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Low temperature calorimetric study of methyl acetate [1]

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Abstract

The heat capacities of solid and liquid methyl acetate were measured from 13 to 290 K with an adiabatic calorimeter. A broad heat capacity anomaly with its peak value at 36 K was observed in the crystalline state. The overall shape of the excess heat capacity resembles closely the Schottky heat capacity function with a two-level equidegenerate system. This suggests a gradual ordering effect of the methyl group belonging to the carboxyl function of the molecule in the crystalline state. The methyl group has been reported to have two orientations with respect to the hydrogen atoms at high temperature. The melting of the crystal takes place at 174.90 ± 0.001 K with an associated enthalpy change of 7.486 ± 0.012 kJ mol^{-1}. No anomalous heat capacity behavior was observed around 260 K, at which temperature a normal–mesogenic liquid–liquid transition was suggested from an NMR T_1 measurement.

INTRODUCTION

Vibrational spectra obtained by IR absorption and Raman scattering of methyl acetate and its deuterated analog [1] showed that methyl acetate is present as a single skeletal conformation in the vapor, liquid and solid states. The molecule has a planar structure with two methyl groups in the trans configuration. Later, an X-ray structural analysis [2] showed that methyl acetate crystallizes in a monoclinic system with the space group $C_{2h}^5 - P2_1/n$. The methyl group belonging to the acetyl moiety was reported to have two orientations with respect to the hydrogen atoms around the C–C axis. The observed electron density was modeled fairly satisfactorily by dividing the methyl hydrogen atoms into two groups, each consisting

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of three partial hydrogen atoms. One group of hydrogen atoms has a population parameter of 0.57 ± 0.04 and the other has one of 0.43 ± 0.04 at 145 K. Each of the conformers can be converted to the other through internal rotation of the methyl group around the C–C axis by $\pi/3$ rad. Since such a disordered molecule cannot build up an equilibrium structure of methyl acetate at 0 K, an ordering process of the methyl group would be expected to occur in the crystalline state at low temperatures. This situation motivated us to undertake heat capacity measurements of the substance at low temperature. Surprisingly, there has been no report of the thermodynamic properties of this simple organic ester.

Further motivation was provided by a recent report of a possible liquid–liquid phase transition in methyl acetate around 260 K. Kawanishi [3] had reported a discontinuous jump of the spin–lattice relaxation time T_1 in the proton NMR experiment and a discontinuous slope of the molar volume in dilatometric experiments. The author ascribed these changes to a mesomorphic–normal phase transition in the liquid state. It is hard to imagine the existence of an ordered liquid phase in such a simple organic compound. It is of interest, therefore, to observe the associated heat capacity effect around the possible phase transition in the liquid state.

EXPERIMENTAL

Methyl acetate of special grade purchased from Wako Pure Chemicals was purified by fractional distillation with a concentric type of rectifier (HC-5500F, Shibata Kagakukikai Kogyo). The amount of impurities contained in each fraction was monitored by gas chromatography (F21, Perkin–Elmer). The main part was dried in vacuo over Linde molecular sieve 5A which had been thoroughly evacuated in advance. The liquid was decanted into another vessel and then subjected to vacuum distillation. The middle fraction was used for the calorimetric measurement.

Heat capacity was measured by an adiabatic calorimeter with a built-in cryorefrigerator [4] which produced temperatures as low as 13 K without use of any external refrigerant. A gold-plated copper calorimeter cell was fitted with an iron–rhodium thermometer. The resistance value was read automatically using an a.c. double bridge (A-7, Automatic Systems Laboratory, UK). The energy input measurement was made with a digital multimeter (Tr 6875, Takeda Riken). These measuring systems were coupled to a personal computer (MZ-2000, Sharp Corp.) to give "on-line" automated heat capacity data [5]. The whole system has the characteristic ability to follow for a long period any spontaneous temperature change arising from any relaxation processes that a sample might exhibit [6].

In the first heat capacity measurement, the ester sample was transferred into the copper calorimetric cell. A small heat capacity peak appeared at 10 K below the melting temperature. The peak area was observed to

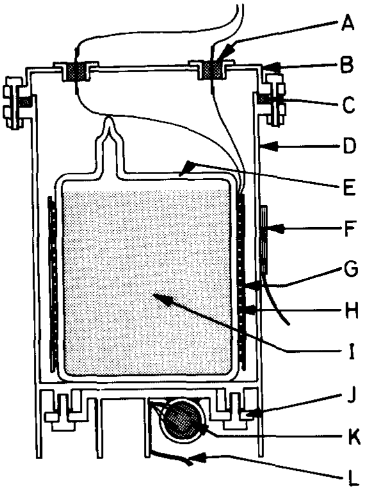

Fig. 1. Newly designed calorimetric cell comprising a glass ampoule and a gold-plated copper can: A, hermetic seal; B, lid; C, indium gasket; D, copper vessel; E, Pyrex sample cell; F, thermocouple sheath; G, aluminum foil; H, heater; I, sample; J, mounting for thermometer; K, rhodium-iron thermometer; L, lead wires.

increase with repeated measurements. Occurrence of a chemical reaction of the sample with the calorimetric cell was suspected. This might happen if the sample contains small amounts of water to induce hydrolysis of the ester so as to produce a mixture of acetic acid and alcohol.

A new calorimetric cell was devised in order to avoid direct contact of the sample with copper metal. The sample was transferred into a Pyrex glass ampoule and the inlet part was sealed off. The outside of the ampoule was wound tightly with a calorimeter heater. The internal volume

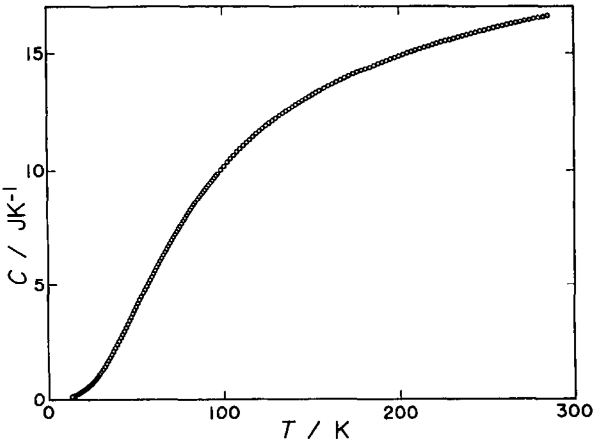

Fig. 2. Heat capacity of the new calorimetric cell.

of the ampoule was 27.3 cm^3. The ampoule was fitted into the copper calorimetric cell, maintaining vacuum tightness with an indium O-ring. The gap between ampoule and cell was filled with helium gas at 0.1 MPa

TABLE 1

Molar heat capacity under saturated vapor pressure of methyl acetate

T_{av} (K)	C_s (J K^{-1} mol^{-1})	T_{av} (K)	C_s (J K^{-1} mol^{-1})	T_{av} (K)	C_s (J K^{-1} mol^{-1})	T_{av} (K)	C_s (J K^{-1} mol^{-1})
13.08	4.022	58.37	45.22	125.02	73.39	212.09	133.2
13.67	4.510	59.85	46.07	127.03	74.11	214.11	133.2
14.38	5.162	61.35	46.95	129.04	74.74	216.12	133.2
15.15	5.904	62.85	47.77	131.05	75.44	218.13	133.3
16.06	6.845	64.37	48.60	133.07	76.13	220.14	133.4
17.11	7.983	65.90	49.40	135.09	76.77	222.14	133.5
18.17	9.201	67.43	50.19	137.11	77.49	224.15	133.6
19.18	10.42	68.98	51.00	139.14	78.13	226.15	133.7
20.74	12.42	70.54	51.77	141.17	78.87	228.15	133.7
21.78	13.79	72.11	52.55	143.21	79.66	230.15	133.9
22.83	15.21	73.70	53.33	145.25	80.60	232.14	134.0
23.89	16.65	75.29	54.09	147.30	81.66	234.13	134.3
24.95	18.12	76.89	54.84	149.34	83.14	236.11	134.3
26.00	19.60	78.51	55.56	151.42	84.40	238.10	134.2
27.05	21.12	80.14	56.33	154.25	84.29	240.09	134.3
28.10	22.67	81.77	57.01	157.05	86.22	242.08	134.7
29.14	24.27	83.42	57.77	159.82	89.09	244.07	134.8
30.17	25.83	85.08	58.47	162.52	92.97	246.07	135.0
31.19	27.30	86.76	59.20	165.17	97.79	248.06	135.1
32.22	28.83	88.44	59.90	167.74	102.2	250.07	135.2
33.25	30.32	90.13	60.61	170.23	111.4	252.07	135.5
34.29	31.63	91.84	61.30	172.44	158.1	254.08	135.7
35.34	32.67	93.56	62.02	176.70	133.7	256.09	135.9
36.41	33.31	95.30	62.71	178.90	133.7	258.10	136.2
37.51	33.48	97.04	63.40	181.87	133.3	260.12	136.3
38.63	33.49	98.80	64.08	183.79	133.3	262.14	136.4
39.77	33.69	100.57	64.75	185.71	133.2	264.16	136.7
40.94	34.13	102.35	65.43	187.74	133.2	266.18	137.0
42.12	34.74	104.15	66.09	189.78	133.1	268.21	137.3
43.30	35.45	105.96	66.80	191.82	133.1	270.23	137.5
44.50	36.23	107.78	67.45	193.86	133.2	272.26	137.8
45.70	37.04	109.61	68.11	195.89	133.1	274.30	137.9
46.90	37.83	111.64	68.64	197.92	133.0	276.33	138.2
48.10	38.68	113.33	69.40	199.95	133.0	278.37	138.5
49.72	39.70	115.20	70.08	201.98	133.0	280.41	138.9
51.13	40.65	117.09	70.72	204.01	133.1	282.45	139.2
52.55	41.61	119.01	71.40	206.03	133.1	284.49	139.5
53.99	42.52	121.01	72.06	208.05	133.1	286.54	139.9
55.44	43.44	123.02	72.78	210.07	133.1	288.58	140.2
56.90	44.34						

pressure for the acceleration of thermal equilibration. The new calorimetric cell is shown schematically in Fig. 1. The resulting heat capacity data of the ester are considered naturally to be somewhat inferior in their accuracy and precision to those of the usual method owing to the increased heat capacity of the empty cell.

RESULTS AND DISCUSSION

The heat capacity of the new empty cell is plotted in Fig. 2 as a function of temperature. The time required to reach thermal equilibrium was normally 5–10 min, depending on temperature, and was not essentially different from that for a conventional calorimetric cell made of metal only. The deviation of each data point from a polynomial smoothed curve was less than 0.3% over most of the temperature range. Thus the new calorimeter cell has proved to be of the same good quality as that normally used. The polynomial smoothed curve was subtracted from the total heat capacity to derive the molar heat capacity data of the sample. The measurement was actually done after the sample heat capacity has been measured.

The amount of sample used for the heat capacity measurement was 9.4784 g, corresponding to 0.127 95 mol. The liquid sample was crystallized slowly in the cell and then annealed for a week at around 150 K. The first series of measurements was then initiated from 13 K after slow cooling of the calorimetric cell. When the sample had been heated to 45 K, a slow exothermic effect was found to occur, and continued up to 55 K. The effect was observed to cease when the sample had been annealed for 160 h around 50 K. The second series of measurements was started again from 13 K for this well-stabilized crystalline phase. No relaxational behavior of the heat capacity was observed in the new series of measurements.

The experimental molar heat capacities under saturated vapor pressure $C_{s,m}$ from 13 to 290 K are listed in chronological order in Table 1 and illustrated in Fig. 3. The data above the melting temperature are representative ones. Several series of measurements were repeated in the liquid region, especially around 260 K. Since there was no anomalous heat capacity behavior in this temperature region, these additional data were omitted from the table.

It is immediately apparent from Fig. 3 that there are three temperature regions which show anomalous heat capacity behavior. The first one is observed around 36 K. The heat capacity anomaly closely resembles the Schottky heat capacity function C_{Sch} with a two-level equidegenerate system [7]

$$C_{\mathrm{Sch}} = R[(x/2)\,\mathrm{sech}(x/2)]^2 \tag{1}$$

where $x = \epsilon/kT$, ϵ being the energy difference between the two levels. This function gives a maximum value of 3.6 J K^{-1} mol^{-1} at $kT/\epsilon = 0.417$.

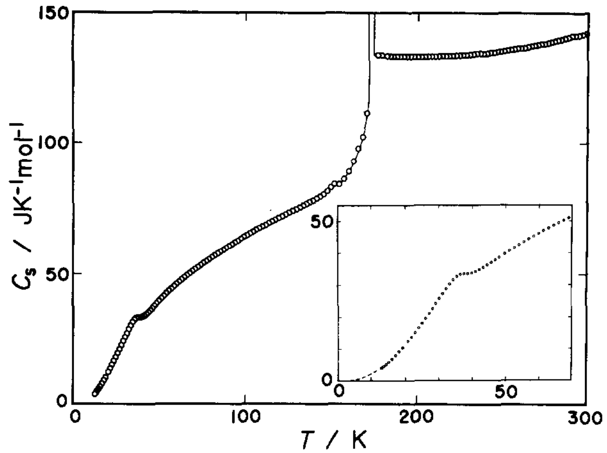

Fig. 3. Molar heat capacity under saturated vapor pressure of methyl acetate.

Since there is no disorder other than that of the hydrogen atoms of the methyl group in the reported crystal structure, it is reasonable to ascribe the anomalous heat capacity to their ordering process. However, separation of the observed heat capacity into the Schottky and lattice-vibrational contributions is not easy in the absence of a knowledge of the phonon spectrum of the present crystal. The following analysis was attempted.

Putting $T_{\mathrm{max}} = 0.417\epsilon/k = 36$ K, we obtain 0.72 kJ mol^{-1} for the energy separation of the two levels. If this value can be regarded as the energy difference between the two conformers of the methyl group (belonging to the acetyl moiety) with respect to the hydrogen atoms, we can calculate the fraction of each conformer to be 0.64 and 0.36 at 145 K. These figures do not differ much from those obtained by X-ray analysis: 0.57 ± 0.04 and 0.43 ± 0.04 respectively. Therefore it seems likely that the disordering process of the methyl group proceeds by thermal excitation between the two orientations with increase in temperature, starting from the ground state configuration at low temperature. This visualization is consistent with the fact that the molecules of methyl acetate exist as discrete entities [2] with no short intermolecular contacts in the crystalline state. Reorientational motion of the CH_3 groups might take place independently of each other without any cooperative effect. A neutron scattering experiment on a deuterated specimen is highly desirable in order to support this conjecture.

It is worthy of note that the methyl group of the acetyl function has a generally low value of the barrier hindering internal rotation. The low barrier height causes quantum-mechanical tunneling by the hydrogen atoms to result in a splitting of their vibrational states. This has been typically observed in the $CaCu(CH_3COO)_4 \cdot 6H_2O$ crystal, for which the barrier height of the methyl internal rotation was reported to be as small as 1.2 kJ mol^{-1} [8]. In the present case, the corresponding methyl group has two orientations with respect to its hydrogen atoms and orders into the lowest energy configuration at temperatures as low as 20 K, without any indication of freezing-out of the motion by virtue of a similarly low hindering potential. Investigation of the dynamic situation of the methyl group in the present crystal at lower temperatures should be fascinating.

The second anomaly appears at 155 K. The effect is too small to be ascribed to a phase transition effect. Most probably the slight peak is due to eutectic melting of the crystal with an unidentified impurity.

The third anomalous region corresponds to melting of the crystal. The enthalpy change associated with melting was determined as the isothermal segment of the enthalpy required to heat from an initial equilibrium temperature of the crystal to a final temperature of the liquid by assuming appropriate baselines for the liquid and the solid phases. Three independent runs of the total enthalpy analysis gave the value 7.486 ± 0.012 kJ mol^{-1} for the molar enthalpy of melting. For the determination of the temperature of melting and the purity of the sample, a fractional melting experiment was carried out. The equilibrium temperatures, $T(f)$, were observed at several fractions f of the sample already melted. The melting temperature plotted against the reciprocal fraction of f gives a straight line, as shown in Fig. 4. The slope of the line combined with the cryoscopic constant gives rise to the total amount of impurities, x. The data of the fractional melting experiment are summarized in Table 2. The amount of impurities, 0.14 mole fraction, is rather large in view of our careful purification. The difficulty in purifying this ester may be not unrelated to

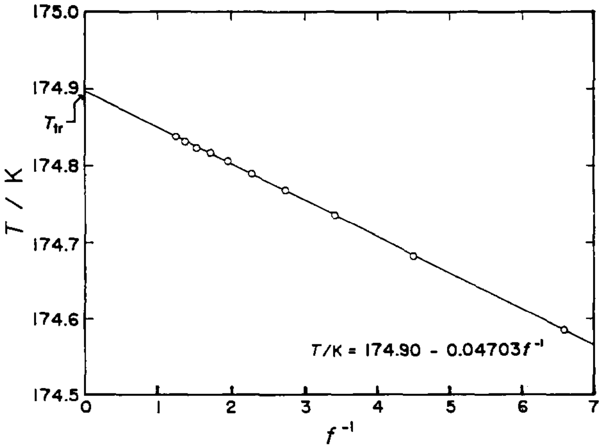

Fig. 4. Plot of the melting temperature as a function of the reciprocal fraction of sample already melted.

TABLE 2

Summary of the fractional melting experiments for methyl acetate [a]

f	f^{-1}	$T(f)$ (K)
0.36581	2.7336	174.7686
0.43860	2.2800	174.7900
0.51151	1.9550	174.8064
0.58458	1.7106	174.8173
0.65768	1.5203	174.8236
0.73096	1.3781	174.8312
0.80419	1.2435	174.8383

[a] $\Delta_{\text{fus}}H_{\text{m}} = 7.486 \pm 0.012$ kJ mol^{-1}; $T_{\text{tr}} = 174.897$ K; $x = 0.0014$.

the fact that the ester easily undergoes hydrolysis even with a trace amount of water to produce twice the quantity of impurities.

In summary, the heat capacity of solid methyl acetate showed an anomalous broad hump in the temperature range between 20 and 40 K, this being possibly related to an ordering of the hydrogen atoms belonging to one of the methyl groups. There was no indication of a heat capacity anomaly around 260 K, which supports the proposed liquid–liquid phase transition.

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