram in the immediate vicinity of the NAC in the $\bar{6}0\bar{8}$-$\bar{6}0\bar{1}0$ mixture.

of the formula (I) because of lacking of data on the NA line in the immediate vicinity of the NAC point and smallness of the A coefficient on the NC line. So $T_{NAC} - T_{NC} \approx B(x_{NAC} - x)$ as could be seen from the Figure 2, one should rather admit the continuity of the NC and AC lines, than NC and AN.

One possible universal feature for NAC points should be noted: the NAC point may coincide with the reentrant point on the AN line.[13] It was this reason that made us unable to carry out the detailed study of the AN line close to the NAC point (heat capacity anomaly on the AN line vanishes in the NAC point).

On the NI line we discovered weak anomaly at concentration corresponding to the NAC-point concentration (Figure 3). However the latent heat of the NI transition within the limits of the experimental errors shows no deviations from approximately linear dependence.

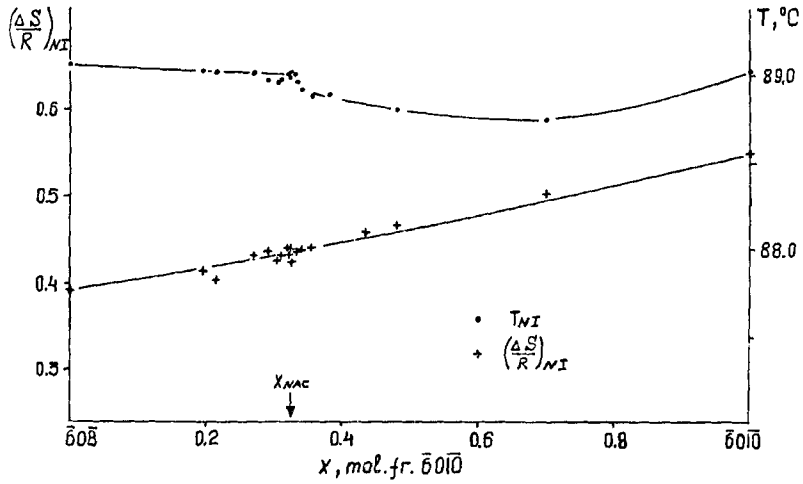


FIGURE 3 NI transition line (dots) and NI transition entropy (crosses) in the $\bar{6}0\bar{8}$-$\bar{6}0\bar{1}0$ mixture.

NC transitions line

The NC transitions are first order ones however their latent heat is drastically decreasing while approaching the NAC point†. The extrapolation of the latent heat depression down to zero gives the following concentration of the NAC point: $x_{NAC} = 0{,}326$ mol.fr. $\bar{6}0\bar{1}0$. Certainly we cannot claim that the point where latent heat vanishes on the NC line and the NAC point be just the same, because we do not known exactly the intersection region of the AN line.

Contrary to Ref. 12 the obtained latent heat dependence on $(x_{NAC}-x)$ is not linear. In the whole range of concentrations corresponding to NC line, the quantity $(\Delta S/R)_{NC}$ (Figure 4) is described by the power law:

$$\left(\frac{\Delta S}{R}\right)_{NC} \sim (x_{NAC} - x)^{\varphi} \qquad (2)$$

with exponent $\varphi = 0.84 \pm 0.02$.

†Whereas the N-C transition entropy in the pure $\bar{6}0\bar{8}$ is about 0.1 R (R is a gas constant), it is only $4 \cdot 10^{-4}$ R in the 32.58% $\bar{6}0\bar{1}0$ mixture. Such a paltry latent heat becomes noticeable only when the slowest scanning rate is used (Figure 5b). Otherwise the transition looks as a second order one (Figure 5a). The change of the concentration only in 0.04% leads to the second order transition within the limits of our accuracy.

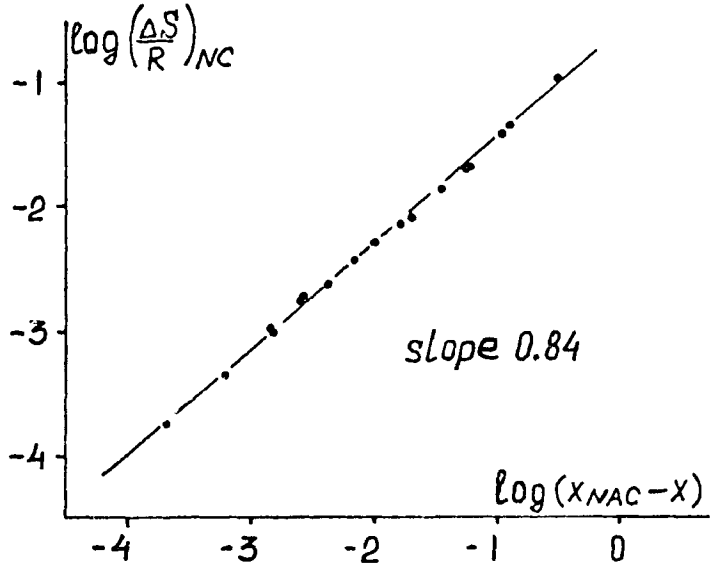


FIGURE 4 Concentration dependence of the NC transition entropy in the $\bar{6}0\bar{8}$-$\bar{6}0\bar{1}0$ mixture.

The nonlinear concentration dependence of the NC transitions entropy could be explained by the nonlinearity of the NC line in the vicinity of the NAC point.

The NC transition can be qualitatively described in the framework of the Landau expansion with a negative fourth-order term coefficient in the free energy:

$$F - F_o = a\frac{(T - T^*)}{T_{NC}}\psi^2 + b\psi^4 + c\psi^6 \tag{3}$$

where F is a molar free energy (in RT_{NC} units), F_o is the regular part of the free energy, T_{NC} is the NC transition temperature, T^* is the absolute stability limit of nematic phase, $T_{NC} - T^*/T_{NC} = b^2/4ac$, ψ is the smectic-C order parameter, a and c are positive constants, $b < 0$. Then for transition entropy one obtains

$$\left(\frac{\Delta S}{R}\right)_{NC} = -\frac{ab}{2c} \tag{4}$$

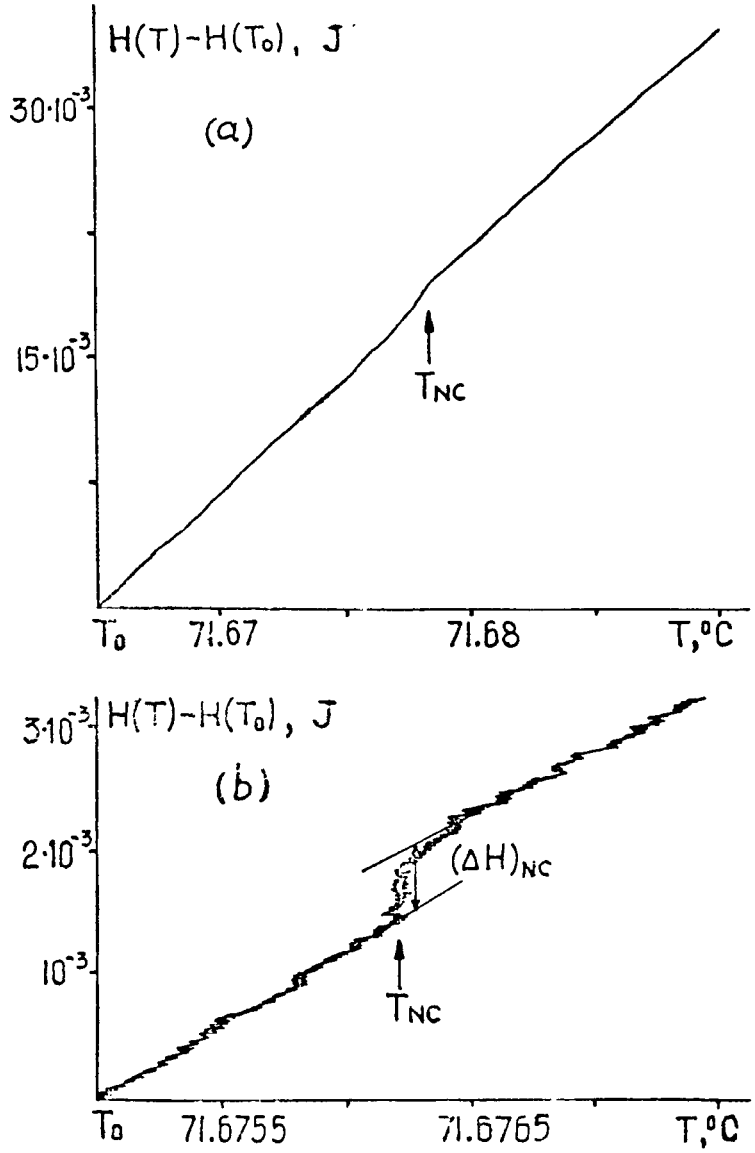


FIGURE 5 Temperature dependence of the enthalpy near the NC transition in the immediate vicinity of the NAC point:
a) the rate of scanning is $1.4 \cdot 10^{-5}$ K/s;
b) $2.2 \cdot 10^{-6}$ K/s.

Here $b \sim (T_{NC}\text{-}T_{NAC})$, but $T_{NAC}\text{-}T_{NC}$ (x) is proportional to $(x_{NAC}\text{-}x)^{\eta}$ (see (1)) and hence the NC transition entropy should be described by expression (2) with the same value of φ as η in expression (1). In this case our value of $\varphi = 0{,}84$ differs significantly from $\eta = 0{,}57$ obtained in Ref. 6 from the NC line fit procedure. There is an alternative explanation of such a discrepancy. In the fluctuation theory of the NAC point the exponent φ in Eq. (2) should be a universal critical exponent different from that determined by the NAC topology.[23] In this connection it would be interesting to have the latent heat data for mixtures studied in Ref. 8 in order to compare the exponent values for the NC line and the concentration dependence of the transition entropy.

For the heat capacity (see Figure 6) we used the expression following from the expansion (3)

$$\frac{C_p}{R} = A_o[(t + t_o)^{-0.5} - 1] + A_1 + A_2 t + A_3 t^2 \qquad (5)$$

where $t = T - T_{NC}/T_{NC}$, t_o characterizes the proximity of the NC transition to the tricritical behaviour (in the meanfield approach $t_o = b^2/12ac$), $(A_1 + A_2 t + A_3 t^2)$ is the regular part of the heat capacity. However as we already reported,[21] such heat capacity dependence is inadequate to our experimental data in the vicinity of the NAC point. A good description for all concentrations ($x = 0.0$, 0.310, 0.319, 0.324, 0.3258 mol.fr. $\bar{6}0\bar{1}0$) in the whole temperature range ($5 \cdot 10^{-2} > t > 3.6 \cdot 10^{-5}$) was obtained with the help of the crossover function

$$\frac{C_p}{R} = A_o\,[(t + t_o)^{-0.5} - 1] + \tilde{A}_o(t^{-\alpha} - 1) + A_1 + A_2 t + A_3 t^2 \qquad (6)$$

where $t = T - T^{**}/T_{NC}$, T^{**} is the divergence temperature of the fluctuation part of heat capacity. The exponent values vary here from 0,35 to 0,55. If one fixes $\alpha = 0{,}5$, the description does not become worse as T^{**} (because of the first order character of the NC transition) happens to be an adjustable parameter. The values of the fitting parameters obtained with the assumption $\alpha = 0{,}5$ in (6) are listed in Table I. In the asymptotic region ($t < 10^{-3}$) with $A_o = 0$, the values of exponent α are also close to 0.5. In this case the term $A_o\,(t + t_o)^{-0.5} - 1$ plays the role of a regular part. It could be noted that t_o

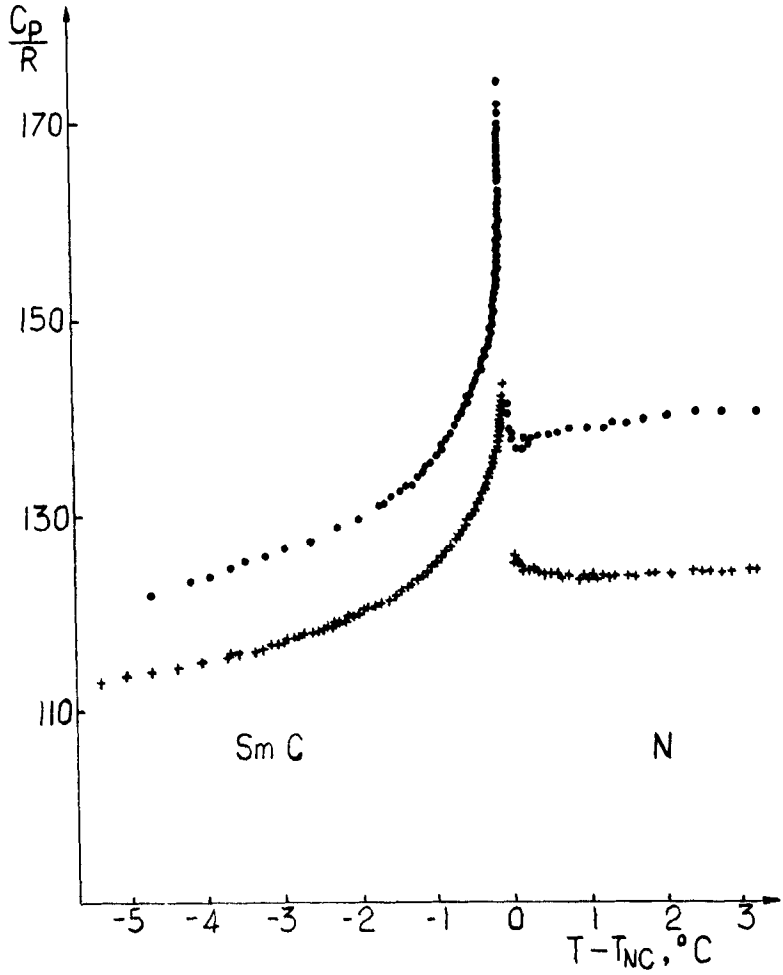


FIGURE 6 Heat capacity near the N-C transition: crosses are $\bar{6}0\bar{8}$, dots are 0.3258 mol.fr. $\bar{6}0\bar{1}0$ in $\bar{6}0\bar{8}$.

changes a little upon going away from the NAC point and the role of the term $\tilde{A}_o(t^{-\alpha}-1)$ in the heat capacity increases.

A-C transitions line

In addition to measurements already reported by us[21] we carried out measurements of the AC transition heat capacity far from the NAC point at x = 0,698 mol.fr. $\bar{6}0\bar{1}0$ ($\bar{6}0\bar{8}$-$\bar{6}0\bar{1}0$ mixture) and in pure $\bar{6}0\bar{1}2$

TABLE I

Fit by formula (6) of the smectic C heat capacity near the N-C transitions in the $\bar{6}0\bar{8}$-$\bar{6}0\bar{1}0$ mixture

x	A_o	t_o	$\tilde{A}_o$	A_1	A_2	A_3	t	T_{NC}	T^{**}	χ^2_ν
0.3258	1.602	$2.14 \cdot 10^{-3}$	0.144	112.5	−223	1860	$5 \cdot 10^{-2} - 3.5 \cdot 10^{-5}$	344.835	344.8364	1.32
	±0.088	$\pm 1.8 \cdot 10^{-4}$	±0.01	±0.9	±28	±350		±0.0004	±0.001	
0.3240	1.765	$2.51 \cdot 10^{-3}$	0.155	110.7	−182.5	1440	$5 \cdot 10^{-2} - 3 \cdot 10^{-5}$	344.808	344.8130	1.11
	±0.13	$\pm 2.5 \cdot 10^{-4}$	±0.01	±1.2	±35	±397		±0.002	±0.0014	
0.3190	2.148	$3.26 \cdot 10^{-3}$	0.179	107.0	−62.2	—	$5.3 \cdot 10^{-2} - 3 \cdot 10^{-5}$	344.737	344.7420	1.15
	±0.068	$\pm 1.7 \cdot 10^{-4}$	±0.01	±0.5	±6.7			±0.002	±0.0015	
0.3097	1.84	$3.04 \cdot 10^{-3}$	0.206	109.5	−137.8	870	$5 \cdot 10^{-2} - 6.1 \cdot 10^{-5}$	344.477	344.4907	1.22
	±0.16	$\pm 2.4 \cdot 10^{-4}$	±0.013	±1.5	±40	±440		±0.002	±0.002	
0.0000	1.30	$3.13 \cdot 10^{-3}$	0.300	104.5	−93.8	—	$2 \cdot 10^{-2} - 2.48 - 10^{-4}$	338.481	338.545	1.18
	±0.24	$\pm 1.12 \cdot 10^{-3}$	±0.08	±2.4	±50			±0.003	±0.02	

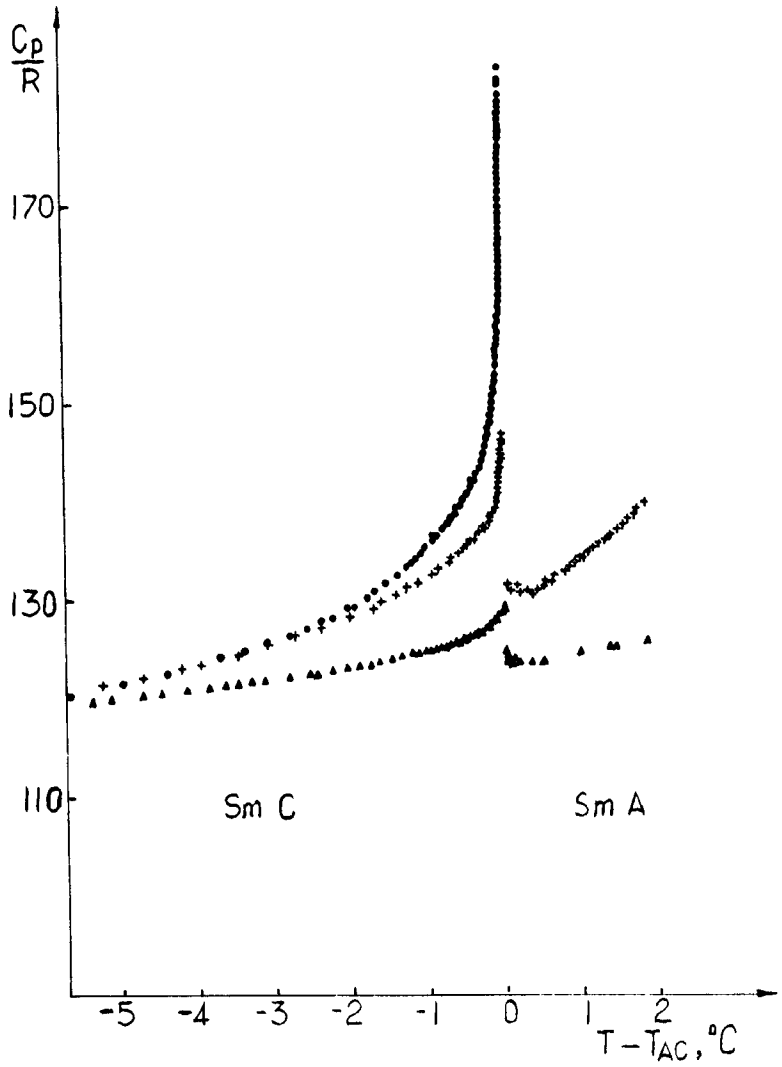


FIGURE 7 Heat capacity near the A-C transition: dots are 0.3262 mol.fr. $\bar{6}0\bar{1}0$ in $\bar{6}0\bar{8}$, crosses are 0.48 mol.fr. $\bar{6}0\bar{1}0$ in $\bar{6}0\bar{8}$, triangles are $\bar{6}0\bar{1}2$. (The latter are shifted down by 17 units of R.)

(see Figure 7). The Landau theory predicts for a second order transition close to a tricritical point (the coefficient b in the expansion (3) is positive but small) the same heat capacity behaviour (5) as for a weak first order one ($b < 0$).

As in the case of the NC transition we could not obtain good

agreement with the experimental data using expression (5), though it becomes better upon going away from the NAC point. On the contrary, expression (6) gives good agreement with experiment in the whole temperature range and for all concentrations. For a fixed value of $\alpha = 0{,}5$ the fitting parameters are listed in Table II. One can see that pure mean-field description ($\tilde{A}_o = 0$ in (6)) is essentially worse than the description taking into account the fluctuation term. The necessity of the $\tilde{A}_o$ ($t^{-\alpha}$-1) term in expression (6) underlines the significant role of fluctuations in the heat capacity, which increases upon approaching the NAC point (coefficient $\tilde{A}_o$ increases from 0,016 to 0,142). The tricritical region also increases (at $x \to x_{\mathrm{NAC}}$, parameter t_o gets smaller, but still is large enough ($t \approx 2 \cdot 10^{-3}$) for the closest to the NAC point concentration $x = 0{,}326$ ($x_{\mathrm{NAC}} - x \approx 0{,}0002$)).

Thus we can draw the following conclusion: side by side with the mean-field quasitricritical heat capacity behaviour in the C phase of AC transition there exists a narrow ($t \lesssim 10^{-3}$) fluctuation region which depends on the proximity of the NAC point. Both AC ($x = 0{,}3262$, Table II) and NC ($x = 0{,}3258$, Table I) heat capacities in the immediate vicinity of the NAC point behave similarly. It can mean that mean-field interpretation of the AC and NC transitions should be revised at least in the vicinity of the NAC point.

N-A transition line

On the basis of the experimental heat capacity studies results in 8CB-10CB mixture[24] it was concluded that the heat capacity behaviour at the N-A transition depends on the nematic region width and has a crossover from the helium behaviour (large nematic region) to the tricritical one (narrow nematic region). The heat capacity critical exponent changes from $\alpha = 0$ to $\alpha = 0.5$. It means that the whole NA line is a crossover one. In our previous measurements,[21] where we studied NA transition heat capacity dependence in the $\overline{6}0\overline{8}$-$\overline{6}0\overline{1}0$ mixture, this qualitative result was continual. However, the mixture studied had no tricritical point on the NA line. Measurements presented here fill in this gap. The $\overline{6}0\overline{8}$-$\overline{6}0\overline{1}0$ and $\overline{6}0\overline{1}0$-$\overline{6}0\overline{1}2$ mixtures provide the whole NA transition line (Figure 1), beginning from the NAC point and ending in the NAI triple point, having also a tricritical point (TCP) on the line. The TCP position was obtained by extrapolation of the latent heat concentration dependence down to zero value on the first order part of the NA line. We got $x_{\mathrm{TCP}} = 0{,}40 \pm 0{,}10$. It happened that concentration dependence $(\Delta S/R)_{\mathrm{AN}}$ passes from the quadratic (Figure 8) (in the vicinity of the TCP) to the linear one (far from the TCP) (Figure 9). In contrast to the NC transition,

TABLE II

Fit by formula (6) of the smectic C heat capacity near the A-C transitions in the $\bar{6}0\bar{8}$-$\bar{6}0\bar{1}0$ mixture

x mol.fr. 6010	A_o	t_o	$\tilde{A}_o$	A_1	A_2	A_3	t	χ^2_ν	$\frac{T_{AC}}{T_{NAC}} - 1$
0.3262	1.455(0.08)	$1.96(0.13) \cdot 10^{-3}$	0.142(0.003)	114.1(0.9)	−272.9(31)	2523(418)	$4.7 \cdot 10^{-2} - 2.2 \cdot 10^{-5}$	1.180	$2.087 \cdot 10^{-5}$
	0.603(0.034)	$2.07(0.26) \cdot 10^{-4}$	—	126.6(0.7)	−745.5(43)	8843(776)	"	4.450	
0.3266	1.505(0.07)	$1.94(0.14) \cdot 10^{-3}$	0.137(0.004)	113.2(0.8)	−232(31)	1820(372)	$5.3 \cdot 10^{-2} - 2.9 \cdot 10^{-5}$	1.393	$5.22 \cdot 10^{-5}$
	0.730(0.035)	$3.17(0.3) \cdot 10^{-4}$	—	124.1(0.7)	−603.5(35)	6174(550)	"	3.54	
0.331	1.736(0.09)	$2.05(0.13) \cdot 10^{-3}$	0.072(0.003)	111.9(0.9)	−222.5(30)	1986(397)	$4.7 \cdot 10^{-2} - 2.4 \cdot 10^{-5}$	1.33	$2.78 \cdot 10^{-4}$
	1.077(0.05)	$7.85(0.57) \cdot 10^{-4}$	—	119.7(0.7)	−475.6(33)	5073(524)	"	2.57	
0.339	2.017(0.17)	$2.39(0.20) \cdot 10^{-3}$	0.037(0.004)	109.4(1.4)	−133.0(45)	702(540)	$4.7 \cdot 10^{-2} - 4.3 \cdot 10^{-5}$	1.26	$4.32 \cdot 10^{-4}$
	1.43(0.07)	$1.39(0.9) \cdot 10^{-3}$	—	115.7(0.9)	−318.4(36)	2856(500)	"	1.64	
0.436	2.876(0.17)	$5.53(0.34) \cdot 10^{-3}$	0.0293(0.002)	104.5(1.0)	−28.8(11)	—	$6.8 \cdot 10^{-2} - 5.1 \cdot 10^{-5}$	1.26	$3.70 \cdot 10^{-3}$
	0.95(0.11)	$1.67(0.2) \cdot 10^{-3}$	—	121.3(1.4)	−413.2(52)	3240(566)	"	2.24	
0.481	3.5(0.05)	$8.03(0.2) \cdot 10^{-3}$	0.063(0.03)	101.2(0.2)	—	—	$6.7 \cdot 10^{-2} - 4.3 \cdot 10^{-5}$	1.23	$4.24 \cdot 10^{-3}$
	0.573(0.07)	$9.04(1.6) \cdot 10^{-4}$	—	124.6(1.1)	−516(48)	4371(573)	"	4.17	
0.6988	2.716(0.12)	$7.27(0.33) \cdot 10^{-3}$	0.0289(0.002)	109.1(0.7)	−43.8(7.2)	—	$5.6 \cdot 10^{-2} - 4.13 \cdot 10^{-5}$	1.155	$9.55 \cdot 10^{-3}$
	0.835(0.09)	$2.14(0.23) \cdot 10^{-3}$	—	123.6(0.9)	−364.3(30)	2992(373)	"	2.02	
$\bar{6}0\bar{1}\bar{2}$	2.54(0.36)	$1.31(0.13) \cdot 10^{-2}$	0.016(0.001)	124.2(0.8)	20.2(17)	—	$3.6 \cdot 10^{-2} - 4.6 \cdot 10^{-5}$	1.11	$1.97 \cdot 10^{-2}$
	0.095(0.01)	$4.63(0.6) \cdot 10^{-4}$	—	141.6(0.2)	−412.2(10)	5397(218)	"	1.23	

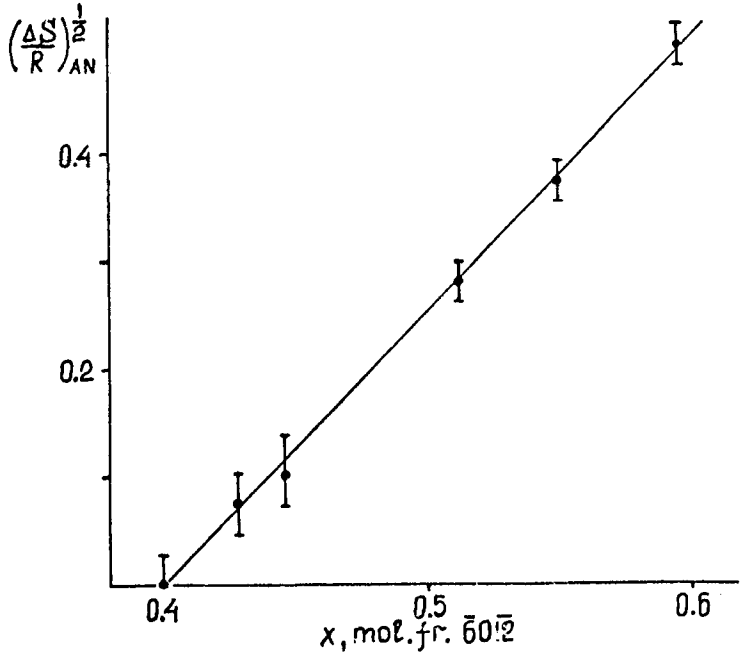


FIGURE 8 Concentration dependence of the square root of AN transition entropy near the TCP in the $\bar{6}0\bar{1}0$-$\bar{6}0\bar{1}2$ mixture.

the latent heat on the NA line is determined with greater experimental error. The great NA transition heat capacity anomaly can "smear" the enthalpy jump (compare Figure 5 and Figure 10). The upper limit of the possible latent heat value at $x_{TCP} = 0{,}40$ amounts to $(\Delta S/R)_{AN} < 6 \cdot 10^{-3}$ (15 J/mole).

The possibility of the tricritical point on the NA line was predicted by McMillan,[25] as a result of the nematic and smectic order parameters coupling. This coupling renormalizes the coefficient of the ψ^4 term in the free energy expansion(I), which goes to zero at a certain proximity of the NA transition to the NI one. This is a usual Landau TCP with the root-square divergence of the heat capacity ($\alpha = 0{,}5$) in ordered phase and the infinite jump of C_p with $(\Delta S/R)_{NA} \sim (T - T_{TCP})$ on the first order part of the NA transition line.

The results of the NA transition heat capacity data analysis for $t < 10^{-3}$ are presented in Table III as a function of concentration. For fitting we used the following formula:

$$\frac{C_p}{R} = A^{\pm}(t^{-\alpha^{\pm}} - 1) + C^{\pm} \tag{7}$$

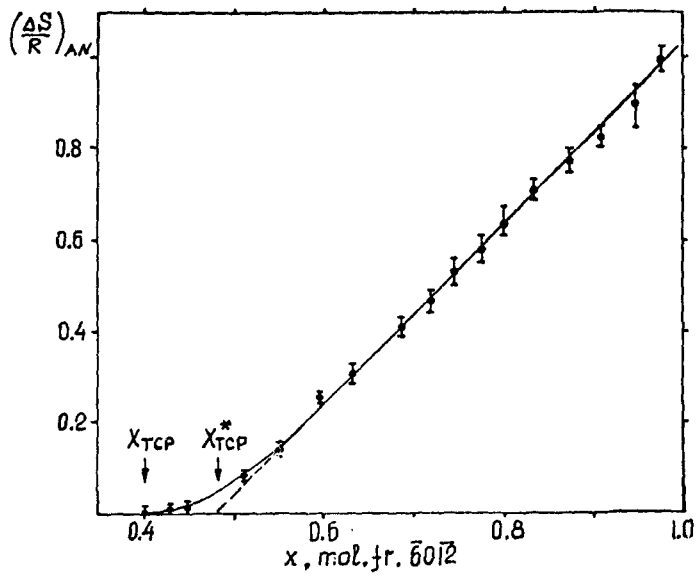


FIGURE 9 Concentration dependence of the AN transition entropy in the $\bar{6}0\bar{1}0$-$\bar{6}0\bar{1}2$ mixture.

where indices plus or minus correspond to the regions $T > T_{AN}$ and $T < T_{AN}$ accordingly. $C^{\pm}$ may be considered to be constant for $t < 10^{-3}$. The results of the fitting make it possible to say the following: a) in the TCP ($x_{TCP} = 0.40$) the heat capacity critical exponent value is close to 0,5 and decreases to $\alpha \approx 0$ upon approaching the NAC

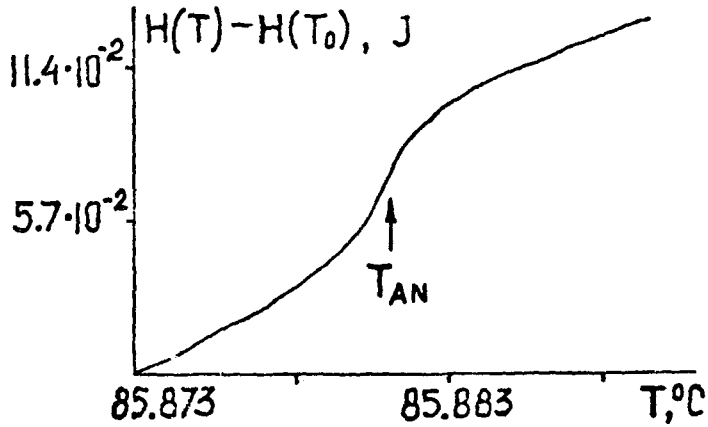


FIGURE 10 Temperature dependence of the enthalpy near the tricritical point (x = 0.40 mol.fr. $\bar{6}0\bar{1}2$) in the $\bar{6}0\bar{1}0$ – $\bar{6}0\bar{1}2$ mixture. The rate of scanning is $1.4 \cdot 10^{-5}$K/s.

TABLE III

Fit by formula (7) of the heat capacity near the NA transitions in the $\bar{6}0\bar{8}$-$\bar{6}0\bar{1}0$ and $\bar{6}0\bar{1}0$-$\bar{6}0\bar{1}2$ mixtures ($\tilde{A}^-$, $\tilde{C}^-$ and $\tilde{A}^+$, $\tilde{C}^+$ correspond to fit with $\alpha^- = \alpha^+$)

X	α^-	α^+	A^-	A^+	C	C^+	$\alpha^- = \alpha^+$	$\tilde{A}^-$	$\tilde{A}^+$	$\frac{\tilde{C}^-}{(\tilde{C}^+)}$	$\frac{T_{AN}}{T_{NI}}$
0.400 mol.fr.	0.576	0.476	2.18	4.20	111.9	163.5	0.518	3.79	2.75	94.0	0.9923
$\bar{6}0\bar{1}2$ in $\bar{6}0\bar{1}0$	(0.012)	(0.015)	(0.1)	(0.7)	(1.7)	(5.2)		(0.02)	(0.01)	(177.5)	
$\bar{6}0\bar{1}0$	0.246	0.255	28.2	14.9	69.8	136.1	0.25	26.0	16.5	76.7	0.9843
	(0.02)	(0.03)	(6.8)	(7.7)	(10.7)	(10)		(1.2)	(1.1)	(1.35)	
0.481 mol.fr.	−0.065	−0.039	−177.8	−107.8	85.3	127.2	−0.05	−204.2	−95.7	90	0.9644
$\bar{6}0\bar{1}0$ in $\bar{6}0\bar{8}$	(0.033)	(0.04)	(42)	(76)	(5.5)	(1.0)		(3.2)	(3.7)	(124.3)	

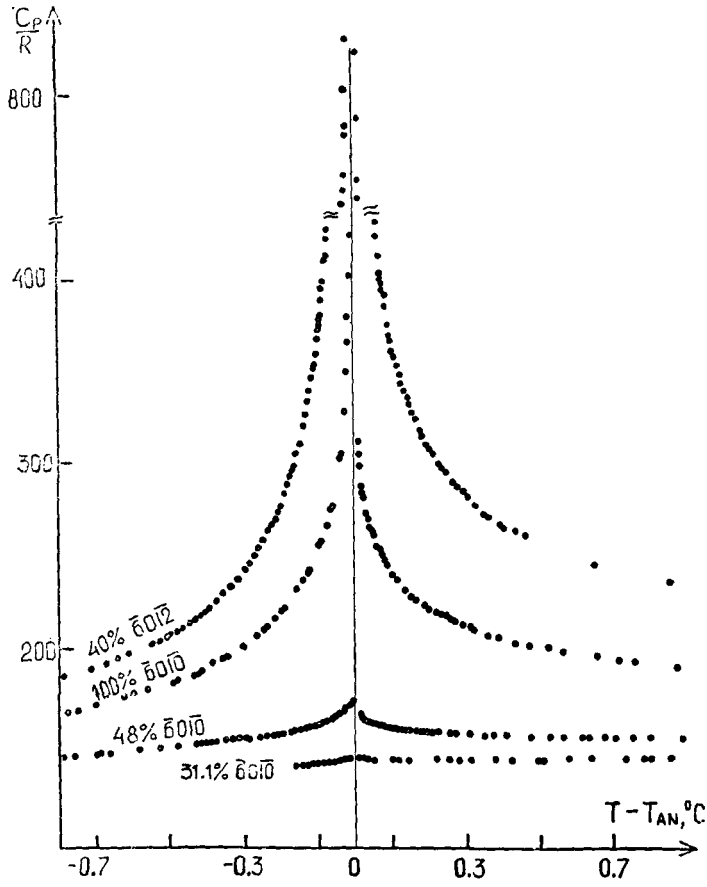


FIGURE 11 Heat capacity near the NA transitions.

point; b) the heat capacity anomaly has approximately symmetric form (A^+/A^- is close to unity) and rests so in the vicinity of TCP (Figure 11); c) the anomaly amplitude drastically decreases upon approaching the NAC point. These results are close to the results of the study of 8CB-10CB mixture presented in Ref. 24, though our liquid crystals are monolayer smectics otherwise those are bilayer ones. However, the more accurate analysis shows some discrepancies between the TCP behaviour in two discussed mixtures. In our case there is a slight asymmetry of the heat capacity anomaly (see Table III). The best values of $\alpha^{\pm}$ are different for smectic and nematic phases. Besides C^+ and C^- (for $\alpha^+ = \alpha^-$) are different (Table III). This does not follow from the scaling approach.

We would like to draw attention to the unusual character of the TCP heat capacity anomaly. This is not the Landau tricritical behaviour. The anomaly in the high-temperature phase is almost as large as in the low-temperature one. It means that strong fluctuations exist here. The asymmetry of the exponents α^+ and α^- could be caused by the fluctuation logarithmic corrections,[26] however the ratio of the amplitudes would not agree with the theory.

The latent heat dependence on the first order part of the NA line gives us a rise to the following speculations. If TCP on the NA line was due to McMillan model, in the vicinity of TCP, $(\Delta S/R)_{NA}$ would depend linearly on $T - T_{TCP} \sim x - x_{TCP}$ and TCP would appear at $x = x^*_{TCP}$ (Figure 9). The quadratic dependence of the $(\Delta S/R)_{NA}$ on $T - T_{TCP} \sim x - x_{TCP}$ observed experimentally in two mixtures (see Figure 8 and also Ref. 24) prompts us that de Gennes TCP ($x = x^*_{TCP}$) would appear in the model having negative coefficient at a third order invariant in a free energy expansion. The third order term may be due to the coupling of smectic order parameter with the director fluctuations,[27] which gives rise to a weak first order transition along the whole NA line. Podnek[28] has shown recently that this effect becomes experimentally observable only for the small distance between NA and NI transitions (in the vicinity of de Gennes TCP). In this case the NA latent heat tends to a small but non-zero limit while broadening of the nematic zone. Then apparent quadratic dependence of $(\Delta S/R)_{NA}$ mentioned above reveals this tendency.

References

1. a) D. Jonson, D. Allender, R. Dehoff, E. Oppenheim, C. Maze and R. Reynolds, *Phys. Rev.*, **B16**, 470 (1977). b) R. Dehoff, R. Biggers, D. Brisbiń and D. L. Johnson, *Phys Rev.*, **A25**, 472 (1982).
2. C. A. Schantz and D. L. Johnson, *Phys. Rev.*, **A17**, 1504 (1978).
3. C. C. Huang and S. C. Lien, *Phys. Rev. Lett.*, **47**, 1917 (1981).
4. C. C. Huang and S. C. Lien, *Phys. Rev.*, **A31**, 2621 (1985).
5. R. J. Birgeneau, C. W. Garland, A. R. Korton, J. D. Litster, M. Meichle, B. M. Ocko, C. Rosenblatt, L. S. Yu and J. Goodby, *Phys. Rev.*, **A27**, 1251 (1983).
6. D. Brisbin, D. L. Johnson, H. Feller and M. E. Neubert, *Phys. Rev. Lett.*, **50**, 178 (1983).
7. R. Shashidhar, B. R. Ratna and S. Krishna Prasad, *Phys. Rev. Lett.*, **53**, 2141 (1984).
8. Y. Galerne, *J. Physique*, **46**, 733 (1985).
9. C. R. Safinya, L. J. Martinez-Miranda, M. Kaplan, J. D. Litster and R. J. Birgeneau, *Phys. Rev. Lett.*, **50**, 56 (1983).
10. J. Chen and T. Lubensky, *Phys. Rev.*, **A14**, 1202 (1976).
11. L. Benguigui, *J. Physique*, **40**, 419 (1979).
12. J. Swift, *J. Chem. Phys.*, **72**, 3430 (1980).
13. E. Gorodetskii and V. Podnek, *JETP Lett.*, **39**, 624 (1984).

14. E. Gorodetskii and V. Podnek, *Sov. Phys. Crystallograhy* (*Kristallographia*), **29**, 1054 (1984).
15. E. I. Kats and V. V. Lebedev, *JETP*, **90**, III (1986).
16. M. Meichle and C. W. Garland, *Phys. Rev.*, **A27**, 2624 (1983).
17. J. Thoen and G. Seynhaeve, *Mol. Cr. Liq. Cr.*, **127**, 220 (1985).
18. C. R. Safinya, M. Kaplan, J. Als-Nelsen, R. J. Birgeneau, D. Davidov, J. D. Litster, D. L. Johnson and M. Neubert, *Phys. Rev.*, **B21**, 4149 (1980).
19. Y. Galerne, *Phys. Rev.*, **A24**, 2284 (1981).
20. M. Anisimov, V. Voronov, A. Kulkov and F. Kholmurodov, *JETP Lett.*, **41**, 248 (1985).
21. M. Anisimov, V. Voronov, A. Kulkov and F. Kholmurodov, *J. Physique*, **46**, 2137 (1985).
22. V. Voronov, "The problems of a calorimetry and a chemical thermodynamics," *10-th Sov. Conf.*, v. 2, p. 2, Chernogolovka, 1984.
23. V. V. Lebedev, private communication.
24. H. Marynissen, J. Thoen and W. van Dael, *Mol. Cr. Liq. Cr.*, **124**, 195 (1985).
25. M. L. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
26. M. Anisimov, E. Gorodetskii and V. Zaprudskii, *Sov. Phys. Uspekhi* (*Adv. in Phys.*), **133**, 103 (1981).
27. B. Halperin and T. C. Lubensky, *Sol. St. Commun.*, **14**, 997 (1974).
28. M. Anisimov, E. Gorodetskii, V. Voronov, V. Podnek and F. Kholmurodov, *JETP Lett.*, **45**, 336 (1987). V. Podnek, private communication.