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EXPERIMENTAL DETERMINATION OF THE THERMODYNAMIC PROPERTIES OF THREE NEMATIC LIQUID CRYSTALS

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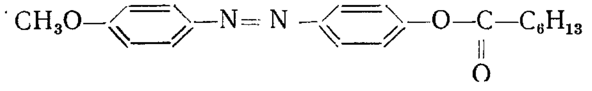
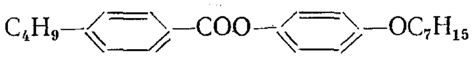
The results of measurements of the density, the magnetic susceptibility, the molar specific heat, and the heat of the nematic–isotropic transition are reported.

The efficient design of new types of liquid-crystal devices, the development of theoretical concepts about the liquid-crystalline state, and advances in the well-conceived synthesis of promising liquid-crystal materials may be attributed to the extent of knowledge of the most important physical properties of existing liquid crystals. Unfortunately, despite the heightened interest in liquid crystals both in the Soviet Union and abroad, experimental data on the physical properties of these objects are extremely sparse, and those which are available suffer from low accuracy and have been obtained from samples with varying degrees of purity. Consequently, the postulated models and the analytical relations derived theoretically on the basis thereof have not been adequately tested, so that their application for calculating the properties of liquid crystals is not yet justified. For example, it has been shown previously [1] within the framework of molecular-statistical theory [2] that the calculated values of the specific heats are in good agreement with the experimental, but large (four- to sixfold) discrepancies are observed for the heats of the nematic–isotropic transition. It is difficult to ascertain the causes of such a large discrepancy, because the data of different authors are used in the calculations and comparisons. Naturally, it is preferable to base the verification and substantiation of any particular model on results obtained from the same sample or from samples having the same degree of purity.

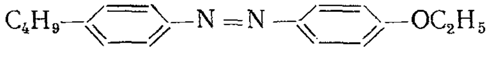
In the present article, therefore, we report an experimental study of the temperature dependences of the density, the magnetic susceptibility, and the molar specific heat, as well as the heat of the nematic–isotropic transition. We investigated the three analytically pure nematics N-62, N-72, and N-100, which were not subjected to additional purification. The structural formulas of these substances have he following form:



(N-62)



(N-72)



(N-100)

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TABLE 1. Temperature Dependence of the Density of Nematics

N-62		N-72		N-100	
T, K	$\rho\cdot10^3$, kg/m^3	T, K	$\rho\cdot10^3$, kg/m^3	T, K	$\rho\cdot10^3$, kg/m^3
331,62	1,07970	309,77	1,01296	324,93	1,02828
335,16	1,07679	311,54	1,01130	331,76	1,02275
338,60	1,07387	312,77	1,01010	335,33	1,01971
342,22	1,07089	313,87	1,00898	338,92	1,01670
345,78	1,06776	314,93	1,00784	342,50	1,01356
349,33	1,06470	315,64	1,00698	346,08	1,01033
352,93	1,06152	316,20	1,00634	347,86	1,00867
356,71	1,05869	316,62	1,00576	349,63	1,00702
360,28	1,05485	316,93	1,00525	351,41	1,00520
363,86	1,05145	317,15	1,00473	353,19	1,00393
366,00	1,04930	317,29	1,00421	354,25	1,00211
367,77	1,04748	317,36	1,00389	354,97	1,00119
369,11	1,04599	317,43	1,00351	355,30	1,00069
370,08	1,04485	317,51	1,00326	355,56	1,00031
370.77	1,04395	317,59	1,00317	355,72	0,99962
370,95	1,04368	317,96	1,00281	355,93	0,99728
371,28	1,04318	318,67	1,00214	356,01	0,99709
371,46	1,04289	319,74	1,00120	356,73	0,99641
371,53	1,04272	321,87	0,99936	358,55	0,99478
371,60	1,04246	324,01	0,99758	360,33	0,99327
371,68	1,04142	326,18	0,99581	362,14	0,99179
371,75	1,04074	328,32	0,99405	363,93	0,99032
371,81	1,04058	330,47	0,99231	365,69	0,98888
371,98	1,04037			367,46	0,98743
373,04	1,03937			369,28	0,98595
374,10	1,03838			371,05	0,98452
375,89	1,03676			374,58	0,98167
377,68	1,03518			378,50	0.97857

The experimental study of the temperature dependence of the density was performed with the use of a single-capillary pycnometer on the apparatus and according to the procedure described in [1]. To extend the temperature range and increase the accuracy of the measurements near the phase transition we modified the thermostatting system [3]. The relative error of determination of the density did not exceed 0.06%, and the contribution of random error in the analysis of its temperature dependence was ~ 0.01%. The measurements were carried out in the isotropic state and in the mesophase up to the crystallization temperature. The resulting data (Table 1) were processed by the least-squares method in the form

$$\rho = [A + B\tau + C\tau^n]\cdot 10^{-3},$$

where $\tau = T_t - T$ in the mesophase and $\tau = T - T_t$ is the isotropic state. The temperature of the nematic–isotropic transition was determined from the maximum of the coefficient of thermal expansion, which was calculated concurrently maximum of the coefficient of thermal expansion, which was calculated concurrently with the density. As a result of processing, we obtained the values of the coefficients A, B, C, and n in the mesophase and in the isotropic state (Table 2). The deviation of the experimental points from the smoothed curves for the investigated substances does not exceed 0.01%. Using the values of A, B, C, and n, we readily obtain analogous relations for the coefficient of thermal expansion and the molal volume.

We used the data of the experimental density measurements to calculate the jump of the molal volume at the nematic–isotropic transition according to the procedure of [4] (Table 2). It is important to note that a rather large (~ 0.5°) temperature interval of the two-phase state was observed in the case of the N-72 liquid crystal, and this affects the value of the molar volume jump.

The magnetic susceptibility was measured by the relative method of Gouy on the apparatus and according to the procedure described in [1]. The relative error of determination of the magnetic susceptibility did not exceed 0.5%, and the contribution of random error in the analysis of its temperature dependence was ~ 0.2%. All the investigated substances are diamagnetic. In the isotropic state the specific magnetic susceptibility is independent of the temperature within the experimental error limits. The resulting average values of this quantity are given in Table 2. The results obtained in the mesophase (Table 3) were processed by the least-squares method in the form

$$\varkappa_{\parallel} = -[A + B(T_t - T)^n]\cdot 10^{-9}.$$

TABLE 2. Coefficients of the Empirical Formulas, Temperature and Heat of the Nematic–Isotropic Transition, Molal Volume Jump, Magnetic Susceptibility in the Isotropic State, and Degree of Order at the Transition Point for the Experimental Nematics

Processed quantity	Coefficient	N-62	N-72	N-100
ρ_{mes}	A	1,042472	1,003868	0,999223
	B	0,0006520	0,0007302	0,0007119
	C	0,0010562	0,0016005	0,0014738
	n	0,64	0,40	0,46
ρ_{is}	A	1,041165	1,003504	0,997594
	B	—0,0000055	—0,0007127	—0,0007838
	C	—0,0013565	—0,0003125	—0,0004778
	n	0,82	0,68	0,31
$\varkappa_{\parallel}$	A	0,5569	0,6473	0,5878
	B	—0,02497	—0,01265	—0,01700
	n	0,26	0,34	0,35
C_p^{mes}	A	507,65	310,98	479,07
	B	0,009904	—7,7345	0,6580
	C	316,42	630,52	204,33
	n	—0,19	—0,19	—0,29
	T_{t}	371,6	317,3	355,8
	$\Delta V/V_{\mathrm{t}}$	0,18	0,13	0,20
	$\overline{\varkappa}\cdot 10^9$	—0,5787	—0,6727	—0,6323
	$S_{\mathrm{t}}^{\mathrm{e}}$	0,302	0,287	0,368
	$S_{\mathrm{t}}^{\mathrm{c}}$	0,413	0,309	0,427
	ΔH^{e}	573	490	655
	ΔH^{c}	1194	582	1221

TABLE 3. Temperature Dependence of the Magnetic Susceptibility of Nematics in the Mesophase

N-62		N-72		N-100	
T, K	$-\varkappa_{\parallel}\cdot 10^9$, m³/kg	T, K	$-\varkappa_{\parallel}\cdot 10^9$ m³/kg	T, K	$-\varkappa_{\parallel}\cdot 10^9$, m³/kg
371,41	0,5407	317,14	0,6405	355,53	0,5766
371,17	0,5361	316,93	0,6387	355,23	0,5734
370,72	0,5327	316,51	0,6355	354,84	0,5717
370,18	0,5300	316,17	0,6347	354,03	0,5686
370,11	0,5297	315,94	0,6328	352,85	0,5629
369,99	0,5282	315,62	0,6326	352,32	0,5605
369,14	0,5263	314,60	0,6298	350,99	0,5585
367,88	0,5216	313,01	0,6259	348,64	0,5552
366,33	0,5182	310,69	0,6227	347,73	0,5517
363,09	0,5130	308,43	0,6213	345,51	0,5481
357,21	0,5061			342,55	0,5470
357,12	0,5068			341,72	0,5441
351,88	0,5030			337,82	0,5402
351,55	0,5033			333,93	0,5379
346,50	0,4989			329,37	0,5347
341,16	0,4959			323,28	0,5305
335,85	0,4936				
330,51	0,4917				

The deviation of the experimental points from the smooth curves does not exceed 0.2%. The values of the coefficients A, B, and n are given in Table 2.

The degree of long-range orientational order can be calculated if the anisotropic of the susceptibility in the solid state is known. It was assumed to be equal to $60\cdot 10^{-12}$ m³/mole for the investigated liquid crystals [1]. The results of calculations for this case are shown in Fig. 1. The curve of the degree of order for N-72 lies well below the curves for N-62 and N-100. This is probably attributable to the difference in the structure of the central group of atoms. The degree of order for the compounds N-62 and N-100 far from T_t is practically identical. The existing slight disparity increases as the transition tem-

TABLE 4. Temperature Dependence of the Molar Specific Heat of Nematics

N-62		N-72		N-100	
T, K	c_p, J/K•mole	T, K	c_p, J/K•mole	T, K	c_p, J/K• mole
351,84	685,9	312,14	793,4	325,49	535,0
353,80	690,9	313,73	812,6	329,85	541,4
355,75	692,7	314,77	834,3	334,27	548,6
357,69	699,7	315,66	872,3	338,65	557,3
359,62	705,6	316,29	925,0	342,87	568,0
361,54	713,2	316,77	994,3	347,01	581,8
363,44	719,8	317,19	1278,0	350,58	601,7
364,66	727,8	317,50	2329.4	353,06	630,5
365,32	730,5	317,86	910,6	353,23	630,7
365,67	733,2	318,39	780,9	353,62	639,3
367,17	745,8	319,21	767,6	354,01	648,7
368,82	767,7	320,59	757,7	354,39	659,9
368,88	766,7	322,52	750,3	354,76	679,8
369,29	776,3	328,32	742,6	355,48	750,2
369,70	785,0	332,75	743,7	355,72	2299,3
370,11	799,8	337,18	744,8	355,83	3708,0
370,51	817,3	341,59	746,6	355,97	1036,6
370,91	849,3	347,35	750,7	356,30	599,3
371,28	914,6	354,45	756,6	356,70	582,2
371,56	2318			357,11	578,4
371,72	2588			357,52	575,0
372,01	745,6			357,93	573,5
372,55	725,5			359,66	569,4
373,20	716,6			360,36	569,7
373,6	714,7			361,39	569,3
373,9	707,7			362,83	567,8

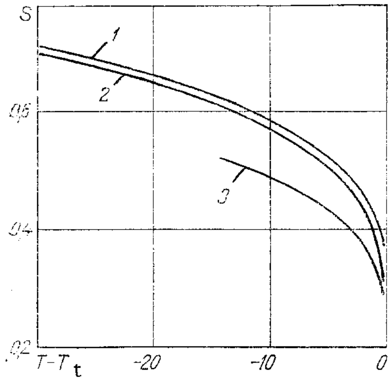

Fig. 1. Degree of order of nematic liquid crystals vs temperature. 1) N-100; 2) N-62; 3) N-72.

perature is approached, and at the level τ = 0.1 it is ~ 20%. The degree-of-order data are shown in Table 2. To determine it by extrapolation of the curves into the range $\tau < 0.1$ is clearly not sufficiently reliable, because it depends strongly on the refractive index n.

The molar specific heat was measured on an adiabatic calorimeter by an incremented-heating procedure [5]. The relative error of its determination did not exceed 0.5%. The results of the investigations are shown in Table 4. The specific heat increases with the temperature. At the nematic–isotropic transition point it attains a maximum and then falls off abruptly. Far from the phase-transition temperature, the specific heat once again increases almost linearly. The data in the mesophase were processed according to the least-squares method in the form of the relation

$$C_p^{\text{mes}} = A + B(T_t - T) + C(T_t - T)^n.$$

The numerical values of the coefficients of this equation are given in Table 2. The deviation of the experimental points from the smoothed curves does not exceed 0.5%. The heat of the nematic–isotropic transition (Table 2) was determined by a special experiment, in which the calorimeter–sample system was heated from the temperature T_1 to T_2, where $T_1 < T_t < T_2$. The calculations were carried out according to the relation $\Delta H^e = Q - Q_C - Q_{sam}$, where $Q_C = M_C C_C (T_2 - T_1)$ and $Q_{sam} = M \int_{T_1}^{T_t} [A + B(T_t - T) + C(T_t - T)^n] \alpha T + MC_p(T_2 - T_t)$.

To find the average value of the specific heat of the sample (C_p) in the interval $T_2 - T_t$

we extrapolated its temperature dependence according to a linear law from the far range of the isotropic state. This procedure is closest to the procedure proposed in [2] and used by us for calculating the heat of the nematic–isotropic transition.

The experimental results made it possible to perform numerical calculations within the framework of molecular-statistical theory [2], which were carried out on a computer according to the procedure described in [1]. It was assumed that the energy of molecular interaction is proportional to V^{-3}. Owing to the lack of data on the isothermal compressibility, we invoked the same assumptions as in [1] for the calculations of the specific heat in the mesophase and the heat of the nematic–isotropic transition. The calculated values of the heat of the nematic–isotropic transition (Table 2) for the compounds N-62 and N-100 are approximately twice the experimental values. However, if the short-range order parameter m = 2 is adopted. The agreement with experiment for these substances is good. For the compound N-72, on the other hand (without regard for short-range order), the disparity between the calculated and experimental values is ~ 20%. Attention should be called to the fact that the calculated and experimental values of the degree of order at the transition point are very close for this compound, whereas a large disparity is observed for the other substances. This can probably explain in part the discrepancy between the calculated and experimental values of the heat of the nematic–isotropic transition for N-62 and N-100.

The calculations indicate qualitative agreement with the experimental. Experimental results on the isothermal compressibility are needed in order to refine the existing analytical relations.

NOTATION

ρ, density, kg/m³; T_t, nematic–isotropic transition temperature, °K; T, instantaneous temperature; ρ_{mes}, density in the mesophase, kg/m³; ρ_{is}, density in the isotropic state, kg/m³; $\Delta V/V_t$, relative jump of the molal volume at the nematic–isotropic transition, %; κ, magnetic susceptibility in the isotropic state, m³/kg; $\kappa_{\parallel}$, magnetic susceptibility in the mesophase, m³/kg; S_t^e, extrapolated value of the degree of order for $\tau = 0.1$; S_t^c, calculated values of the degree of order at the transition point; C_p^{mes}, molar specific heat in the mesophase, J/K·mole; M, mass of the investigated sample, kg; ΔH^e, experimental value of the heat of the nematic–isotropic transition, J/mole; ΔH^c, calculated value of the heat of transition; C_C, specific heat of the calorimeter; M_C, mass of the calorimeter; Q, total quantity of heat.

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