SPECIFIC HEAT OF ETHYL CYANOACETATE

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The temperature dependence of the isobaric specific heat has been examined over the range 90-300 K for ethyl cyanoacetate. Phase transitions are detected whose type is dependent on the solid-state structure. The mechanisms giving the various structures are discussed.

Organic substances cannot be used efficiently in chemical engineering unless there are reliable data on their thermophysical parameters. Such a data bank enables one to forecast behavior and sometimes to optimize processes for making major compounds [1-3].

We have examined the temperature dependence of the isobaric specific heat $C_p(T)$ for ethyl cyanoacetate, which is an important intermediate in making some vitamins.

Specimens and Methods of Measuring $C_p(T)$. The technical product was purified by vacuum rectification ($P = 2.26 \times 10^3$ Pa) before use, the fraction boiling at 102°C being taken. The purity was tested by GLC and by IR and UV spectroscopy and found to be 99.6%.

The measurements were made with a UNTO universal standard system, whose error of measurement over the range 90-300 K was not more than 0.5% [4].

Experimental Results. Figure 1 shows these. With rapid cooling ($v \approx 0.15\ \mathrm{K \cdot sec^{-1}}$) from 300 to 77 K, there were two anomalous regions (curve 1). At 160 K, there was a sharp increase, which characterizes melting in a vitreous structure. Further heating in the supercooled metastable liquid causes spontaneous crystallization to begin at 175 K. The internal energy in the disordered liquid is higher than that in the ordered solid, so the crystallization releases a certain amount of heat Q. The second anomaly is associated with melting in the crystalline phase at 247 K. With slow cooling ($v \approx 2 \times 10^{-5}\ \mathrm{K \cdot sec^{-1}}$), the curve rises smoothly without anomalies up to the melting point. As that temperature is approached, the specific heat increases sharply, which also characterizes the crystalline-phase melting (curve 2).

Quasistatic thermograms showed that the transitions under the various cooling conditions near 247 K are first-order phase ones.

Analysis and Discusion. 1. Crystalline Phase. This phase is obtained on cooling the liquid from 300 to 77 K at $v \approx 2 \cdot 10^{-5}\ \mathrm{K \cdot sec.^{-1}}$.

Thermodynamic and molecular-kinetic factors are important in the production of the crystalline or metastable phases. The thermophysical parameters and the rheological ones indicate the intramolecular and intermolecular processes, while models enable one to interpret the relation between the properties and the structure [5].

We examined not only $C_p(T)$ but also $\nu(T)$, $\rho(T)$, and $\lambda(T)$ at 273-353 K.

An organic compound having $n_C \geq 4$ carbon atoms frequently tends to form a glass [6], while the formation of crystalline clusters is governed by features of the liquid such as chain branching and symmetry, the scope for heat dissipation at the liquid–nucleus interfaces, and the tendency to form intermolecular hydrogen bonds.

The $\nu(T)$, $\rho(T)$, and $\lambda(T)$ together with the $C_p(T)$ data suggest that all the molecular-kinetic parameters favor the formation of crystalline clusters during slow cooling [7].

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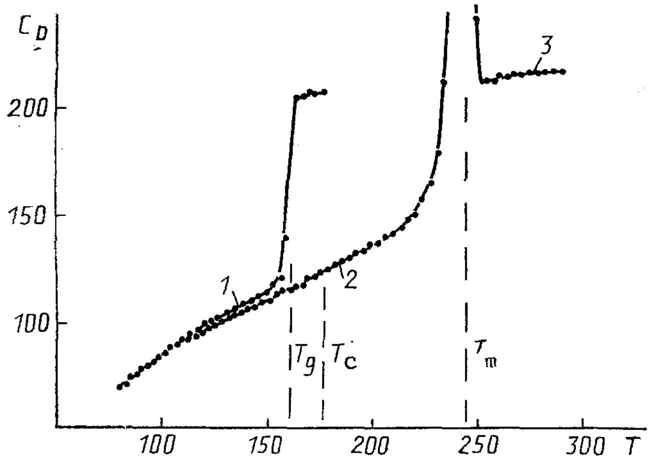

Fig. 1. $C_p(T)$ for ethyl cyanoacetate: 1) vitreous state; 2) crystalline state; 3) liquid state; C_p in $J \cdot mole^{-1} \cdot K^{-1}$, T in K.

TABLE 1. Thermodynamic Functions for the Ester Calculated from the Smoothed $C_p(T)$

T	$C_p(T)$	H_t-H_0	S_t	$\Phi(T)$
		Crystal		
90	79,58	1805,76	66,76	46,69
100	85,24	2629,31	75,43	49,14
110	90,93	3510,59	83,82	51,91
120	96,15	4446,44	91,96	54,91
130	101,07	5432,72	99,86	58,07
140	105,98	6467,90	107,52	61,33
150	111,12	7553,23	115,01	64,65
160	116,57	8691,51	122,36	68,03
170	122,25	9885,55	129,59	71,44
180	127,92	11136,57	136,74	74,87
190	133,20	12442,66	143,80	78,31
200	137,60	13797,62	150,75	81,76
210	142,12	15193,37	157,59	85,24
220	146,05	16633,71	164,21	88,60
230	149,45	18111,21	170,85	92,11
240	153,16	19623,98	177,21	95,44
247	155,25	20703,41	183,43	99,61
		Liquid		
247	213,98	32483,54	231,12	99,61
250	214,44	33126,17	235,41	102,90
260	215,96	35278,17	243,80	108,12
270	217,48	37445,39	252,03	113,35
280	219,01	39627,82	260,11	118,58
290	220,52	41825,46	267,58	123,35
300	222,04	44038,31	275,33	128,53

The measured $C_p(T)$ for the crystalline phase were used to calculate the thermodynamic functions (Table 1).

2. Vitreous State. Here one needs to examine the effects from the structure on the thermodynamic parameters, which has in particular confirmed that vitrification is similar in type for many different liquids.

Vitrification theory [8-10] emphasizes the importance of the configuration energy in the liquid state. For various reasons, such energy can be frozen to an extent such that anticrystalline-cluster nucleation and growth become thermodynamically preferable.

Many organic liquids and glasses differ from crystals in that two or more rotational isomers may exist in equilibrium [6]. The equilibrium isomer concentrations are frozen on cooling below T_g. These isomers occur because parts of the molecule can rotate around C—C and C—O bonds and so on. Internal rotation is thermally activated and involves a potential barrier E. With rapid cooling of this ester, various configurations may be taken up, while there is more stringent conformation selection when the liquid crystallizes. In most cases, only elongated conformations enter the crystal lattice, since this is the only way in which the potential energy can be reduced. With rapid cooling, the various conformations of this ester molecule will probably be determined by the carbon atoms. The high ν also indicate that molecular interactions are important, and consequently the configuration energy is insufficient to provide the necessary rearrangement at T_c.

These measurements and the data on the molecular interaction energies can be used as input in designing and optimizing engineering processes for making vitamins as well as for forecasting the properties of liquid systems.

NOTATION

T is absolute temperature; C_p is isobaric specific heat; v is cooling rate; Q is quantity of heat; T_c is crystallization temperature; T_g is glass temperature; T_m is melting point; ν is kinematic viscosity; ρ is density; λ is thermal conductivity; S_t is absolute entropy; $H_t - H_0$ is enthalpy change; $\Phi(T)$ is reduced isobaric—isothermal potential.

LITERATURE CITED

1. L. P. Filippov, Measuring Thermophysical Properties [in Russian], Moscow (1984).
2. E. Westram and J. McCullough, Physics and Chemistry of the Solid State for Organic Compounds [Russian translation], Moscow (1967).
3. D. Stall, E. Westram, and G. Zinke, The Chemical Thermodynamics of Organic Compounds [Russian translation], Moscow (1971).
4. T. S. Ismailov, B. G. Iskhakov, and M. G. Khodzhaeva, in: Proc. of the 5th All-Union Conference on Metrological Support to Thermophysical Measurements at Low Temperatures, [in Russian], Part 2, Khabarovsk (1988), p. 14.
5. V. G. Dashevskii, Conformation Analysis Applied to Organic Molecules [in Russian], Moscow (1982).
6. S. V. Nemilov, Fiz. Khim. Stekla, 3, No. 5, 423-432 (1977).
7. A. R. Ubbelhode, The Molten State [Russian translation], Moscow (1982).
8. N. Parsonage and L. Stavely, Disorder in Crystals [Russian translation], Part 2, Moscow (1982).
9. G. Leibfried, The Microscopic Theory of the Mechanical and Thermal Parameters of Crystals [Russian translation], Moscow (1963).
10. H. Suga, Amorphous-Substance Calorimetry [in Russian], All-Union Translation Center, Translation No. G-25416, Moscow (1981).