CALORIMETRIC STUDIES OF LIQUID CRYSTALLINE MATERIALS

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Values of heat capacity C_p are obtained and thermodynamic properties are calculated for three nematic liquid crystals.

There is not much data available on the thermodynamic properties of liquid crystalline materials. Interesting results for a small number of compounds were presented in [1, 2, 3]. Using a sensitive differential thermograph, the authors in [1] studied n-azoxyanisol, anisaldazine, and p-n-methoxybenzolydene-p-phenylazoanaline. Transition temperatures and heats were obtained and the nature of the nematic state was discussed. In [2] the dta* method was used to obtain transition temperatures in cholesterine ethers. Results of these studies were used for identification of the mesophase. In [3] a DSC-2 differential scanning calorimeter manufactured by Perkin-Elmer was used to obtain the heats of transition of the same nine ethers of cholesterine. These compounds are interesting in that they are capable of forming both a smectic and a cholesteric mesophase.

Expanded studies of the thermodynamic properties of compounds capable of forming a mesophase were undertaken by Arnold and co-workers [4-11]. Experimental values of heat capacity C_p were obtained with an adiabatic calorimeter [4] over the temperature range 293-453°K by the multistep-heating method. The error in determining heat-capacity values was estimated by the authors at 0.3%, while the error in heat of transformation was 0.2%.

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*dta – differential thermal analysis.

TABLE 1. Experimental Values of Heat Capacity C_p

T	C_p	T	C_p	T	C_p
Compound I					
278,5	568,4	304,9	730,9	315,9	774,1
281,8	584,6	307,1	734,6	317,7	790,0
285,4	608,4	309,1	735,7	320,0	821,4
289,0	640,6	311,1	748,28	325,1	773,0
292,4	692,8	313,1	756,4	327,2	754,9
298,7	1478,0	314,2	758,8	329,1	762,4
300,55	3385,0	315,0	766,0		
Compound II					
278,7	616,7	316,4	10133	337,7	872,8
282,3	629,2	316,7	17900	347,1	928,1
298,0	672,8	316,9	18293	312,4	1012
309,2	749,7	320,2	827,7	319,7	829
312,0	902,2	324,5	835,4	357,1	911,3
314,4	1660,0	328,9	844,5	359,8	891
315,8	4533,0	333,4	857,1	361,4	894
Compound III					
296,8	511,7	337,8	13526	342,9	752,8
299,7	524,9	338,0	23280	347,5	770,4
312,6	556,9	338,12	36820	350,3	797,7
327,0	607,7	338,2	42410	352,2	844,7
328,8	654,6	338,4	48560	355,6	749,3
333,9	839	342,6	739,5	358,2	746,1
336,3	2093	341,2	739,7	360,8	752,1
337,3	6052				

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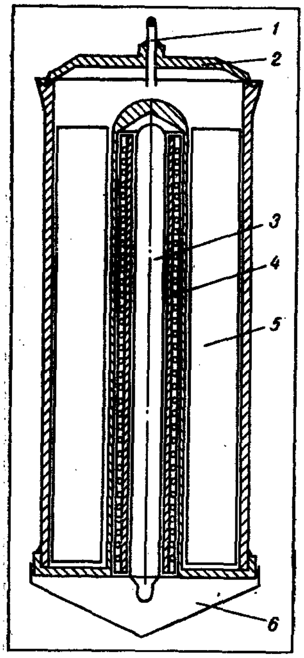


Fig. 1

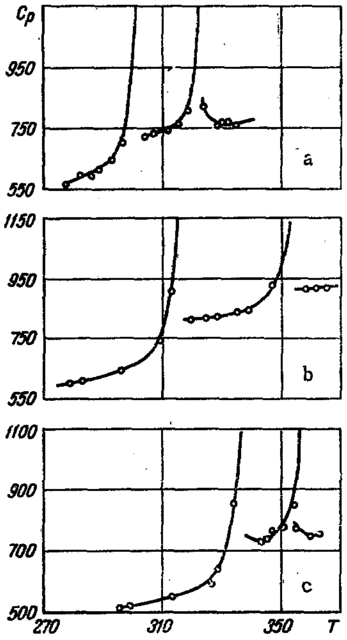
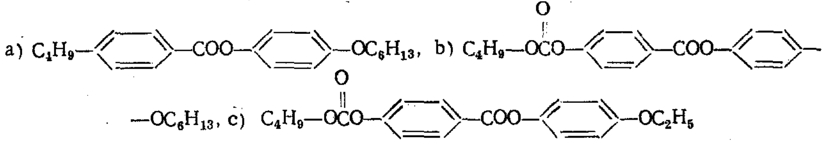


Fig. 2

Fig. 1. Calorimeter construction.

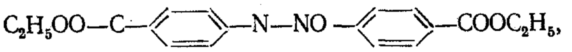
Fig. 2. Behavior of heat capacity C_p (J/mole • deg) near phase transformations (T, °K):



Arnold [5, 6] presented data on the heat capacity of the solid crystalline phase of the smectic and nematic mesophases of the first 12 members of 4,4 di-p-alkoxybenzol. Latent heats of the phase transitions were also obtained. These measurements were intended for a study of the effect of slight changes in molecular structure on liquid crystalline properties.

Results of measurement of heat capacity C_p and heat of transformations of the two compounds:

I



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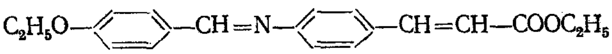


were presented in [7]. For the ethyl ether of 4-ethoxybenzol-4-aminic acid (compound II), which has one nematic and two smectic modifications, the energy of transition between the two smectic modifications was presented for the first time. This energy comprised about 38% of the heat of the following transition from the smectic state through the nematic to the isotropic liquid, and about 8% of the heat of fusion.

It was shown in [8] that the heat of transformation between the two smectic phases was not more than 100 J/mole. This is the smallest value which has ever been observed for transformations between two liquid crystalline modifications.

Arnold and Roediger [9] presented results of a study of cholesterine ethers, which are capable of forming a cholesteric mesophase. It was shown that the heats of transformation of the cholesteric and nematic crystals into isotropic liquid were of the same order. Transformation temperatures were also approximately equal. Thus, the difference in molecular ordering between cholesteric and nematic mesophases does not lead to a noticeable difference in changes in enthalpy and entropy. This fact again supports the theory of the similarity of these states.

Arnold, Jacobs, and Sonntag [10] considered heats of transformation and configurations of the smectic modifications, as well as evaluating factors affecting the heat of transformation between the smectic modifications A, B, and C.

TABLE 2. Thermodynamic Characteristics of Liquid Crystalline Materials

Substance	T_1	ΔH_1	ΔS_1	T_2	ΔH_2	ΔS_2
I	302,6	20800	68,7	323,8	3010	09,3
II	316,6	28230	89,2	353,6	6230	17,6
III	338,4	36000	106,4	353,8	4060	11,48

Results of a study of a large number of liquid crystalline compounds by the dta method were evaluated in [11]. The results were compared with data obtained by an adiabatic calorimeter, presented in [3]. Analysis of these studies permits a number of general conclusions.

1. Comparison of the results of [1-3] with the data of [4-11] indicates that the existing discrepancies cannot be explained by the experimental error (±4%) claimed in [1-3].

2. It was not possible to establish a dependence on molecular structure for temperatures and heats of transformation of members of a single homologous series. At the same time, for heats of transformation from the nematic state to isotropic liquid, together with even–odd changes, there exists a general tendency toward increase in heat of transformation with increase in number of carbon atoms.

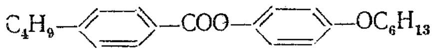
3. The change in entropy upon the transition nematic mesophase to isotropic liquid comprises approximately 2% of the total change in entropy for the transition solid to isotropic liquid. The change in entropy for the transition smectic mesophase to isotropic liquid is approximately 10 times larger.

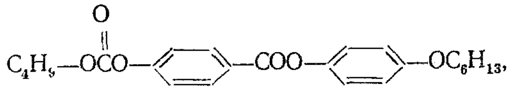
4. Because of pre- and postfusion effects in the homogeneous phase near the transition point the heat capacity rises sharply. In the phenomenological classification of McCallough and Westrum [12], in the phase transformations of the substances considered there occur type 2I and 3I transitions.

5. Comparison of experimental results with values obtained with the molecular static theory of the nematic state proposed by Maier and Saupe [13, 14] allows the conclusion that details of the heat-capacity curve are described poorly by the theory. Formation of valid theoretical concepts of the liquid crystal state requires wider studies of the temperature dependence of heat capacity, as well as measurements of the coefficient of thermal expansion and isothermal compressibility.

6. The form of the heat-capacity curve is significantly affected by the number of impurities in the specimen; thus, purity of specimens studied must be controlled carefully.

The purpose of the present study was the production of reliable values of heat capacity and temperature and heat of transformation for three compounds capable of forming a nematic mesophase: the compounds were complex ethers of n-oxybenzoic acid:


(I)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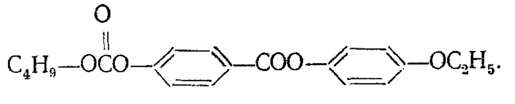
(III)

The specimens studied were synthesized at the All-Union Scientific-Research Institute of Chemical Reagents and Specially Pure Substances by B. M. Bolotin and co-workers.

Measurements of heat capacity as a function of temperature at constant pressure C_p were performed with an adiabatic calorimeter. The apparatus and methodology are described in [15]. The construction of the calorimetric ampoule is depicted in Fig. 1. The copper calorimeter body was plated with silver. The outer surface was polished to reduce heat transfer by radiation. Heater 4 was made of a conductor 0.1 mm in diameter, $R = 120\ \Omega$. The heater was shaped into a bifilar winding in the gap between the two coaxial cylinders. A platinum resistance thermometer 3, type TSPN-2V, constructed and calibrated at the All-Union Scientific-Research Institute of Physicotechnical and Radiotechnical Measurements ($R_0 = 50.066\ \Omega$) was used to measure specimen temperature in the calorimeter. A table was used to determine temperature [16]. Radiator 5 promotes rapid attainment of temperature equilibrium in the specimen after introduction of energy and is made of silvered copper foil. The ampoule is covered with lid 2 and soldered. The lid contains a capillary 1, through which air is exhausted and the ampoule filled with heat-exchange helium. Radiation screen 6 serves to reduce losses by radiation from the heater.

The heat capacity of the empty ampoule was measured over the temperature range 80–360°K at 32 points. To verify the reliability of the heat capacity values obtained, measurements were made of the heat capacity of type K-2 benzoic acid, prepared by the D. I. Mendeleev All-Union Scientific-Research Institute of Metrology, over the temperature range 120-360°K. Deviation of the experimental values from the values presented in [17] did not exceed ±0.3%.

The heat capacity C_p of substance I was measured at 22 points over the temperature range 280-330°K. Specimen weight was 2.0197 g. Specimen II, weighing 1.6869 g, was measured at 21 points in the range 280-360°K. The heat capacity C_p of substance III was measured at 22 points over the range 297-361°K. Specimen weight was 2.2581 g. The heat capacity C_p values obtained for the three specimens are presented in Table 1. Behavior of heat capacity near the phase transformations is depicted in Fig. 2.

Other thermodynamic characteristics obtained from the experimental data are presented in Table 2. Impurities in the specimens, as determined by the method of [18], did not exceed 2% molar.

NOTATION

t, temperature, °K; C_p, molar heat capacity at constant pressure, J/mole · deg; R, resistance, Ω; ΔH, change in enthalpy upon phase transition, J/mole; ΔS, change in entropy upon phase transition, J/mole · deg Indices 1 and 2 correspond to transition from solid state to liquid crystal and from liquid crystal to isotropic liquid.

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