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Simultaneous determination of the heat capacity and the heat of the transitions for long-chain compounds with a heat-flux type DSC

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Abstract

The heat capacity method of DSC measurements, for which sapphire was used as a standard, was applied to determine simultaneously the heat of the transitions and the heat capacity for long-chain compounds. A heat-flux DSC was used because of its relatively high sensitivity at slow scanning rates. The data were analyzed with a computer system. Measurements on indium were performed to obtain information about factors affecting the accuracy. Fairly satisfactory results were obtained for the heat of melting and the heat capacity at heating rates of 0.5 and 2 K min^{-1}. Long-chain symmetrical ketones were also used to test the reliability of the measurement because their thermal behavior is very simple. Solution-grown crystals of henpentacontane and dopentacontane clearly showed high-temperature modifications with a high heat capacity. Analysis by the present method indicates that the heat capacities of these modifications have a relatively large contribution to the overall change in enthalpy from the stable crystal at room temperature to the liquid.

INTRODUCTION

Polymorphism is one of the thermal characteristics of long-chain *n*-alkane crystals. The widely known phase is the hexagonal phase, observed just below melting for *n*-alkanes whose number of carbon atoms in the molecule is below about 40. The nature of this phase is important in dynamic conformational disorder [1]. Recently, other types of high-temperature modifications have been discovered [2–5]. In these modifications the sub-cell structure remains in the same orthorhombic sub-cell as in

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the room-temperature modifications. The presence of longitudinal disorders along the chain axes in the high-temperature phase of tritriacontane has already been discussed [6]. The high-temperature phases just below the hexagonal phase or the melt, abbreviated as the C-phase for the odd *n*-alkanes and the C′-phase for even *n*-alkanes [5, 7], may belong to the phase of dynamical or at least quasi-dynamical conformational disorders. A feature of these phases is a heat capacity higher than those of the crystal that is stable at room temperature or of the liquid. When the thermodynamic parameters of the phase transition occurring between them are considered, it is necessary to know both the heat capacity of the disordered phase and the heat of the transitions. This becomes more important for long-chain *n*-alkanes crystals because the C- or C′-phase regions are wide and their contribution to the total enthalpy or entropy changes becomes large with increasing *n*. DSC measurements are preferable for pure *n*-alkane samples because of the restricted amount of material available.

Improved heat capacity Cp data from DSC measurements are available in several laboratories. In order to obtain the precise Cp data from DSC, it is recommended that the sample mass is reduced and the scanning speed increased [8]. Although Lau et al. [9] performed the simultaneous determination of Cp and the heat of the transitions for polytetrafluoroethylene with a heat-compensating DSC, the high heating rate of $10\,\mathrm{K\,min^{-1}}$ that they used resulted in the superheating of the solid–solid transition and the melting. Takahashi [10] reported that the heat of melting for indium determined by the heat capacity DSC method was in good agreement with the literature value. However, heat-flux type DSC instruments generally have high sensitivity but do not have as rapid a response as the heat-compensating types. Because the thermal behavior of the high-temperature modifications of *n*-alkane crystals is complicated, for example as shown in ref. 5, it is desirable to adopt a slow heating rate in the DSC measurements to avoid the superheating effect.

The purpose of this paper is to examine the accuracy of the simultaneous measurement of the heat capacity and the heat of fusion using a heat-flux type DSC with a slow heating rate. When sapphire is used as the calibration standard for the determination of the heat of transition, one of the factors that affect the accuracy of the data obtained may be the magnitude of the deflection. Compared with the deflection from sapphire, the magnitude of the deflection for a melting peak becomes very large for a sufficient mass of sample. Therefore, the linearity of the electrical amplitude and the similarity of the thermal circumstances during the transitions have to be taken into consideration. These effects were examined for the melting of indium at different scanning rates. The heat of melting of long-chain symmetrical ketones was also determined in order to examine the reliability of the method for chain compounds. These compounds were suitable for examination because their melting occurs without any solid–solid transition. Finally, we applied the method to *n*-alkane crystals.

EXPERIMENTAL

Materials

The indium measured was supplied by Rigaku Denki Co. and its purity was 99.999%. An NBS standard, sapphire 720, was used as the reference material. The symmetrical ketones used were 16-hentriacontanone and 20-nonatriacontanone, abbreviated as K31 and K39, respectively, where the numeral is the number of carbon atoms in the molecule. They were synthesized through a ketene dimerization reaction [11]. The homologous purity of K31 and K39 were 99.9 and 99.7%, respectively. The DSC measurements were made on samples crystallized from heptane and toluene solutions for K31 and K39, respectively. The *n*-alkanes measured were henpentacontane and dopentacontane, abbreviated as C51 and C52. Their syntheses were described briefly in a previous paper [5]; their purities were 99.4% and 99.8%, respectively. The DSC measurements were performed on crystals grown from dilute hexane or octane solutions, because this method of crystallization yields crystals that are stable at room temperature which enabled us to obtain information on the solid–solid transitions [5].

Measurements

The DSC measurements were performed on a Rigaku DSC 8240B at a standard heating rate of 0.5 K min^{-1} in a flow of dry nitrogen. The effect of the heating rate was also examined. The data acquisition and analyses were made with a Rigaku TAS-100 and a personal computer. Samples were weighed with a supermicro balance (Sartorius 4504MP8), the precision of which was $\pm 0.2\,\mu$g.

The measurements were made on samples sealed in a standard aluminium pan with a lid. The differences in the weights of the sample pans, after approximately matching the masses, were corrected using the known heat capacity of aluminum. The pulverized sapphire, mixed with rod-like sapphire, was sealed in the sample pan in order to obtain a good thermal contact with the pan and to increase the sample weight in the pan. The maximum weight was about 67 mg. Measurements made using a sapphire disk resulted in an oscillation of the signal, which might be due to poor thermal contact with the sample pan. It became difficult to discern this oscillation at higher scanning rates. The use of pulverized sapphire reduced the oscillation, even at a slow scanning rate.

Over all the initial to final isothermal conditions, 4095 data points for the deflection were recorded. The maximum temperature rate of the scan was about 80 K for the n-alkanes. In these cases, about 35 data points were recorded per kelvin.

The heat capacity $C_{p_{sa}}$ of a sample was calculated by the equation

$$C_{p_{sa}} = \left[\left(\frac{h_{sa}}{h_{st}}\right)C_{p_{st}}Wt_{st} - \left[\left(\frac{h_{sa}}{h_{st}}\right)(W_{bl} - W_{st}) - (W_{bl} - W_{sa})\right]C_{p_{Al}}\right]\Big/ Wt_{sa} \qquad (1)$$

where h represents the difference in the deflection between a sample and the empty blank, Wt is the net weight of material measured and W that of a pan and lid. Subscripts sa, st Al, and bl stand for sample, the standard material (sapphire), aluminum (from which pan and lid are made) and an empty blank, respectively. In the present case, h_{st} was expressed with polynomials that were best fitted by the least squares calculation. Because the measuring temperature range was relatively narrow, the polynomials were usually linear. We assumed that the absorbed heat over the region of the phase transiton could be obtained from eqn. (1).

RESULTS AND DISCUSSION

Indium

Integration of the C_p data calculated by eqn. (1) may give an approximate relationship between relative enthalpy and temperature. Figure 1 shows a typical relationship for indium for about 4.8 mg of sample

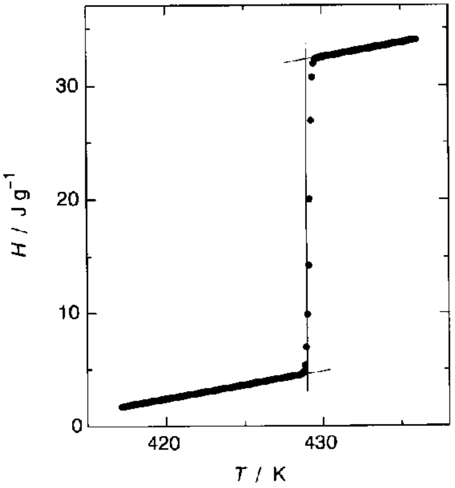

Fig. 1. Apparent enthalpy–temperature relationship for indium. Weight, 4.8 mg; heating rate, 0.5 K min^{-1}; standard, sapphire. The symbols represent every fifth experimental data point. The fine vertical line represents the melting.

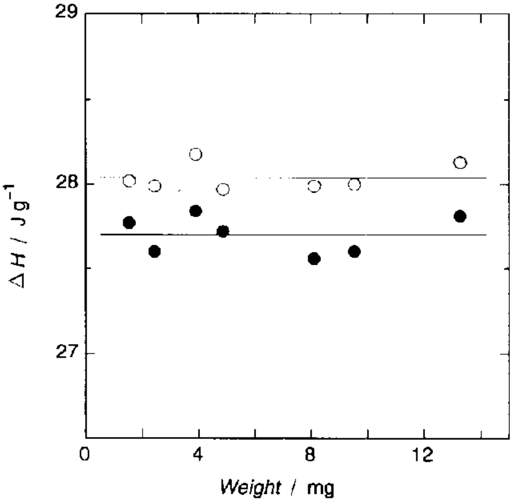

Fig. 2. Dependence of the heats of melting obtained for indium on the sample weight at the heating rates of 0.5 (●) and 2 (○) K min^{-1}. The fine lines indicate the average values for each data set.

at a heating rate of 0.5 K min^{-1}. Here, the temperature of the abscissa is not corrected. The jump in enthalpy, i.e. the heat of melting, can be easily determined from the data obtained over the crystalline and liquid regions. In the usual way, the melting point is defined as the onset temperature at which the crystalline line and the line over the melting region intersect. The heat of melting was calculated from the jump at the melting temperature, as shown in Fig. 1.

As stated above, the effect of the ratio h_{sa}/h_{st} at the peak temperature on the heat of melting has to be examined. In Fig. 2, the heat of melting per unit weight is plotted as a function of the sample weight. Experiments were also run at a scanning rate of 2 K min^{-1}. The data are compared in Fig. 2. The literature value for the heat of melting of indium is 28.5 ± 0.2 J g^{-1} [12]. For this magnitude of sample weight, the ratio of h_{sa}/h_{st} at the peak varies between 1 and 13. It may be concluded that the linearity, especially with electrical amplification, has no effect on the results when the ratio is within this range. Moreover, it seems that there is no error inherent in simple integration over the melting range of indium because there were 40–60 data points over this region. The average heat of melting is 27.7 ± 0.1 J g^{-1} for a scan rate of 0.5 K min^{-1} and 28.0 ± 0.1 J g^{-1} for 2 K min^{-1}, respectively. Although these are both outside the literature values, the experimental results may approach the literature values with increasing scan rate. This behaviour corroborates the recommendation of Suzuki and Wunderlich [8]. The present results may be attributed to the subtle difference in the thermal circumstances.

The C_p values at 420 K (crystal) and 434 K (liquid) for indium are

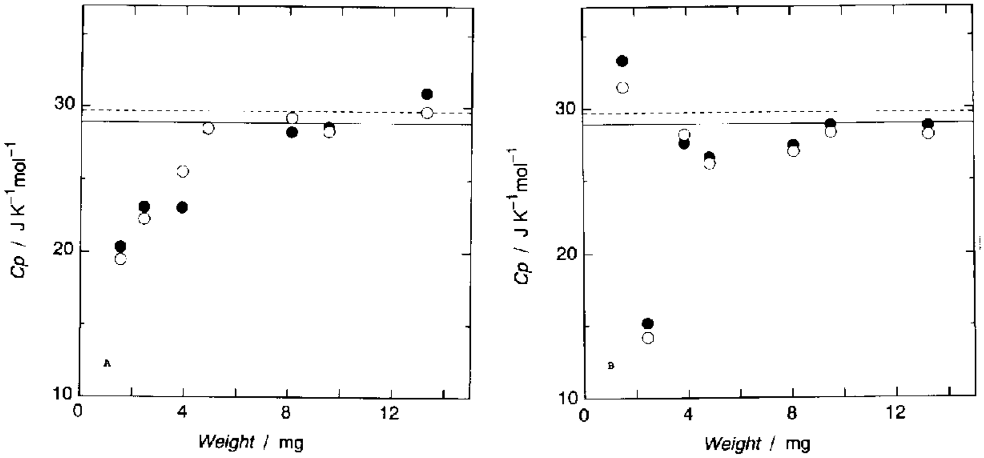

Fig. 3. Dependence of the heat capacities obtained for indium on the sample weight. A. Heating rate of 0.5 K min^{-1}. B. 2 K min^{-1}. ●, at 420 K (crystal); ○, at 434 K. The broken and fine lines represent the literature values at each temperature.

plotted against the sample weight in Fig. 3A and 3B for data obtained at rates of 0.5 and 2 K min^{-1}, respectively. The latter data points are all good, except one. Although the C_p data for a smaller sample weight deviate from the literature values, the results obtained suggest that the heat of melting and the heat capacity can be determined simultaneously with a limited accuracy.

Long-chain symmetrical ketones

Ketones are suitable long-chain compounds with which to test the simultaneous determination. Because they melt without any solid–solid transitions, there are no problems in determining the heat capacity of the crystalline phase. The relationship between the apparent enthalpy and temperature for K31 is plotted in Fig. 4. Table 1 lists the experimental data for K31 and K39 which were obtained using the procedure described above at heating rates of 0.5 and 2 K min^{-1}. The agreement of the data implies that the effect of the heating rate and also of the sample weight are relatively small for organic substances, in contrast to the case of indium. Here, the sample weights were from 0.5 to 3.0 mg. The heat of melting obtained may have a sufficient accuracy. The melting points of K31 and K39 are 356.4 and 365.6 K, respectively. This difference may have no effect on the proportionality constant, even when the calibration is made at the single temperature of the melting of indium, as usually adopted. However, in general, the use of sapphire as the standard is preferable because its

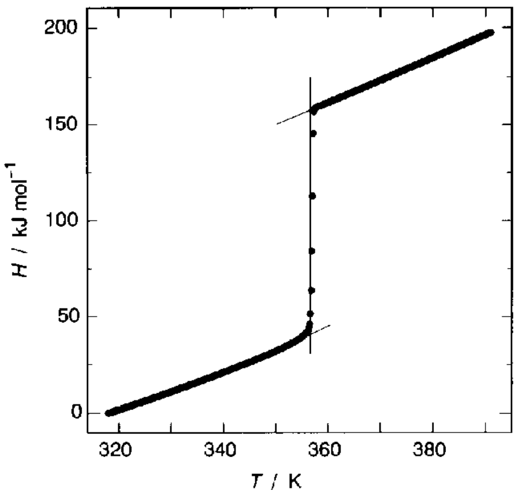

Fig. 4. Apparent enthalpy–temperature relationship for 16-hentriacontanone crystallized from dilute heptane solution. Weight, 1.07 mg; heating rate, 0.5 K min^{-1}; standard, sapphire. The symbols represent every fifth data point. The fine vertical line reprents the melting.

temperature dependence is taken into consideration, as Takahasi has stressed [10]. Using indium as the standard, slightly higher values were obtained: 119.8 kJ mol^{-1} for K31 and 154.2 kJ mol^{-1} for K39.

The heat capacities for the crystal (at 335 K) and the liquid (380 K) are listed in Table 1. In general, the scanning rate does not seem to have an effect on the data. In order to increase the precision it is desirable to use larger sample masses.

TABLE 1

Thermodynamic quantities for the symmetrical ketones K31 and K39 determined using sapphire as a standard

Sample	Heating rate/K min^{-1}	
	0.5	2
Heat of melting in kJ mol^{-1}		
K31	117.1 ± 0.1	116.6 ± 0.4
K39	153.0 ± 0.3	152.0 ± 0.8
Heat capacity at 335 K (crystal) in kJ K^{-1} mol^{-1}		
K31	1.02 ± 0.02	0.95 ± 0.03
K39	1.13 ± 0.03	1.21 ± 0.08
Heat capacity at 380 K (liquid) in kJ K^{-1} mol^{-1}		
K31	1.16 ± 0.02	1.09 ± 0.02
K39	1.36 ± 0.01	1.46 ± 0.10

n-*Alkanes*

As stated above, the purpose of the present investigation is to establish the reliability of the estimation of the total enthalpy change for *n*-alkanes between the crystals stable at room temperature and the liquid. We applied the present method to C51 and C52 crystals. The DSC curves of both are shown in Fig. 5A and 5B. The samples measured were crystals grown from a dilute solution in suitable solvents. The structure at room temperature for C51 was orthorhombic, whereas C52 was monoclinic. Small transition peaks are observed before the melting peak for both C51 and C52. In order to enhance the small peaks, a curve in which the ordinate is expanded about 25 times is also shown. C51 melts via two modifications and C52 via one modification. The symbols for the modifications of C51 and C52 are given at the top of their respective figures. The characteristic of the high-temperature modifications is a heat capacity that is higher than those of the crystal stable at room temperature and the liquid. This is why the simultaneous determination of the heat capacity and the heat of the transitions is necessary. The small peak observed on the magnified curves at 362 K for C51 and at 357 K for C52 may be ascribed to artifacts resulting from the quasi-dynamic properties of the modifications [5]. The measurement using the sapphire standard was also made at a heating rate of 0.5 K min^{-1} for the solution-crystallized samples. After melting, the stable crystalline forms were not recovered even if the cooling rate was very slow. The apparent enthalpy is plotted against uncorrected temperature for C51

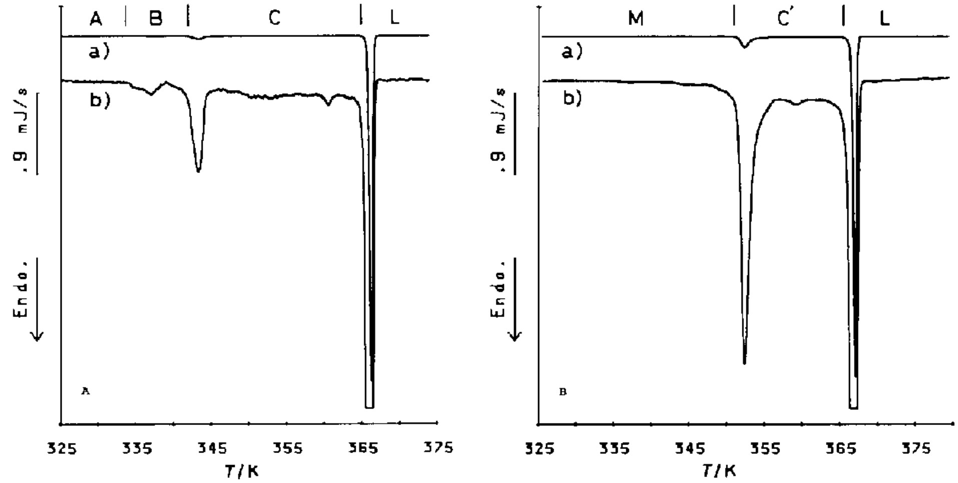

Fig. 5. DSC curves of henpentacontane (A) and dopentacontane (B). The former was crystallized from a hexane solution and the latter from a toluene solution. Weight, 1.00 mg; heating rate, 0.5 K min^{-1}. Curve (b) has a magnification of 25 times that of curve (a).

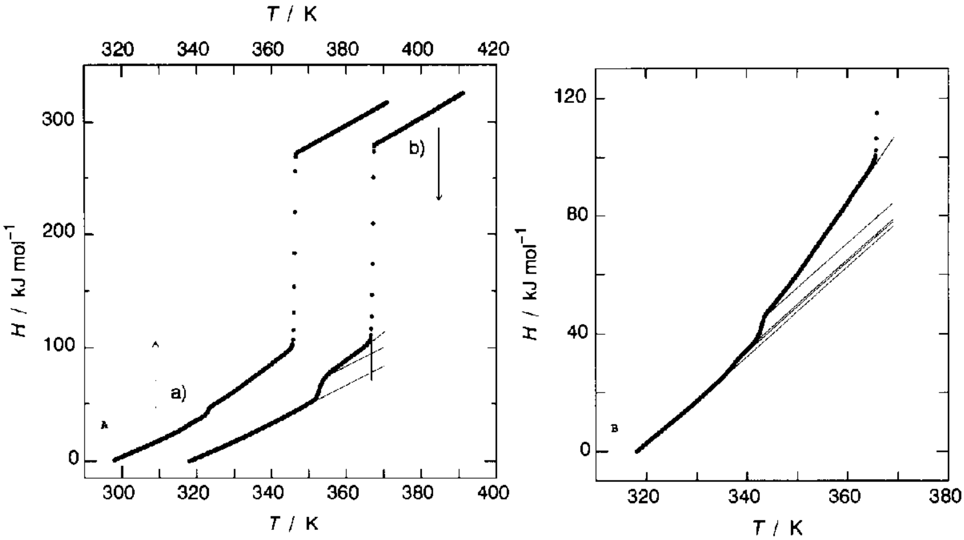

Fig. 6. A. Apparent enthalpy–temperature relationships of henpentacontane (a) and dopentacontane (b). Weight, 1.0 mg; heating rate, 0.5 K min^{-1}; standard, sapphire. The symbols represent every fourth data point. Fine lines represent the linear change of enthalpy for each phase, and the vertical lines represent the melting. B. Magnified enthalpy–temperature relationship for henpentacontane to elucidate the solid–solid transitions.

and C52 in Fig. 6. In theoretical studies, the linearity of the dependence of the enthalpy of melting of *n*-alkanes on the number of carbon atoms in the molecule *n* was assumed [13, 14]. Previously, it has been thought that the transition of the *n*-alkane crystals was simple, i.e. that the crystals of the homologue with *n* greater than approx. 40 melt directly from the orthorhombic crystals. The results presented here suggest that this assumption is not valid and that it is impossible to evaluate the total enthalpy change at the reference temperature without a knowledge of the temperature dependence of the enthalpy over the high-temperature modifications, as shown in Fig. 6A. In order to show the subtle solid–solid transition of C51, the scale of the ordinate is magnified by about ×2 in Fig. 6B. When the melting point is chosen as a reference temperature and the enthalpy changes are assumed to be linear with temperature, it is possible to evaluate the contribution from the transition and the high-temperature phases. This situation is shown by the fine lines in Fig. 6A for C52 and in Fig. 6B for C51. The tentative values are listed in Table 2. The high-temperature modification, the C- or C′-phase, makes a contribution that cannot be negligible. The C-phase of C51 extends over a wide temperature range and its contribution becomes larger than the sum of the transition heat.

Most of the theoretical considerations on the melting of a polymer chain is based on the entropy change arising from the conformational change

TABLE 2

Contributions of the transitions and the enthalpy change to the overall heat of melting ($kJ\ mol^{-1}$) [a] for samples C51 and C52

	C51 ($T_m = 365.6$ K)	C52 ($T_m = 366.7$ K)
$\Delta H_{(A\rightarrow B)}$	1.75	–
$\Delta H_{(B\rightarrow C)}/\Delta H_{(M\rightarrow C')}$	5.33	17.1
$\Delta H_{(C,C'\rightarrow L)}$	170.4	171.8
$H_{(B)}$	0.84	–
$H_{(C\ or\ C')}$	14.5	10.7
$\Delta H_{(A\rightarrow L)}/\Delta H_{(M\rightarrow L)}$	192.9	199.5

[a] The contribution is obtained approximately by assuming a linear variation of the enthalpy of the A or M phase. The symbols used for the phases are indicated in Figs. 5A and 5B.

[15, 16]. The present data may be easily converted to an expression for entropy. This will be done in further investigations on *n*-alkanes.

CONCLUSIONS

It has been demonstrated that the heat of melting and the heat capacity can be determined at relatively low heating rates using a heat-flux DSC for indium and long-chain symmetrical ketones, which were shown simply to melt. The present measuring method was very useful for evaluating the contribution from the high-temperature modifications of *n*-alkane crystals to the total enthalpy change from the stable crystals at room temperature to the liquid.

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