Dilatometric investigation of phase transitions in a BBOA liquid crystal at high pressures

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Results are presented of a dilatometric investigation of phase transitions in the liquid crystal *N*-(4-*n*-butylhydroxybenzylidene)-4-*n*-octylaniline (BBOA or 40.8) at high hydrostatic pressures (up to 6 kbar). The phase diagram and the orders of the phase transitions in BBOA are found. A critical end point corresponding to the crossing of the lines for the continuous S_A-N phase transition and for the first-order S_B-S_A phase transition is found. The thermodynamic quantities ($\Delta V, \Delta S$) that are indicative of the thermodynamics of first-order phase transitions are calculated. It is concluded that the nature of the variation of ΔV and ΔS along the S_B–S_A equilibrium line point to a crossover between two- and three-dimensional melting. The behavior of the thermal expansion in the vicinity of the continuous S_A–N phase transition is analyzed.

INTRODUCTION

Liquid-crystal substances are an example of a surprising variety of forms of the ordered state of matter. An important property of these substances is the strongly pronounced anisotropy of interparticle-interaction energy, determined in the general case by certain characteristic energies and lengths. For this reason, the transition from the crystalline state to an isotropic liquid proceeds in liquid crystals not as ordinary melting, but breaks up into a sequence of phase transitions that correspond to vanishing of various order elements. An analysis of this situation requires, generally speaking, the introduction of an entire set of order parameters that interact with one another and with other degrees of freedom. The problem is aggravated also by the fact that the two-dimensional order, as well as the one-dimensional one possessed by a number of mesophases, is generally speaking not long-range,[1] but it is not at all clear how this circumstance influences the thermodynamics of the phase transition.

Naturally, the problem of physically describing the liquid-crystal phases and of phase transitions in liquid crystals is quite complicated and in many respects unclear, and its solution requires first and foremost a reliable experimental foundation.

We report here the results of a dilatometric investigation of phase transitions in *N*-(4-*n*-butyloxybenzylidene)-4-*n*-octylaniline (BBOA or 40.8) at high pressure. The BBOA liquid crystal is distinguished by having good chemical stability and a classical sequence of phase transitions at atmospheric pressure:

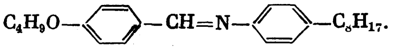
$$Cr \xrightarrow{311.5\,\mathrm{K}} S_B \xrightarrow{323.05\,\mathrm{K}} S_A \xrightarrow{336{,}95\,\mathrm{K}} N \xrightarrow{352.0\,\mathrm{K}} I.$$

In the last few years BBOA became the object of intensive investigations.[2–7] Principal attention was paid in this case to the nature of the smectic *B* phase. It was established in the upshot that the S_B phase of BBOA is actually a true three-dimensional crystal, but with an anomalously low interlayer shear modulus.[7–11] It was just this circumstance which prompted the present investigation. We have previously[12] established that the S_B–S_A phase transition in MBMBAC (β-methyl-butyl-methoxybenzilidene-amino-cinnamate) terminates at a critical point, and according to structure data there is practically no interlayer correlation in this substance.

We have therefore deemed it of interest to track the evolution of the S_B–S_A phase transition at high pressure for the case of strong interlayer correlation. It became clear in the course of the investigation that a detailed study is needed also of the S_A–N phase transition. We obtained simultaneously certain data on the *N*–*I* and *Cr*–S_B transitions.

EXPERIMENTAL PART

The investigated material was obtained from "Princeton Laboratories" (USA) and used, after additional purification by recrystallization, as the absolute standard. The structural formula of BBOA is:



Two experimental procedures were used for the investigation: a piston piezometer[12] and a specially developed bellows micropiezometer with a capacitive displacement sensor of sensitivity ~10^{-7} cm^3. The temperature and pressure were stabilized in these experiments to within ~10^{-3} K and ~0.1 bar. The temperature was measured with a TSPN-1 platinum resistance thermometer accurate to ± 10 bar. We used in the experiment an electronic system of automatic gathering and reduction of the data.

Figure 1 shows the temperature dependence of the specific volume *V* of the investigated substance and of its derivative $\partial V/\partial T$ at atmospheric pressure. It can be seen from the figure that the S_A–N phase transition can be classified as continuous, whereas the remaining ones are of first order. On the basis of the experimentally obtained *P*–*V*–*T* data we determined the volume and entropy discontinuities ΔV and ΔS in the first-order phase transitions. ΔS was calculated using the Clausius-Clapeyron equation, and the slope of the phase-equilibrium curves was obtained by analytic differentiation of the equations for the transition lines.

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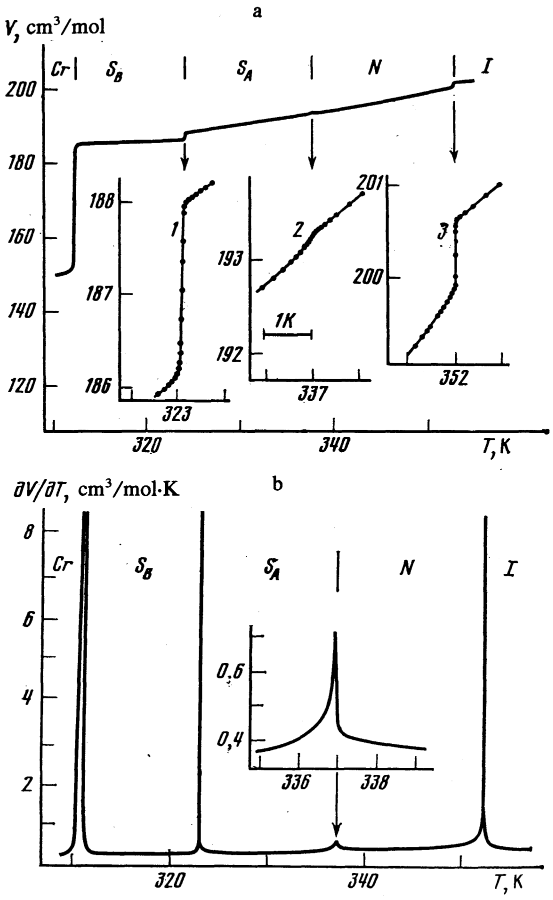

FIG. 1. a. Behavior of the specific volume V of the liquid crystal BBOA at atmospheric pressure: 1—near the S_B–S_A phase transition; 2—in the vicinity of the S_A–N transition; 3—in the vicinity of the N–I transition. b. Temperature dependence of the derivative $\partial V/\partial T$ at atmospheric pressure for BBOA.

It was established experimentally that pressure does not alter the character of the phase transitions in BBOA (Tables I and II). In contrast to the Cr–S_B and N–I phase transitions, the S_B–S_A transition has an unusual behavior of the volume jump ΔV and of the entropy along the phase-equilibrium line (Table II, see also Ref. 15).

DISCUSSION OF RESULTS

The Cr–S_B and N–I transitions

Since our main purpose was to study phase transitions in smectic mesophases, we shall not discuss here in detail the data on the Cr–S_B and N–I phase transitions. It should only be indicated that the values of the thermodynamic quantities that characterize the N–I transition in BBOA (see Table I) are perfectly typical for transitions of this type.[4,14,16] As for the Cr–S_B phase transition, a few remarks are in order. We note first that if the "crystallinity" of the smectic phase S_B is taken as a final and immutable fact, the Cr–S_B phase transition is not melting but a transition of the orientational and conformational ordering type. The large values of the volume and thermal effects obtained by us for the Cr–S_B transition in BBOA are therefore not surprising. On the other hand, our values for the entropy of this transition at atmospheric pressure exceed by an order of magnitude the data obtained in Refs. 4 and 16. Our measured temperatue $\approx 37°$ of the Cr–S_B transition at atmospheric pressure agrees with the data of Refs. 4 and 16. The value ≈ 33 °C sometimes cited for the temperature of this transition in the literature[10] corresponds apparently, as follows from our observation, to a metastable phase transition. It should be noted in general that BBOA at atmospheric pressure tends to form metastable phases, and reproducibility of the values of the specific volume for the Cr–S_B transition at atmospheric pressure could be obtained only if the substance was crystallized beforehand under pressure.

The S_A–N transition

Out of the many predictions of the theory concerning to the character of th S_A–N phase transition,[17–23] experiments confirmed only one conclusion, that this transition can take place both jumpwise and continuously. At present, however, no unambiguity whatever exists in the results of investigations of continuous phase transitions. Studies of the heat capacity near the S_A–N transition and work on the determination of the critical exponent α yielded values of α from 0 to 0.45 (Refs. 24–30). In Ref. 24 were investigated a number of liquid-crystal homologs of the type $\bar{n}S5$ and it was concluded that crossover exists between the critical and tricriti-

TABLE I. Thermodynamics of the Cr–S_B and N–I phase transitions in BBOA.

T, K	P, kbar	ΔV, cm³/mol	$\Delta V/V$, %	$\Delta S/R$	Source
		Cr–Sb transition			
311,2	0,001	–	–	1,9	[4]
310	0,001	–	–	1,9	[16]
311,5	0,001	35	20	19,8	Present work
374	3,060	16,5	–	9,6	»
		N–I transition			
352	0,001	–	–	0,02–0,1	[4]
351,7	0,001	–	–	0,48	[16]
352,0	0,001	0,75	0,3	0,26	Present work
384,2	1,075	0,4	–	0,18	»

TABLE II. Thermodynamics of the S_B–S_A and S_B–N phase transitions in the liquid crystal BBOA.

T, K	P, kbar	V, cm^3/mol	ΔV, cm^3/mol	$\Delta V/V$, %	$\Delta S/R$	Source
			S_B–S_A transition			
322,91	0.001	–	–	–	0.67	[4]
321,95	0.001	–	–	–	0.74	[16]
–	0.001	–	–	–	0,81	[30]
323.05	0.001	186.1	1,9	1.02	0.82	Present work
332.4	0,32	181.9	1,95	1.07	0.86	»
348.1	0.89	175.9	2.01	1.14	0.92	»
375,2	1,97	167.3	2.13	1.27	1,05	»
			S_B–N transition			
397.6	2.95	161.2	2.34	1,45	1.25	»
418.4	3.93	155.7	2.39	1,53	1,39	»
430,1	4.51	152.8	2.38	1.56	1.45	»
437,9	4.9	150.9	2.34	1,55	1.48	»
448.9	5.49	148.2	2,33	1,57	1.56	»
462.4	6.25	145.0	2,27	1.57	1.65	»

cal behavior when the length of the chain $\bar{n}$ is increased. An exponent $\alpha \approx 0$ is suggested in Ref. 24 for the substance $\overline{8S}\,5$, thus confirming the de Gennes superconducting analogy.[17–18] At the same time the value $\alpha = 0.45$ for the liquid crystal $\overline{10S}\,5$ corresponds to a tricritical behavior.[30] For 8OCB a value $\alpha \sim 0$ (logarithmic singularity) was obtained in Ref. 29 and $\alpha = 0.25$ in Refs. 26–28. An interesting result is that of Ref. 25, where two values of the exponent, $\alpha = 0$ and $\alpha = 0.25$ were obtained for two 8OCB samples from different sources. The heat capacity of the liquid crystal BBOA was investigated in Ref. 27 and $\alpha = 0.2$ was obtained. There is no agreement in the data for the other exponents.

Great interest attaches to the vanishing (at pressures above 1 kbar), observed in Ref. 26, of the thermal anomalies that accompany the S_A–N transition in 8OCB (this question is discussed in Ref. 31). A similar phenomenon was observed by us for S_B–S_A transitions in MBMBAC.[12]

It can be suggested that the vanishing of the thermal singularities means that at a pressure of approximately 1 kbar the phase diagram of 8OCB has a critical point analogous to the critical point of a one-component liquid, meaning that the smectic phase A and the nematic crystal have different symmetries. Inasmuch as even in an ideal smectic A there is no true long-range order, it can be suggested that in some objects (by virtue of the presence of impurities, of the influence of boundaries, etc.), particularly in 8OCB, there is strictly speaking no S_A phase, but a nematic phase with a large but finite correlation length of the smectic A fluctuations, and this can serve as the order parameter. This case, of course, cannot agree with the de Gennes helium analogy.[17] We note that measurements of the correlation length in the vicinity of the S_A–N transitions, performed in a magnetic field that suppresses the fluctuations of the director, values not exceeding $90/q_A$ were obtained for the direction perpendicular to the director (q_A is the reciprocal-lattice vector for smectic A).[32]

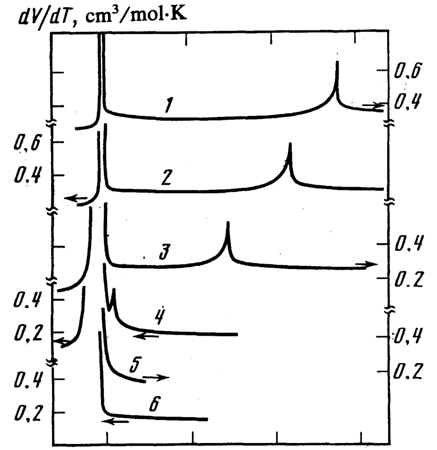

FIG. 2. Dependence of the derivative $\partial V/\partial T$ in BBOA on the temperature for different pressures: 1—1 bar; 2—0.89 kbar, 3—1.97 kbar, 4—2.5 kbar, 5—2.7 kbar, 6—2.95 kbar.

Our investigation has shown that the S_A–N phase transition in the BBOA liquid crystal is continuous (Fig. 1). The thermodynamic singularities that acompany this transition, in contrast to 8OCB,[20] are not altered in any substantial way up to a pressure on the order of 2.5 kbar. This gives grounds for assuming that a true smectic A phase exists in BBOA.

The analysis of our experimental data on $\partial V/\partial T$ was carried out by the maximum-likelihood method.[33] The adequacy criterion used was the quantity

$$F = \frac{1}{N-M} \sum_{i=1}^{N} \frac{\Delta y_i^2}{\sigma_i^2},$$

where Δy_i are the deviations from the approximation curve, σ_i^2 is an estimate of the variance of one measurement, and N and M are the numbers of the experimental points and of the approximation parameters. It was found that the data on $\partial V/\partial T$ in the S_A phase, obtained at atmospheric pressure, cannot be adquately described ($F = 5 - 7$) by the usual expression

$$y = K_0 + K_1 |\tau|^{-\alpha}; \qquad \tau = \tau_{AN} = (T - T_{AN})/T_{AN}. \qquad (1)$$

The exponent α in this approximation turned out to depend on the range of the employed τ. A natural explanation of this fact is the presence of crossover, not taken into account in (1), between the critical and tricritical regions. This account is necessary also because the homolog 40.6 which is close to BBOA (40.8) apparently undergoes a first-order phase transition.[30] A second circumstance that must be taken into account is the proximity of the S_B–S_A transition ($[T_{AN} - T_{AB}]/T_{AN} < 0.05$). When these factors are taken into account we can write for the second derivatives of the thermodynamic potential the expression

$$y=K_0+K_1|\tau_{AN}|^{-\alpha'}+K_2|\tau_{AB}|^{-\alpha_1}+K_3|\tau_{AN}{}^+|^{-1/2}, \tag{2}$$

where

$$\tau_{AB}=(T-T_{AB})/T_{AB}, \quad \tau_{AN}=(T-T_{AN})/T_{AN},$$

$$\tau_{AN}{}^+=(T-T_{AN}{}^+)/T_{AN}{}^+.$$

The last term in (2) makes it possible to take into account the possible presence of crossover[34] (T_{AN}^+ exceeds somewhat the temperature T_{AN} of the S_A–N transition and is determined in the course of the approximation). The third term in (2) was introduced to take into account the pre-transition phenomena connected with the S_B–S_A transition. Since these phenomena are weakly manifested (see Fig. 1), the exponent α_1 in (2) cannot be determined reliably. It was found that α_1 has little effect on the quality of the approximation and on the value of α^1. We have therefore postulated the presence of logarithmic divergence for the S_B–S_A transition ($\alpha_1 = 0$).

At the same time, a search for the values of K_0, K_1, K_2, K_3, α', $T_{AN}{}^+$ in (2) for the entire region of the existence of the S_A phase ($\tau < 0.05$) at fixed T_{AN} and T_{AB} yielded the following values:

$$K_0=0{,}347; \quad K_1=0{,}0092;$$

$$K_2=0{,}0415; \quad K_3=0{,}0132;$$

$$\alpha'=0.23;$$

$$T_{AN}{}^+=337{,}04; \quad F=0.98$$

$$(T_{AN}=336{,}954\,\mathrm{K},\ T_{AB}=323{,}05\,\mathrm{K}).$$

The confidence interval for a 0.95 probability yields a range of α' from 0.1 to 0.3. We emphasize that the assumption that the coefficient K_2 or K_3 is equal to zero yielded respectively $F_2 = 5.5$ and $F_3 = 2.5$, which negates the adequacy of the approximation.

A similar analysis of the data obtained at high pressure is not effective, in view of the rapid reduction of the region where the phase S_A exists (see Fig. 2) and of the additional error due to the instability of the pressure.

The experimental data on $\partial V/\partial T$ at T/T_{AN} can be described in the interval $\tau_{AN} < 0.01$ by the expression (1) with a fixed value of the exponent $\alpha = 0.2$ ($F = 1.0$). The weakness of the pretransitional phenomena in this region prevents a direct search for the exponent α.

Thus, even though BBOA is apparently a "true" smectic A and the S_A–N transition is continuous, the exponent α obtained from thermal-expansion data does not agree with the helium analogy.(1)

Terminal critical point

It follows from the BBOA phase diagram that the smectic A phase of this substance exists only in a limited pressure interval, since the line of the S_A–N phase transitions terminates at a pressure close to 2.7 kbar in a triple point of a special type, in the vicinity of which nematic and smectic A and B phases coexist.[15] In contrast to the usual triple point, in this so-called terminal critical point (TCP) there converge not three first-order phase-transition lines, but two first-order phase-transition lines and one continuous-transition line.(2)

Thus, at the TCP the first-order S_B–N transition takes place only at the instant when the high-temperature phase loses stability, in analogy with the phase transition within the framework of the Slater model.[35] This leads to the appearance, near the TCP, of clearly pronounced pretransitional phenomena from the side of the nematic phase (see Fig. 2). However, the analogy with the Slater model is not complete, since the ordered smectic B phase in the TCP does not lose stability and can be metastable in the region of the nematic phase.

The existence of a TCP on the phase diagram of a liquid crystal points to the presence of a strong interaction between the order parameter ρ_B that corresponds to two-dimensional ordering in a direction perpendicular to the director axis, and the order parameter ρ_A corresponding to one-dimensional ordering along the director.

The behavior of the jumps ΔV of the volume and ΔS of the entropy of the first-order phase transitions S_B–S_A and S_B–N in the vicintiy of the TCP is determined principally by the destruction of the one-dimensional smectic order ρ_A on the S_B–S_A transition line as the TCP is approached and by the decay of the smectic fluctuations in the nematic phase on the S_B–N transition line with further increase of the pressure.

The S_B–S_A transition

Since the smectic B of BBOA is a true three-dimensional crystal,[2,3] the S_B–S_A phase transition can be regarded as two-dimensional melting in a three-dimensional system. At the TCP and at higher pressure the transition is into a positionally disordered nematic phase and is ordinary three-dimensional melting. By comparing the data on the thermodynamics of the transition at atmospheric pressure and at the TCP, we can obtain some information on the thermodynamics of two-dimensional melting. Unfortunately, the purely positional contribution made to the entropy by the pressure of the smectic B is masked by contributions from other degrees of freedom: the entropy of the S_B–N transition is $(1.2$–$1.5)R$, much higher than the melting entropy of simple three-dimensional systems ($\approx 0.7R$, Ref. 38). Exclusion of this excess entropy in one way or another (see Ref. 15) yields for the jump of the entropy of two-dimensional melting a value $\Delta S = (0.3$–$0.45)R$. It is interesting that the ratio of the entropies of the S_B–S_A transition at atmospheric pressure (maximum two-dimensionality $d \approx 2$) to the entropy of the S_B–N transition at the TCP ($d = 3$) is almost exactly 2/3.

It is logical to attribute the increase of the entropy and volume jumps along the S_B–S_A transition line with increasing pressure to crossover between two-dimensional and three-dimensional melting.

In conclusion, the authors are sincerely grateful to M. S. Costantino for sending the samples, and to B. M. Bolotin for making possible their purification.

[1)] One cannot, however, exclude the possible influence of impurity on the values obtained by us for the exponent α (Ref. 36).

[2)] It appears that such a point was first observed on the phase diagram of He^4 as the point of intersection of the line of the transitions with the melting curve.[37]

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