Thermodynamics of the nematic liquid crystal-isotropic liquid phase transition at high pressures

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The thermodynamics of the nematic phase transition has been investigated experimentally for the first time, for three liquid-crystal substances, at high pressures. The pertinent numerical data are presented. In the case of *p*-azoxyanisole, the thermodynamics of crystallization was also investigated. The possibility is discussed of the existence of an isolated critical point on the nematic transition curve. On the basis of the experimental data, it is concluded that short-range repulsive interaction plays a decisive role in nematic ordering.

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INTRODUCTION

According to Landau's phenomenological theory[1] the phase transition from nematic liquid crystal to isotropic liquid is a phase transition of the first order over the whole extent of the equilibrium curve with the exception of a single point, where this transition may prove to be of second order. It has been shown[2] that the occurrence of an isolated critical point on the nematic transition curve should, in the simplest case, be accompanied by the appearance of yet another uniaxial nematic phase with the "perpendicular" type of ordering. It is obvious that within the framework of the phenomenological theory it is impossible to decide whether an isolated point exists in general.

The semimicroscopic theory of Maier and Saupe[3] describes the nematic-isotropic liquid transition as a first-order phase transition over the whole possible range of pressures and temperatures. It must be emphasized that this conclusion of the theory is entirely determined by the form of the model Hamiltonian.

It is useful to illustrate the deductions of the Maier-Saupe theory by means of results that follow from the so-called Klein theorem[4,5] which states that in a system of particles whose potential energy is a homogeneous function of order n of the coordinates of the particles, the nonideal part of the partition function does not depend separately on the density and the temperature but is a function of the single combined variable $\rho^{n/3}/T$, where ρ is a dimensionless density and T a dimensionless temperature. It is obvious that the presence of angular components of the interaction potential does not destroy the validity of this theorem. From this theorem follow statements of the constancy of the parameter $\rho^{n/3}/T$, the relative discontinuity of volume $\Delta V/V_N$, the entropy of transition $\Delta S/R$, and the order parameter η along the transition curve. All of this is true also in the Maier-Saupe theory, although all the conclusions are stated also for anisotropic van der Waals interaction.

Under the indicated limitation on the interparticle potential, the coefficients of the higher-order terms in the expansion of the dimensionless free energy in powers of the order parameter are power functions of the dimensionless parameter[6] $\rho^{n/3}/T$. Thus the coefficient of the third-order term in the expansion of the free energy is never zero, and this precludes the existence of an isolated point on the transition curve.[1]

Undoubtedly a necessary condition for existence of an isolated point on the transition curve is the presence of a component of the interparticle potential of very special form, capable under certain conditions of leading to the "perpendicular" type of ordering. If we ignore this possibility as being highly improbable, then the details of the behavior of the thermodynamic quantities that describe the nematic phase transition will be determined by the relative contribution of the van der Walls attraction and of the short-range repulsion to the energy of nematic ordering. In any case, the investigation of the thermodynamics of the nematic phase transition at high pressures can cast light on a

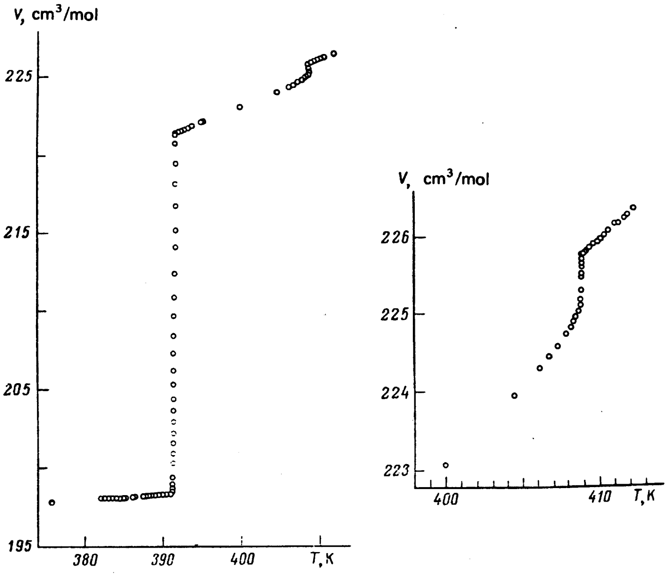
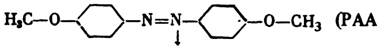


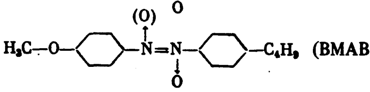
FIG. 1. Variation of the molar volume of PAA with temperature in the range of melting and of the nematic phase transition, at atmospheric pressure. At the right, the region of the nematic phase transition is shown on an enlarged scale.

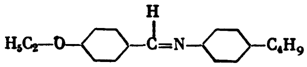
number of controversial questions, and this was the basic motive for the organization of the present experiments.

EXPERIMENTAL PART

We investigated the nematic-isotropic liquid phase transitions in three substances: *p*-azoxyanisole (PAA), *n*-butylmethoxybenzene (BMAB), and ethoxybenzylidene-*n*-butylaniline (EBBA). The structural formulas of these substances have the following form:


(PAA),


(BMAB),


(EBBA).

In one of these substances (PAA), we investigated the crystal-liquid crystal transition.

The choice of objects of research was determined primarily by their availability in sufficiently pure form.$^{2)}$ The method of investigation consisted of measurement of the volume of material, the temperature, and the pressure in the neighborhood of the phase-transition curve. The volume measurements were made with a piezometer with an intermediate liquid.[7] The only difference between the present technique and that described in Ref. 7 lay in the possibility of direct contact of the intermediate liquid (mercury) with the substance under investigation; this increased the accuracy of the pressure measurement. Specially designed experiments showed absence of appreciable interaction between the substances under investigation and the mercury.

To determine the null volume of the piezometer, we used data of dilatometer researches[8] (PAA),[9](EBBA) and data from our picnometer determinations of the density of BMAB. The accuracy of the volume measurements at high pressures was no worse than 0.05%; the temperature and pressure were measured with accuracy ±0.01 °C and ±5 kg/cm^2. As a rule, the measurements were made under isothermal conditions; but for each substance, we also investigated the thermal expansion at atmospheric pressure. Figures 1 and 2 show one of the compression isotherms and an expansion isobar at atmospheric pressure for PAA.

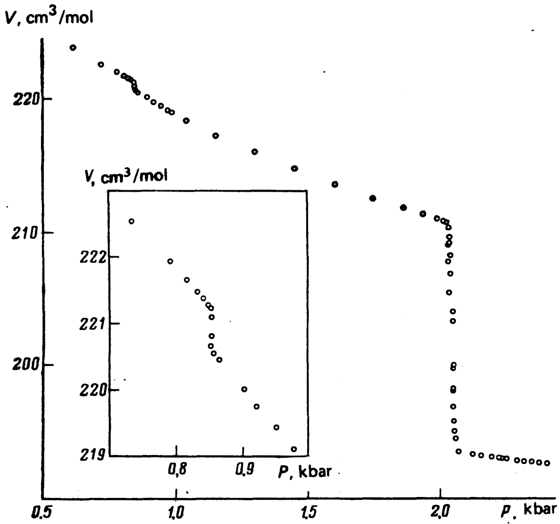


FIG. 2. Compression isotherms of PAA at $T=448.21$ K. The inset shows the region of the nematic phase transition on an enlarged scale.

On the basis of the data obtained, we determined the discontinuities of volume ΔV in the phase transitions. Further, by use of the Clausius-Clapeyron equation we calculated the changes of enthalpy ΔH, entropy ΔS, and internal energy ΔU. Unfortunately the very small values of the discontinuities of volume in the nematic phase transition and the difficulty of determining the start of the phase transition against the background of clearly expressed pretransitional phenomena made it impossible to determine the values of these thermodynamic quantities with accuracy better than 5%. The results of the measurements and calculations are given in Tables I and II and illustrated in Figs. 1–3.

We note that the limits of attainable pressures and temperatures were determined by the thermal stability of the substance. Results describing the thermodynamics of the nematic transition in PAA were published earlier[10]; in the present paper, these data have undergone slight revision.

DISCUSSION OF RESULTS

As is seen from Table II and Fig. 3, the discontinuity of entropy $\Delta S/R$ and the relative discontinuity of volume $\Delta V/Y_N$ in the nematic phase transition decrease with temperature in all three substances investigated. But this decrease is not catastropic and certainly gives no indication of the existence of a critical point anywhere on the transition curve. Especially significant in this respect is the behavior of the discontinuity of entropy $\Delta S/R$, whose change in all three substances is very small and does not exceed 20%. Such behavior of the entropy, in general, is consistent with a very small variation of the order parameter η along the nematic transition curve[11] (according to Landau's theory, $\Delta S \sim \eta^2$).

We turn our attention to Fig. 4, which shows the correlations between the entropy of transition $\Delta S/R$ and the relative discontinuity of volume $\Delta V/V_N$ in the nematic transition. It is evident from Fig. 4 that the behavior trends of $\Delta V/V_N$ and $\Delta S/R$ are such that these quantities cannot vanish simultaneously; with unlimited decrease of $\Delta V/V_N$, which corresponds to unlimited compression, $\Delta S/R$ approaches a finite value.

We shall consider the question of the behavior of the

TABLE I. Thermodynamic parameters of the melting of PAA.

T, K	P, bar	ΔV, cm^3/mol	$\Delta S/R$	ΔU, cal/mol	T, K	P, bar	ΔV, cm^3/mol	$\Delta S/R$	ΔU cal/mol
391.45	1	23.8	8.84	6874	417.90	888	20.52	8.81	6878
394.75	107	23.35	8.84	6873	427.51	1240	19.43	8.75	6856
405.55	443	21.95	8.83	6882	448.21	2043	17.37	8.61	6821
412.66	693	21.09	8.81	6875	448.41	2056	17,37	8,62	6826

TABLE II. Thermodynamic parameters of nematic-isotropic liquid phase transitions.

T, K	P, bar	V_N, cm^3/mol	ΔV, cm^3/mol	$\Delta S/R$	ΔU, cal/mol
		PAA			
408.75	1	225.04	0.72	0.172	140
408.85	1	225.02	0.72	0.173	140
410.61	39	224.80	0.71	0.171	139
412.70	81	224.53	0.70	0.171	139
416.55	161	224.97	0.69	0.173	140
420.78	249	223.49	0.68	0.173	140
427.55	398	222.70	0.65	0.170	138
435.25	564	221.92	0.66	0.171	140
435.23	564	221.92	0.61	0.166	135
448.21	862	220.65	0.59	0.168	138
452.66	968	220.29	0.57	0.164	134
458.23	1104	219.80	0.54	0.160	131
		3MAB			
347.80	1	264.69	0.44	0.120	83
352.80	113	263.89	0.43	0.118	82
356.79	210	263.23	0.42	0.118	81
373.91	617	260.55	0.39	0.115	80
383.22	855	259.08	0.37	0.114	79
403.22	1379	256.32	0.34	0.110	77
413.14	1655	254.93	0.32	0.108	76
423.09	1935	253.61	0.31	0.106	75
433.05	2229	252.26	0.29	0.104	74
		EBBA			
352.41	1	283.50	0.60	0.182	127
354.41	44	283.70	0.57	0.174	122
369.91	471	279.23	0.53	0.173	121
380.74	765	277.11	0.49	0.167	118
387.80	965	275.70	0.47	0.165	116
394.15	1152	274.46	0.46	0.165	117
422.51	2044	269.42	0.40	0.159	114
438.91	2604	266.70	0.38	0.160	116
454.02	3148	264.34	0.34	0.150	110

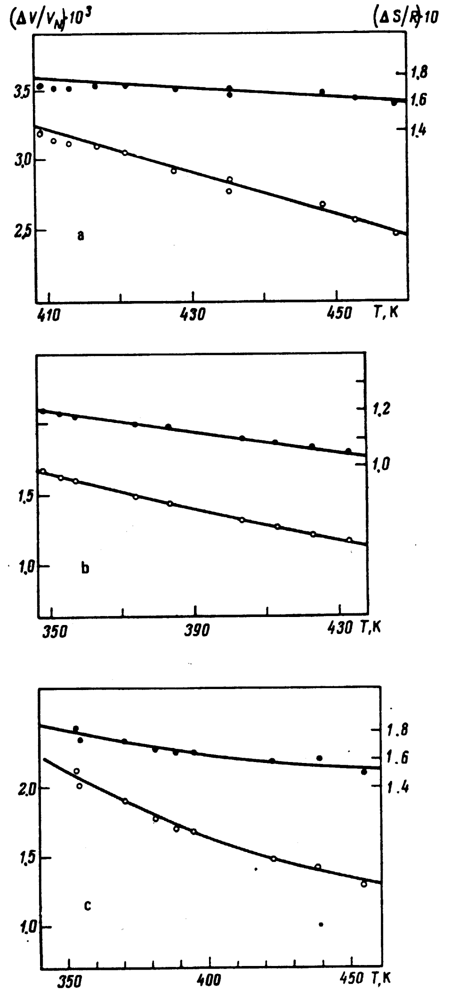


FIG. 3. Variation with temperature of the relative discontinuity of volume $\Delta V/V_N$ and of entropy $\Delta S/R$ in the nematic phase transition: a, for PAA; b, for BMAB; c, for EBBA.

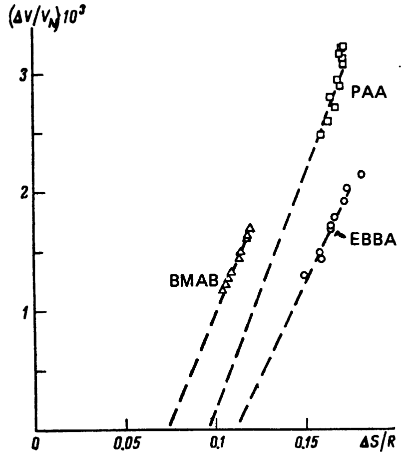


FIG. 4. Correlation of the relative discontinuity of volume $\Delta V/V_N$ and of the discontinuity of entropy $\Delta S/R$ in the nematic phase transition.

relative discontinuity of volume $\Delta V/V_N$. Figure 5 shows $\Delta V/V_N$ as a function of the absolute value of the discontinuity of volume ΔV. It is seen that ΔV approaches zero, the relative discontinuity of volume $\Delta V/V_N$ approaches a small but quite finite value,[3] the same for all three substances and equal to $\sim 0.2 \cdot 10^{-3}$. This is a very curious fact, showing that the flexible alkyl chains on the ends of the molecules make no appreciable contribution to the change of volume in the phase transition.

Thus the experimental data allow us to suppose that in the nematic phase transition the following relations hold:

$$\Delta V/V_N \to \text{const}, \quad \Delta S/R \to \text{const} \quad \text{as} \quad T, P \to \infty, \tag{1}$$

where the limiting values of $\Delta V/V_N$ are apparently the same for all three substances, whereas the limiting values of the entropy of transition are slightly different. It seems that this difference must be due to internal degrees of freedom of the molecule.

From what has been said, it may be concluded that

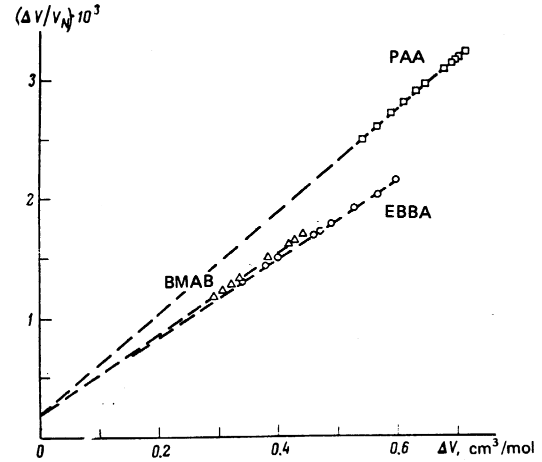


FIG. 5. Variation of the relative discontinuity of volume $\Delta V/V_N$ with the absolute value of the discontinuity of volume ΔV in the nematic phase transition.

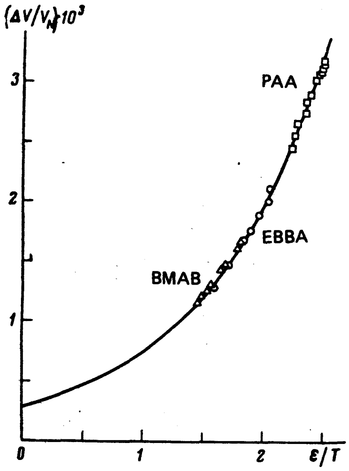


FIG. 6. Illustration of the exponential behavior of the relative discontinuity of volume $\Delta V/V_N$ as a function of the inverse temperature. The solid line shows the function $\Delta V/V_N = 0.27 \cdot 10^{-3} e^{\varepsilon/T}$. The calculation gives the following values of the parameter ε: 1016 K (PAA), 630 K (BMAB), 720 K (EBBA).

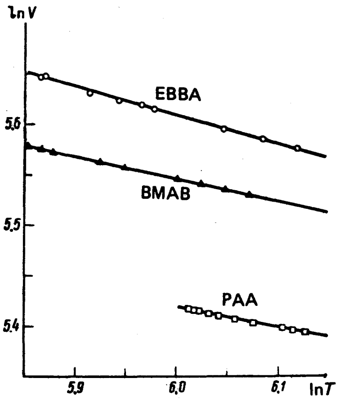


FIG. 7. Graph illustrating the power dependence of the molar volume of a nematic liquid crystal on the inverse temperature along the transition curve. The slopes of the lines correspond to the following values of the exponent n (see text): 14.31 (PAA), 13.74 (BMAB), 10.55 (EBBA).

the possibility of existence of an isolated critical point in substances of the type investigated seems extremely doubtful.

We must point to the astonishing similarity in behavior of the thermodynamic functions in the nematic phase transition and in the crystallization of simple substances of the argon type (on the crystallization of argon, see Stishov[12]). The marked analogy allows us to assume that the chief contribution to the orientational energy comes from the energy of anisotropic repulsion with a pair potential of the form

$$\Phi(\mathbf{r}_{1,2}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) = f(\mathbf{n}_{1,2}, \mathbf{\Omega}_1, \mathbf{\Omega}_2)/|\mathbf{r}_{1,2}|^n.$$

where $\mathbf{\Omega}_1$ and $\mathbf{\Omega}_2$ are unit vectors determining the orientation of the molecules, r is the distance between the centers of gravity of the molecules, and $\mathbf{n}_{1,2} = \mathbf{r}_{1,2}/|\mathbf{r}_{1,2}|$, then, as was mentioned in the Introduction, at high temperatures, when the attractive interaction may be neglected, the parameters of the nematic phase transition will be determined by the relations[12]

$$V_{N,I} \sim T^{-n/3}, \tag{2}$$

$$\Delta V/V_N = \text{const}, \tag{3}$$

$$\Delta S/R = \text{const}. \tag{4}$$

We emphasize that the relations (3) and (4) agree with our conclusions about finite asymptotic values (1) for $\Delta S/R$ and $\Delta V/V_N$.

In the intermediate temperature range, when the energy of attraction may be treated in the van der Waals approximation, the corresponding relations must be written in the form[12]

$$\Delta V/V_N = (\Delta V/V_N)_0 e^{\varepsilon/T}, \tag{5}$$

$$\Delta S/R \approx c + \gamma \Delta V/V_N. \tag{6}$$

In view of the smallness of the discontinuity of volume in the nematic phase transition, it must be supposed that the relation (2) retains its form in the intermediate temperature range also. It is obvious that the experimentally attainable temperatures in the present case are not sufficiently high to satisfy fully the requirements for applicability of the van der Waals approximation; nevertheless, the experimental data do not contradict the relations (5) and (6). As can be seen from Fig. 6, the variation of the relative discontinuity of volume $\Delta V/V_N$ with temperature is excellently described by the exponential formula (5) with the single value $(\Delta V/V_N)_0 \approx 0.27 \cdot 10^{-3}$. The variation of volume with temperature is also well described by the power function (2) with values $n \approx 10$ to 14 (see Fig. 7).[4)] We note that the quantity n in (2) is an exponent that describes the law of interparticle repulsion, and the estimates obtained agree with generally accepted ideas regarding its possible values.[13]

In conclusion, it must be pointed out that the estimates and considerations presented above, in view of the limited range of temperatures and densities investigated, cannot serve as the basis for categorical assertions, but merely favor the idea of the dominant role of anisotropic repulsive interaction in nematic ordering.

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[2)] The samples of PAA and EBBA, purified by repeated recrystallization, were provided by I. G. Chistyakov. The BMAB sample, of NIOPIK manufacture, was a mixture of two isomers and was obtained from M. A. Anisimov and E. L. Sorokin.

[3)] It is not difficult to show that the relative error in determination of the asymptotic value of $\Delta V/V_N$ by linear extrapolation of the function $\Delta V/V_N = f(\Delta V)$ is practically equal to the error of determination of ΔV. At the same time, the legitimacy of the linear extrapolation remains in question.

[4)] Because of improvement of the experimental data, the values of the parameters n and ε (see Fig. 6) differ somewhat from those that we gave earlier for p-azoxyanisole[10].

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Theory of longitudinal magnetoresistance in weak magnetic fields

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Longitudinal magnetoresistance depends on the ratio of the distance between the Landau levels to the level width due to the interaction of the electron with the phonons and the impurities. If the level width exceeds the distance between the levels, resonance effects are impossible and the corresponding terms are exponentially small. The quantum corrections that determine the longitudinal magnetoresistance turn out to be analytically (quadratically) dependent on the magnetic field. The method of translationally invariant kinetic equation makes it possible to calculate these corrections for different scattering mechanisms. In scattering by ionized impurities, owing to the slow decrease of the Coulomb potential with distance, the order of magnitude of the magnetoresistance increases and it is determined by the classical theory, while its sign turns out to be negative.

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According to ordinary kinetic theory, application of a magnetic field does not change the resistance along the direction of the magnetic field. The magnetic field is regarded to be applied along a symmetry axis of the crystal, so that no resistance change due to crystalline anisotropy takes place. The magnetoresistance is zero because the action of the magnetic field on the electron system is taken into account only classically—via the Lorentz force. According to quantum mechanics, a system of Landau levels is produced in a magnetic field and the longitudinal magnetoresistance of the electrons that have a discrete spectrum does not vanish. It was investigated for the case of extremely strong (quantizing) magnetic fields by Adams and Argyres.[1] They have noted that when electrons are scattered by ionized impurities, the longitudinal magnetoresistance can be negative in a definite range of magnetic fields. In the limit of nonquantizing magnetic fields, allowance for the quantum corrections yields a nonzero longitudinal magnetroesistance. Argyres,[2] considering the scattering of electrons by acoustic phonons, reached the conclusion that a region of negative magnetoresistance exists. However, the order of magnitude and the dependence on the magnetic field, which were determined in Ref. 2, turned out to be incorrect, as was demonstrated by Dubinskaya.[3]

According to Argyres[2] and Dubinskaya,[3] the magnitude and sign of the magnetoresistance are determined by the resonant behavior of the state density and of the collision frequency in the vicinity of the Landau levels. This point of view implies tacitly that the system of Landau levels is well defined, i.e., the distance between the levels, Ω, which is equal to the frequency of revolution of the electron in the magnetic field, exceeds their smearing, which is of the same order as the reciprocal relaxation time $1/\tau_p$. It can be assumed that at $\Omega < 1/\tau_p$ the resonance effects are strongly smeared out. Thus, despite the fact that the considered effect is longitudinal, it depends essentially on $\Omega\tau_p$. A theory of magnetoresistance for a small $\Omega\tau_p$ was developed next.

In the first part of the present paper we determine, in the Landau-number representation, the magnetoresistance in the case of elastic scattering of electrons by acoustic phonons. It is shown that the terms that might be resonant, are small for small $\Omega\tau_p$ like $\exp(-\pi/\Omega\tau_p)$, and the density of states and the relaxation time can be regarded as smooth functions of Ω. At a small ratio of the distance between the energy levels to the average energy, the relaxation time, and the state density, meaning therefore also the magneto-

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