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HEAT CAPACITY AND PHASE TRANSITION OF TRIMETHYLOLETHANE*

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SUMMARY

Heat capacities of trimethylolethane (TME) have been measured between 18 and 375 K. The substance underwent a first-order phase transition at 358.2 K. The enthalpy and entropy of the transition were 21.24 $kJmol^{-1}$ and 59.3 $JK^{-1}mol^{-1}$, respectively. The purity of the sample was determined to be 99.96 % by DSC measurement of the melting peak. The plastically crystalline phases of TME, pentaerythritol (PE) and neopentylglycol (NPG), were discussed in relation to the orientational and internal disorder of the molecules in the cubic phase.

INTRODUCTION

Pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediol (PE $C(CH_2OH)_4$)) and related polyalcohols, trimethylolethane (2-hydroxymethyl-2-methyl-1,3-propanediol (TME $CH_3C(CH_2OH)_3$)) and neopentylglycol (2,2-dimethyl-1,3-propanediol (NPG $(CH_3)_2C(CH_2OH)_2$)) undergo solid-solid phase transitions from rigid to plastically crystalline phases at increasingly higher temperatures as the number of the methylol groups increases from two to four (refs. 1-2). The high temperature phases stable just below their temperatures of fusion are known to be highly disordered with respect to the molecular orientations, and crystallize in f.c.c. (ref. 3), which is the most efficient packing of quasi-spherical molecules. The low temperature phases are rigid crystals in which molecules are held together by intermolecular hydrogen bondings between OH groups belonging to the neighboring molecules. In NPG and PE, the hydrogen bond network is such that four hydroxyl groups belonging to the neighboring molecules form a four membered hydrogen bonded ring (refs. 4-5). The present compound is reported to be monoclinic at room temperature, although the structural determination was complicated by four-fold twining which gave the substance an apparent structural similarity to PE (ref. 6). Recently another solid-solid phase transition was found in NPG at 60.4 K (ref. 7). This may be attributed to disordering of the hydrogen atoms in the hydrogen bond system. For PE this type of a phase transition has not been found (ref. 8). Low temperature behavior of TME as studied by heat capacity measurement is reported in this paper.

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The large enthalpies of transitions of these compounds have stimulated many investigations into their thermal properties, some of them aiming at the feasibility of their technological application in heat storage (ref. 9). The crystallographic and thermochemical properties of PE had been studied by Nitta and his co-workers, and the models of disorder involving inter- as well as intra-molecular degrees of freedom in the high tmeperature phase have been proposed (refs. 1, 10). Previous calorimetric studies of TME were limited to those employing DSC. In the previous work of this series, we found that the rigid- to plastically-crystalline transition of NPG is accompanied not only by a large enthalpy of transition but also by a substantial increase of the heat capacity (ref. 7). Unlike the enthalpy of transition, the latter quantity is difficult to be determined by DSC to any useful degree of accuracy. Since both quantities are equally important characteristics of the highly disordered states, we made the heat capacity measurement on TME, using an adiabatic calorimeter which is capable of determining the enthalpy of transition as well as the heat capacity.

EXPERIMENTAL

Sample

The sample of TME was kindly supplied by Mitsubishi Gas Chemical Company, Inc.. It was purified through the following three steps. The first step was recrystallization from ethanol. The second was sublimation under reduced pressure at 380 K. Finally the product was subjected to zone refining in which the material underwent 50 passages of the molten zone. In the second step and afterwards the sample was handled carefully in a dried N_2 atmosphere in order to avoid possible contamination due to moisture.

DSC Measurement

DSC measurement was run between 353 and 483 K. Heating rate was 1.0 $\mathrm{Kmin^{-1}}$ and the mass of the sample was 21.1 mg. The apparatus used was a heat flux type differential scanning calorimeter DSC-50 which was kindly offered for our use by Shimadzu Corporation.

Heat Capacity Measurement

Heat capacity measurement was made with an adiabatic calorimeter between 18 and 375 K (refs. 11-12). Mass of the sample used was 3.6852 g. He gas at 101 kPa was filled into the sample cell for the acceleration of thermal equilibrium.

RESULTS AND DISCUSSION

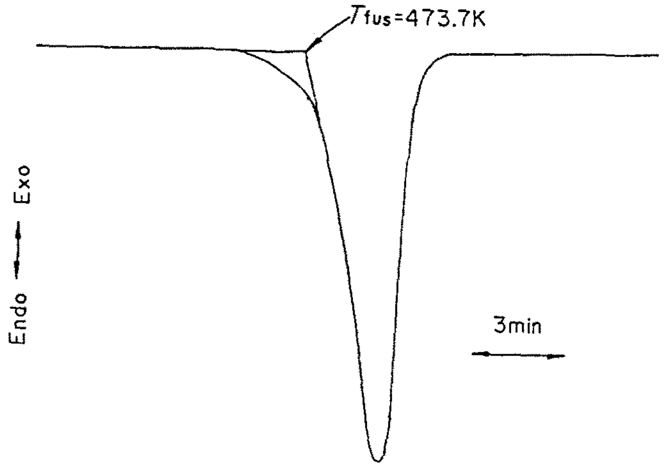

Fig. 1 Melting curve of trimethylolethane by DSC. See text for the determination of the temperature and enthalpy of fusion and the purity of the sample.

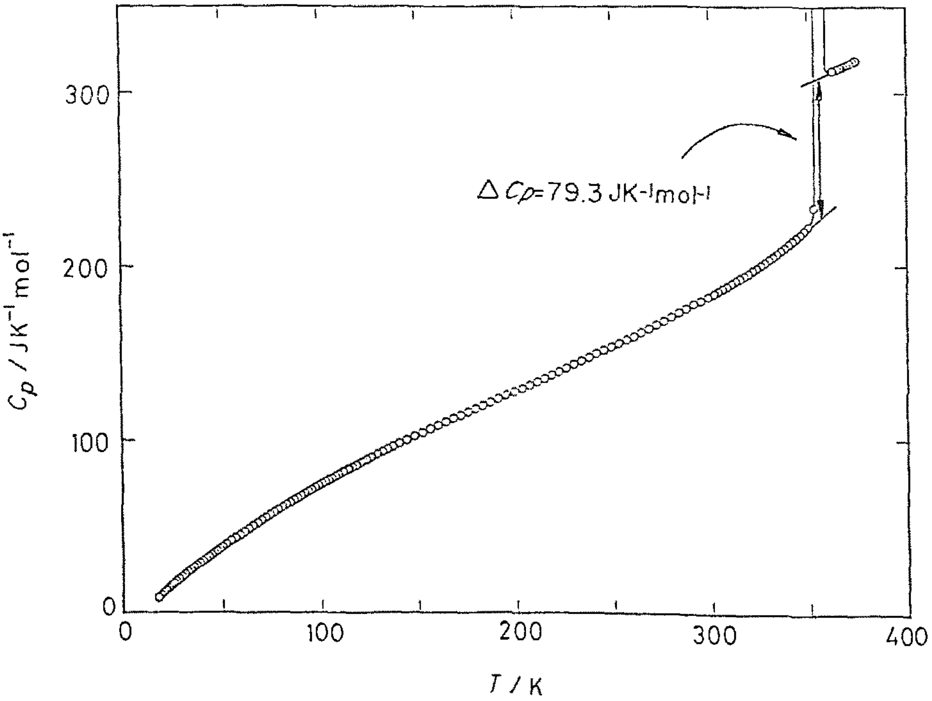

Fig. 2 Molar heat capacity of trimethylolethane between 18 K and 375 K.

TABLE 1

Heat capacities of trimethylolethane.

T	Cp	T	Cp	T	Cp
K	$JK^{-1}mol^{-1}$	K	$JK^{-1}mol^{-1}$	K	$JK^{-1}mol^{-1}$
18.36	9.479	102.29	76.06	272.47	166.4
19.39	10.64	104.04	77.26	276.35	168.6
20.34	11.72	105.78	78.30	280.21	170.9
21.24	12.70	107.56	79.45	284.05	173.3
22.17	13.69	109.39	80.54	287.86	175.7
23.14	14.72	111.20	81.68	291.65	178.3
24.05	15.68	111.82	82.01	295.41	180.2
24.92	16.58	114.10	83.36	299.15	182.6
25.82	17.48	116.36	84.56	302.08	184.2
27.07	18.72	118.59	85.89	304.25	185.6
28.57	20.18	121.09	87.37	306.41	187.2
29.96	21.52	123.85	88.89	308.57	188.4
31.43	22.93	126.58	90.47	310.72	190.0
32.97	24.36	129.27	92.02	312.87	191.4
34.41	25.62	131.94	93.38	315.01	192.9
35.77	26.85	134.58	94.90	317.13	194.4
37.13	28.00	137.19	96.25	319.25	195.8
38.64	29.26	140.45	98.03	321.36	197.4
40.21	30.55	144.33	100.1	323.46	198.9
41.71	31.80	148.32	102.2	325.56	200.4
43.13	32.95	152.42	104.3	327.64	202.0
44.49	34.07	156.48	106.3	329.72	203.7
45.80	35.18	160.48	108.3	331.78	205.2
47.16	36.29	164.43	110.3	333.83	206.9
48.56	37.44	168.35	112.3	335.88	208.6
49.92	38.57	172.22	114.1	337.91	210.3
51.84	40.15	176.06	116.0	339.94	212.1
54.28	42.15	179.85	117.9	341.95	214.1
56.58	43.94	183.63	119.8	343.95	216.1
58.87	45.74	187.51	121.7	345.94	218.0
61.15	47.52	191.50	123.7	347.92	220.2
63.34	49.16	195.46	125.6	351.42	225.0
65.54	50.80	199.39	127.6	352.90	233.6
67.74	52.44	203.28	129.6	353.67	234.1
69.87	54.05	207.14	131.6	355.72	333.2
72.03	55.58	210.98	133.5	356.24	494.3
74.21	57.19	214.78	135.5	357.12	868.6
76.33	58.69	218.55	137.4	(transition at 358.2 K)	
78.39	60.13	222.30	139.3	359.56	560.1
80.41	61.52	226.15	141.4	359.95	311.4
82.39	62.88	230.11	143.7	361.85	312.0
84.41	64.27	234.04	145.7	362.48	312.3
86.35	65.70	237.94	147.7	363.40	312.9
88.16	66.88	241.80	149.9	364.59	313.9
89.94	68.08	245.65	151.7	365.02	313.1
91.70	69.29	249.47	153.7	366.61	313.8
93.44	70.40	253.26	155.6	368.21	314.6
95.16	72.72	257.03	157.8	369.80	315.4
96.92	72.72	260.78	159.8	371.39	316.2
98.73	73.88	264.62	162.0	372.97	317.2
100.52	74.92	268.56	164.1	374.56	318.1

DSC Measurement

The DSC curve is reproduced in Fig. 1. The temperature(T_{fus}), enthalpy($\Delta_{fus}H$) and entropy($\Delta_{fus}S$) of fusion were determined as follows. The leftside slope of the endothermic melting peak was extrapolated to the base-line, and the temperature corresponding to the intersection was taken as T_{fus}. The value of $\Delta_{fus}H$ was calculated as the area of the peak which has been calibrated in advance with the melting peak of indium. The quantity $\Delta_{fus}S$ was calculated as $\Delta_{fus}H/T_{fus}$. The purity was determined by fractional-melting method (ref. 13). A correction was introduced in the purity calculation to account for the thermal resistance in the sample holder. Another correction necessary to linearize the 1/fraction-melted plot was 3.3 % of the area of the melting peak. The magnitude of the correction is not unreasonable in view of the dynamic nature of the DSC experiment. T_{fus}, $\Delta_{fus}H$, $\Delta_{fus}S$ and the purity of the sample thus determined were 473.7 K, 4.7 kJmol^{-1}, 9.8 JK^{-1}mol^{-1} and 99.96 %, respectively.

Heat Capacity

The heat capacity vs. temperature curve is shown in Fig. 2, and the numerical values are given in Table 1. There is a sharp peak of the heat capacity at 358.2 K due to the phase transition. The sudden increase of the enthalpy (the apparent heat capacity approaching the infinity) is a characteristic of a first order transition. Measurement covering the transition temperature was repeated three times (one of which was an enthalpy run), and an excellent reproducibility of the transition enthalpy was obtained. Transition temperature (T_{trs}), transition enthalpy (Δ_{trs}), and transition entropy ($\Delta_{trs}S$) were determined as 358.2±0.1 K, 21.24±0.03 kJmol^{-1} and 59.3±0.1 JK^{-1}mol^{-1}, respectively. For the calculation of $\Delta_{trs}H$ and $\Delta_{trs}S$, heat capacity curves of the high and low temperature phases were extrapolated to T_{trs} and used as the base line representing the normal heat capacity. Besides the strong increases of the enthalpy and entropy, there was a remarkable difference in the heat capacities between the low and high temperature phases. As shown in Fig. 2, the heat capacity of the high temperature phase was higher than that of the low temperature phase by 79.3 JK^{-1}mol^{-1}. There was no additional anomaly between 15 and 358.2 K.

The Phase Transition at 358.2K

The crystal structure of TME has been determined by X-ray diffraction (ref. 6). The low temperature phase is ordered and monoclinic, while the high temperature phase is disordered f.c.c.. The large transition enthalpy is no doubt related to the breaking of the hydrogen bonds. It takes place as the substance undergoes the phase transition into the disordered phase. The transition entropy is a measure of the disorder in the high temperature phase. Denoting by W the number of allowed molecular configuration in the high temperature phase, one finds that the transition entropy $\Delta_{trs}S$ = 59.3 $JK^{-1}mol^{-1}$ corresponds to W = 1250. The number of the equivalent orientations allowed to a molecule situated in an octahedral environment is 48, 24, 12, 8, or 6 depending on the intrinsic symmetry of the molecule and on whether the orientations are general or special in the crystallographic sense. In view of the polarity of the TME molecule we may take the first value 48 as the maximum orientational disorder possible in the f.c.c. phase. The entropy corresponding to this orientational disorder is R ln48 = 32.2 $JK^{-1}mol^{-1}$. This is to be supplemented by conformational disorder. Unlike the orientational disorder, the conformational disorder cannot be discussed based on the symmetry. However, if we remind the fact that the molecule is basically tetrahedral in its shape, we may assume that a methylol group has three minima of the potential energy as the internal rotation angle increases from zero to 2π, one of them being the true minimum. Supposing that this degree of freedom is fully excited, one obtains the entropy of the internal configuration R ln(3×3×3) = 27.4 $JK^{-1}mol^{-1}$, because there are three methylol groups in the molecule. The total entropy is given by 32.2 + 27.4 = 59.6 $JK^{-1}mol^{-1}$. This compares well with the experimental value 59.3 $JK^{-1}mol^{-1}$. The agreement of the experimental and calculated entropies is impressive. However, it has to be kept in mind that the entropy calculation is based on a number of assumptions; three configurations for one methylol group, fully excited configurations and independence of the three methylol groups in the molecule. In view of these, we are inclined to a modest interpretation that a substantial part of the transition entropy comes from the conformational degrees of freedom. It would not be appropriate to emphasize that the assumptions involved in the entropy calculation are fully substantiated by the agreement between the experimental and calculated values.

It is interesting to note that there is a large heat capacity jump associated with the phase transition amounting to 79.3 $JK^{-1}mol^{-1}$. This indicates that the configurational degrees of freedom are still being excited (rather than have been fully excited) in the high temperature phase. Let us suppose for the sake of an order-of-magnitude discussion that there are doubly degenerate excited configurations against a singlet ground state for each of the conformational degrees of freedom. This gives a Schottky anomaly peak of the heat capacity of 6.3 $JK^{-1}mol^{-1}$. Since there are six internal rotational degrees of freedom, they contribute a maximum of 37.8 $JK^{-1}mol^{-1}$ to the heat capacity. On the assumption that these degrees of freedom are frozen in the low temperature phase, this value is to be compared with the experimental heat cpacity jump, ΔCp = 79.3 JK-1mol-1. The agreement between the experimental and calculated values is not completely satisfactory. The latter quantity has to be supplemented by the difference of the $Cp - Cv$ correction terms relevant to the two phases, which we cannot calculate at present for the lack of the necessary data. It does, however, show again that an important part of the transition entropy comes from the internal degrees of freedom.

The comparison of the three polyalcohols (NPG, TME, PE)

Table 2 represents previously reported crystallographic data, and Table 3 summarizes thermodynamic quantities pertaining to the phase transitions obtained in the present work and those taken from the literatures. From Table 2, one sees that as the number of the OH groups in each molecule increases, the molar volume of the high temperature phase decreases, whereas that of the low temperature phase increases. The temperature, enthalpy and entropy of transition also depend systematically on the number of the OH groups as shown in Table 3. Dissociation of hydrogen-bonds and the intramolecular motional degrees of freedom thereby enhanced would play an essential role in the phase transition. The important part of the methylol group played in the phase transitions can be supported by the entropy of transitions plotted as a function of the number of methylol groups in each molecule. Figure 3 draws all the relevant data determined by the precise calorimetry. The transition entropy increases with the increased number of methylol groups, indicating a large contribution arising from the conformational degrees of freedom of molecule on passing through the phase transition. The mono-substituted member (neopentylalcohol) of this series is interesting in this respect and will be the subject of a calorimetric study in near future.

TABLE 2

Crystallographic data of the three polyalcohols cited from various sources.

Substance	Structure	T / K	a / nm	b / nm	c / nm	β / degree	Reference
NPG	Monoclinic P	RT	0.601	1.091	1.018	100.0	[5]
	Cubic F	323			0.82		[14]
TME	Monoclinic C	RT	1.07	0.605	1.21	124.3	[6]
	Cubic F	373			0.886		[3]
PE	Tetragonal I	294	0.6079		0.8745		[4]
	Cubic F	503			0.8963		[15]

NPG - neopentylglycol
TME - trimethylolethane
PE - pentaerythritol

TABLE 3

Thermodynamic quantities pertaining to the phase transitions.

Substance	T_{trs}	$\Delta_{trs}H$	$\Delta_{trs}S$	ΔCp	Reference
	K	kJmol^{-1}	R	JK^{-1}mol^{-1}	
NPG	60.4	0.177	0.352		[7]
	314.5	12.50	4.70	68.9	[7]
TME	358.2	21.24	7.13	79.3	[*]
PE	461.9	43.93	11.46	44.4	[1]
NPG (fusion)	348	4.7	1.19		[2]
TME (fusion)	474	4.7	1.19		[*]
PE (fusion)	531	5.0	1.15		[2]

[1],[2] and [7] were taken from the literature.
[*] were obtained in this work.

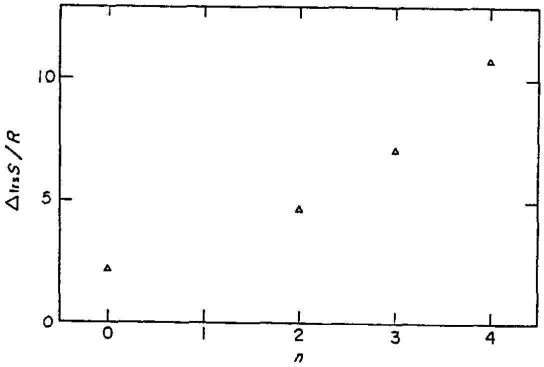

Fig. 3 Transition entropies of neopentane and four polyalcohols $(CH_3)_{n-1}C(CH_2OH)_n$ (n = 0 to 4).

REFERENCES

1 I. Nitta, T. Watanabe, S. Seki and M. Momotani, Proc. Japan Acad., **26** (10), (1950) 11.
2 E. Murrill and L. Breed, Thermochim. Acta, **1**, (1970) 239.
3 N. Doshi, M. Farman, R. Rudman, Acta Cryst., **B29**, (1973) 143.
4 D. Semmingsen, Acta Chem. Scand., **A42**, (1988) 279.
5 E. Nakano, K. Hirotsu, and A. Shimada, Bull. Chem. Soc. Jpn., **42**, (1969) 3367.
6 D. Eilerman, R. Lippman and R. Rudman, Acta Cryst., **B39**, (1983) 263.
7 R. Kamae, T. Matsuo and H. Suga, to be published.
8 E. F. Westrum, private communication.
9 M. Barrio, J. Font, J. Muntsell, J. Navarro and J. Li. Tamarit, Sol. Energy Mater., **18**, (1988) 109.
10 E. F. Westrum, Pure Appl. Chem., **2**, (1961) 241.
11 M. Tatsumi, T. Matsuo, H. Suga and S. Seki, Bull. Chem. Soc. Jpn., **48**, (1975) 3060.
12 T. Matsuo and H. Suga, Thermochim. Acta, **88**, (1985) 149.
13 C. Plato and A. R. Glasgow, Anal. Chem., **41**, (1969) 330.
14 H. P. Frank, K. Krzemicki and H. Volleke, Chem. Z. **97**, (1973) 206.
15 I. Nitta and T. Watanabe, Bull. Chem. Soc. Jpn., **13**, (1938) 28.