ANOMALIES OF THE SPECIFIC HEAT IN THE VICINITY OF THE PHASE TRANSITION FROM ISOTROPIC LIQUID TO NEMATIC LIQUID CRYSTAL

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Precision measurements were made of the specific heat in the vicinity of the phase transition from nematic liquid crystal to isotropic liquid, an analysis of the results indicating that this transition occurs near the tricritical point.

The phase transition from nematic liquid crystal to isotropic liquid ($N \rightleftarrows I$) is one of the first kind. It is characterized by a low heat of transition and by anomalies of various properties over a rather wide temperature range, similar to those occurring near phase transitions of the second kind. Until recently, the behavior of nematics near the $N \rightleftarrows I$ transition was explained in terms of the Landau—de Jean phenomenological theory [1]. Meanwhile, it has been known that the Landau approximation does not apply to phase transitions of the second kind in systems with short-range intermolecular forces. The situation is made more difficult by the often insufficient accuracy and reliability of existing experimental data. Thus, e.g., the readings of the specific heat of the most extensively studied nematic substance MBBA (p-metoxybenzilidene-p'-n-butylaniline) [2-4] defy even an only qualitatively consistent interpretation.

These authors made precision measurements of the specific heat of two nematics: MBBA and BMOAB (p-n-butyl-p'-metoxyazoxybenzene) in the vicinity of the phase transition,* also of MBBA + n-decane and BMOAB + iso-octane mixtures. An analysis of the temperature dependence of the specific heat of these substances has revealed that a description of the $N \rightleftarrows I$ phase transition in terms of the Landau—de Jean theory is inadequate. The anomaly of the specific heat can be consistently described only on the assumption that the $N \rightleftarrows I$ transition occurs near the tricritical point [5].

The specific heat was measured with an adiabatic calorimeter [6] incorporating some inprovements. Two kinds of calorimeter vessels were used: one with heat-exchanger disks made of copper and stacked (≈3 mm apart) in "bookcase" fashion inside the cylindrical housing, and another one of the same shape and size (35 mm in diameter and 60 mm high) but furnished with a plunger-type magnetic stirrer.

The process of synthesizing and purifying these substances has already been described [7]. BMOAB is a mixture of two isomers with an approximately equimolecular composition. Our specimens were not additionally purified. The calorimeter was loaded in an atmosphere of dry nitrogen.

A real specimen always contains a certain amount of impurities. Equilibrium impurities uniformly distributed over the volume split the $N \rightleftarrows I$ transition: within some temperature range $T_T^- < T < T_T^+$ the nematic phase coexists with the isotropic phase. The dependence of the isotropic-phase appearance temperature T_T^+ on the impurity concentration x in MBBA and in BMOAB has been determined earlier [6]. For BMOAB mixture, moreover, has also been determined the isotropic-phase disappearance temperature T_T^-. Aliphatic alcohols, hydrocarbons, benzene, carbon tetrachloride, and naphthalene were used as impurities. These impurities, when added in low concentrations, drop the appearance temperature linearly with the derivative $dT_T^+/dx = 2 \pm 0.2$°K/mole % the same for both nematics. The phase diagram of BMOAB + iso-octane, one of the mixtures in this study, is shown in Fig. 1.

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*The preliminary results were published earlier [6].

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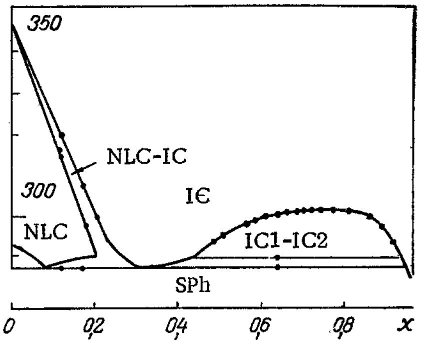

Fig. 1. Phase diagram of the BMOAB + iso-octane system: NLC) nematic liquid crystal; IC) isotropic crystal; SPh) solid phase. The critical equilibrium point IC1-IC2 corresponds to concentration x = 0.740 ± 0.005 (molar fraction) of iso-octane and to temperature T = 301.44 ± 0.01°K.

The most likely impurities to be found in MBBA are water and products of reverse hydrolysis. Inasmuch as the kinetics of the latter process had not been studied yet, we preferred to study the effect of impurities on the anomalous specific heat by adding, rather than water, a substance not interacting with MBBA such as chemically pure n-decane. It was added to raw MBBA in a concentration of 2.93 mole %.

The transition temperatures in the calorimetric experiments with stirring of a specimen were determined according to the method of quasistatic thermograms [8] with temperature drift rates of 10^{-6}-10^{-5} °K/sec. When a thermogram started from a single-phase region, then subcooling or superheating effects and a 1-20 mK hysteresis were found which depended on the rate of change of temperature and on the history of a specimen. With thermograms plotted first from a two-phase region into a single-phase region, there was no hysteresis found. The transition temperatures determined from such thermograms and regarded by us as equilibrium points are given in Table 1.

Thermograms plotted with the calorimeter of the first kind without stirring had no deflection points and were not reproducible. So as to minimize the side effect of stirring, the solenoid current was increased 10-15% above its level at which the stirrer would cease moving. The power dissipated by the stirrer during a 48-sec cycle and a 5-sec lifting time was 30 μW.

The readings of the specific heat of MBBA, BMOAB, and the MBBA + n-decane mixture are shown in Fig. 2. The readings taken directly within the transition range are shown in Fig. 3. The temperature dependence of the specific heat is seen to follow the same trend in all three cases. In the experiments with stirring the mean random error was ≈0.05%, almost no matter how close to the transition, with 0.1°K divisions on the calorimeter scale. In the experiments without stirring the error was just as large, but within a narrow range near the appearance temperature (≈0.3°K wide) the nonrepeatability of readings in various series of measurement reached several percent. Within this range the temperature stabilization time in the calorimeter after heater turnoff was much longer (5-10 h). In the experiments with stirring, the temperature equalization time was always short (a few minutes).

The results obtained with and without stirring can be easily explained, if one considers the presence of about 1% impurity in a test specimen. The manner in which the anomaly of the specific heat is distorted in a specimen containing some impurities depends largely on whether or not the latter are at thermodynamic equilibrium [9]. In a perfectly pure and homogeneous specimen, the transition temperature corresponds to a δ-function of the specific heat. The presence of a small amount of equilibrium impurities transforms the δ-function to a narrow trapezoid, its width depending on the amount of impurity (Fig. 1) and its area determining the heat of transition. The heat of transition calculated in this way was found to be $\lambda/RT_T = 0.102 \pm 0.001$ for MBBA and $\lambda/RT_T = 0.110 \pm 0.001$ for BMOAB (calculated by the "cryoscopic" formula [6] from the transition temperatures given in Table 1 for MBBA and for the MBBA + n-decane mixture, it would be $\lambda/RT_T = 0.106 \pm 0.005$ for MBBA).

TABLE 1. Transition Temperatures

Nematic substances, mixture	T_I^-, °K	T_I^+, °K
MBBA	318,01	318,18
MBBA + n-decane	312,13	312,66
BMOAB	346,74	346,88

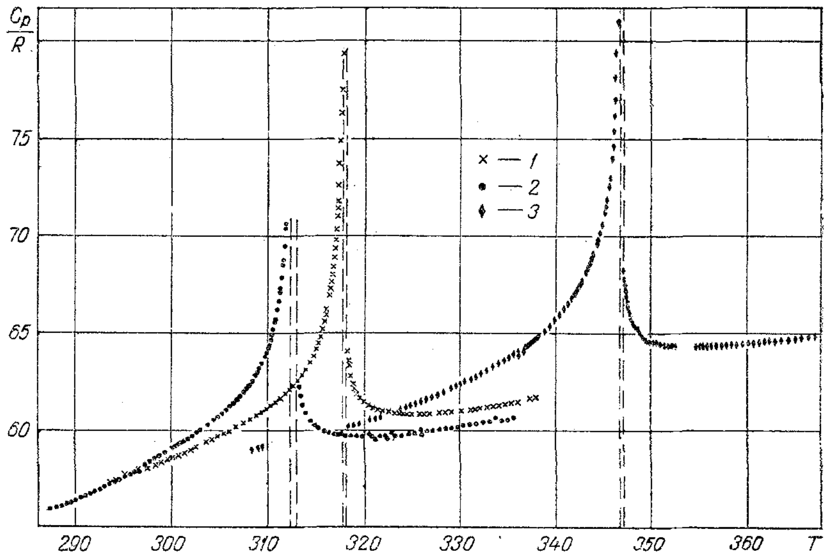

Fig. 2. Specific heat of MBBA, BMOAB, and the MBBA+ (3 mole %) n-decane mixture: 1) MBBA; 2) MBBA + n-decane; 3) BMOAB: the straight dashed lines correspond to, respectively, the disappearance temperature T_T^- and the appearance temperature T_T^+ of the isotropic phase.

Nonequilibrium impurities nonuniformly distributed over the specimen distort the δ-function differently. Each segment of the specimen has its peculiar beginning and end of transition, depending on the impurity concentration in it, so that the δ-function becomes blurred. The readings can be reproduced if the measuring time is much shorter than the time in which the inhomogeneities dissipate. In a two-phase region without stirring, the equilibrium distribution of impurities is established through diffusion and, therefore, very slowly.

Accordingly, measurements without stirring in the vicinity of transition distort the temperature dependence of the specific heat. The form and the extent to which the δ-function becomes blurred depend on the amount, the degree of nonhomogeneity, and the manner of distribution of impurities in the specimen.

The results of equilibrium measurements were first approximated with a power-law relation, viz.,

$$\frac{C_p}{R} = \frac{T}{T_c} A_0|\tau|^{-\alpha} + A_1 + A_2\tau + A_3\tau^2, \tag{1}$$

with $\tau = (T - T_c)/T_c$ and generally $T_c \neq T_T$.

The constants A_i ($i = 0, 1, 2, 3$), α, T_c and their confidence intervals for a confidence coefficient of 0.68 as well the adequacy of model (1) were determined through a nonlinear

TABLE 2. Results of Approximating the Temperature Dependence of the Specific Heat with Expression (1)

Nematic substance, mix.	α	T_c	A_0	A_1	A_2	A_3
			Nematic phase			
MBBA	0,32±0,02	318,12±0,02	2,25±0,21	54,7±0,6	20,3±3,0	—38,0±±15,2
MBBA + n-decane	0,36±0,03	312,36±0,05	1,51±0,16	55,2±0,6	27,3±1,3	—
BMOAB	0,38±0,03	346,92±0,02	1,65±0,20	58,6±0,9	7,4±9,9	—334,7±±197,0
			Isotropic phase			
MBBA	0,18±0,04	318,10±0,04	2,19±0,68	55,6±1,1	31,9±0,4	—
MBBA + n-decane	0,20±0,05	312,52±0,05	1,97±0,63	54,8±1,1	31,0±0,4	—
BMOAB	0,16±0,06	346,89±0,06	2,84±1,57	58,2±2,5	36,8±1,3	—

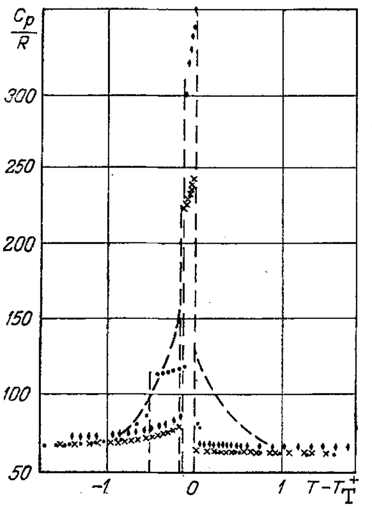

Fig. 3

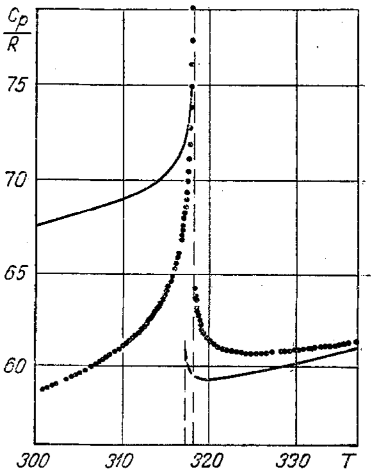

Fig. 4

Fig. 3. Specific heat of MBBA, BMOAB, and the MBBA+ (3 mole %) n-decane mixture within the range of transition from isotropic liquid to nematic liquid crystal, $T - T_T^+$ (°K). Notation the same as in Fig. 2; the dashed-line curve represents smoothing of the data [4].

Fig. 4. Comparison of experimental data on the specific heat of MBBA with calculations according to relations in the Landau—de Jean theory (solid lines); the straight dashed lines correspond to the theoretical temperatures at which the $C_p(T)$ relations diverge.

regression analysis of the data according to an available deck of programs [10]. The results of this analysis are given in Table 2.

The obtained values of the critical exponent are not explainable by any of the known theories. A theoretical curve of specific heat, one which follows from the Landau—de Jean theory and has been calculated according to formulas in an earlier study [6], is shown with a dashed line in Fig. 4. Characteristic of it is the jump of specific heat $\Delta C = a^2/2c$, where a and c are constants in the series expression of the thermodynamic potential in powers of the order parameter Q:

$$\Phi - \Phi_0 = \frac{1}{2} a\tau Q^2 - \frac{1}{3} bQ^3 + \frac{1}{4} cQ^4. \qquad (2)$$

For these calculations, the heat of transition $\lambda/RT_T = 0.1$, the order parameter at the transition point $Q_T = 0.4$ [11], and $T_T^+ - T_c = 1$°K [11] were used; these values yielded $a = 1.4$, $b = 0.06$, and $c = 0.1$ for the constants in the series expansion of the thermodynamic potential. In the theoretical relation, fluctuational corrections to the specific heat in the Ornstein—Zernicke approximation were included, the only addition to the normal specific heat of the isotropic phase. These corrections are [12] $C^+ = \frac{R}{16\pi} \frac{v}{r_0^3} |\tau|^{-1/2}$, and $C^- = 2^{3/2}C^+$, where $r_0 = 6 \pm 1$ Å [11, 13]. The experimental curve differs from the theoretical one in essence by the absence of a jump within the normal region and by a large anomaly in the region of the isotropic phase.*

On the other hand, the fact that the values of the critical exponent given in Table 2 are intermediate (between $\alpha = 0.5$ for a tricritical point [5] and $\alpha \leqslant 0.1$ [14] for an isolated critical point) suggest an idea (for the first time expressed in [6]) that the experimental temperature range ($10^{-1} > |\tau| > 10^{-3}$) falls within the range of transition from tricritical to critical behavior. A qualitative comparison of the temperature dependence of the specific heat near the N⇄I transition and near the tricritical point of NH_4Br, respectively,

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*It is important to note that varying the values of the input constants over a reasonable range will not appreciably change the theoretical trend of the specific heat.

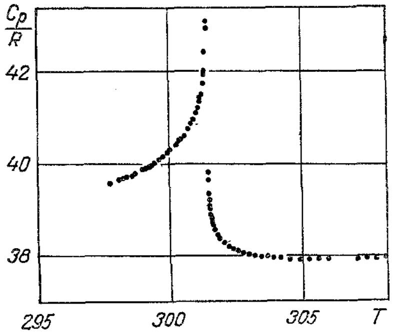

Fig. 5. Specific heat of the BMOAB + (74 mole %) isooctane mixture.

reveals that it is strikingly similar in both cases [15]. Another argument in support of this hypothesis is the small value of constant c in expansion (2), with $c = 0$ at a tricritical point. However, an attempt to describe the temperature dependence of the specific heat by expression (1) with a fixed value of the exponent α, viz., $\alpha^+ = \alpha^- = 0.5$ (as in the case of a tricritical point), reveals an inadequacy of this model. For this reason, the data on the specific heat of MBBA and BMOAB were analyzed on the basis of the simpler interpolation model

$$\frac{C_p}{R} = \frac{1}{B_1|\tau|^{1/2} + B_2|\tau|^{\alpha}} + B_3 + B_4\tau + B_5\tau^2. \tag{3}$$

Expression (3) yields a tricritical behavior at large values of $|\tau|$ and a critical behavior at $\tau \to 0$. With $\alpha = 0.1$ fixed, model (3) adequately describes the temperature dependence of the specific heat of both substances in both their isotropic and nematic phases. The values obtained for $B_1^{\pm}$ and $B_2^{\pm}$ are given in Table 3.

The second term in the denominator of expression (3) is comparable with the first term only when $|\tau| < 10^{-3}$ so that tricritical behavior is determining throughout the entire experimental temperature range in both nematic and isotropic regions.

The proposed interpretation of the $N \rightleftharpoons I$ transition consistently explains the entire body of experimental data: the "classical" values of exponents γ and ν for the susceptibility and the correlation radius [11, 13], respectively, also the exponent $\beta \approx 1/4$ for the temperature dependence of the order parameter first obtained by Keyes [16], without the need to introduce "long-range interaction" [1].

We also measured the specific heat of the BMOAB + iso-octane mixture in the vicinity of the critical point of liquid–liquid equilibrium (Fig. 1). The results of these measurements are shown in Fig. 5. Here the critical exponent was found to be $\alpha = 0.114 \pm 0.011$ and the ratio $A_0^-/A_0^+ = 1.97 \pm 0.40$ correspondingly. Both values are universal for all liquids and liquid mixtures with a short-range intermolecular interaction potential [9], which further confirms the short-range character of intermolecular forces in a liquid crystal.

NOTATION

T_T^-, disappearance temperature of the isotropic phase; T_T^+, appearance temperature of the isotropic phase; x, impurity concentration; λ, latent heat of transition; R, universal gas constant; C_p, specific heat at constant pressure; Φ, thermodynamic potential; Q, order parameter; v, molecular volume; r_0, radius of direct interaction; α, β, γ, ν, critical exponents for the specific heat, the order parameter, the susceptibility, and the correlation radius, respectively.

TABLE 3. Constants in the Interpolation Formula (3)

Nematic substance	B_1^+	B_1^-	B_2^+	B_2^-
MBBA	2,87±0,44	1,10±0,03	0,21±0,03	0,050±0,03
BMOAB	2,90±0,39	1,04±0,12	0,22±0,03	0,032±0,09

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