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Low-temperature heat capacity and phase transition of *n*-hexatriacontane

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Abstract

The heat capacities of crystalline and liquid *n*-hexatriacontane were measured with an automatic adiabatic calorimeter over the temperature range of 80–370 K. Two solid-to-solid phase transitions at the temperatures of 345.397 and 346.836 K, and a fusion at the temperature of 348.959 K have been observed. The enthalpies and entropies of these phase transitions as well as the chemical purity of the substance were determined on the basis of the heat capacity measurements. Thermal decomposition temperatures of the compound were measured by thermogravimetric analysis. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: *n*-Hexatriacontane; Heat capacity; Adiabatic calorimetry; Phase transition; Thermal decomposition

1. Introduction

n-Hexatriacontane has been considered as a kind of energy-storage material with application perspectives due to its high enthalpies of transition [1–3], innoxiousness, noncorrosiveness and good thermal stability. In China, for instance, it has been planned to use this substance as a special heat-storage material in aircraft. For the application of the material, thermodynamic data of this substance are urgently needed. Mazee [1], Schaaer et al. [2] and Compamy [3] reported the enthalpies of phase transitions of *n*-hexatriacontane with the conduction, the adiabatic calorimetric and the cryoscopic method, respectively. In the present work, low temperature heat capacity measurements were carried out with adiabatic calorimetry, and the basic thermodynamic parameters, such as enthalpy and entropy of phase transitions as well as chemical purity and thermal stability were determined on the basis of heat capacity measurement. Thermal decomposition of the compound was also studied by thermogravimetry (TG).

2. Experimental

2.1. Sample

n-Hexatriacontane is white sheet crystals, its molecular formula is $CH_3(CH_2)_{34}CH_3$. The sample used for the present calorimetric study was produced by ACROS ORGANNIS (New Jersey, USA). The labeled chemical purity is >98%. The mass of the sample

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loaded in the calorimeter amounted to 2.3438 g, corresponding to 4.6231×10^{-3} mol based on its molar mass of 506.98 g mol^{-1}.

2.2. Adiabatic calorimetry

Heat capacity measurements were carried out by means of an automatic adiabatic calorimeter for small sample. The construction of the calorimeter has been described previously in detail [4]. Briefly, the calorimeter included a sample cell, a thermometer, a heater, two adiabatic shields, two sets of 8-junction chromel–copel thermocouples and a high vacuum system. The calorimeter cell was made of gold-plated copper with internal capacity of 6 cm^3. A miniature platinum resistance thermometer made by the Shanghai institute of industrial automatic meters, China, was used to measure the temperature of the calorimeter cell. The thermometer with an uncertainty of about 1 mK (in absolute) was calibrated on the basis of the ITS-90 by the station of low temperature metrology, Chinese Academy of Sciences. The thermometer was placed in the copper sheath at the bottom of the sample cell. After loading the sample into the cell, the up-cover and body was sealed with a special kind of cycleweld. The cell was evacuated, and then a small amount of helium gas was introduced through a copper capillary on the up-cover to promote the heat transfer. Finally, the cell was sealed by pinching off the tube. Two adiabatic shields surrounded the cell and controlled its temperature. The whole calorimetric system was kept in a high vacuum with residual pressure of 10^{-3} Pa to obtain good adiabatic conditions.

In order to verify the reliability of the calorimeter, the molar heat capacities of α-Al_2O_3 were measured in the temperature range of 60–350 K. Deviations of the experimental results from the smoothed curve lie within ±0.2%, while the inaccuracy is within ±0.5%, as compared with those of the National Bureau of Standards [5] over the whole temperature range.

3. Result and discussion

3.1. Heat capacity

75 observed points of heat capacity were obtained in the solid region from 78 to 337 K, whereas nine points were obtained in the liquid region of 350–371 K. All the results are listed in Table 1, and plotted in Figs. 1 and 2. Fig. 1 indicates that the structure of *n*-hexatriacontane is stable at temperatures below 340 K and phase transitions in the temperature range of 340–350 K. The transition temperatures shown in Fig. 2 are 345.397, 346.836 and 348.947 K, respectively. Based on our observation, peaks 1 and 2 are solid-to-solid transitions, but peak 3 is the fusion. In detail, the three transitions are $Cry_{III} \rightarrow Cry_{II}$, $Cry_{II} \rightarrow Cry_{I}$, and $Cry_{I} \rightarrow$ liquid phase (where Cry_{III}, Cry_{II} and Cry_{I} represent the crystalline structures at the correspond-

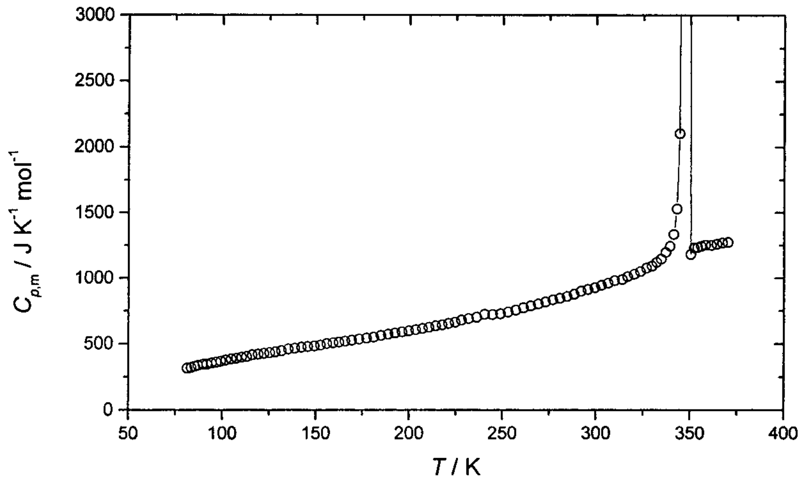

Fig. 1. Heat capacity as a function of temperature for *n*-hexatriacontane.

Table 1
Experimental molar heat capacities of *n*-hexatriacontane (M = 506.98 g mol^{-1})

T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}
81.310	316.06	227.853	680.65	346.724	33756
83.425	321.48	231.71	691.30	346.749	40447
89.498	345.96	236.033	702.41	346.769	39461
91.760	346.92	240.294	723.80	346.787	40267
94.169	354.69	244.51	723.60	346.801	41541
96.719	361.75	248.703	718.75	346.817	41950
99.218	368.97	252.857	730.72	346.836	48962
101.893	379.15	256.958	766.54	346.857	43010
104.744	385.42	261.013	774.81	346.932	14342
107.542	391.74	265.028	790.07	347.278	3603.7
110.293	398.14	268.994	803.34	347.759	3640.5
113.004	404.01	272.908	819.56	348.086	9213.5
115.941	417.89	276.773	833.89	348.295	14257
119.094	422.93	280.599	846.30	348.436	19237
122.198	428.08	284.391	860.11	348.541	24012
125.258	433.84	288.141	877.07	348.612	30715
128.279	438.69	291.84	901.27	348.674	37854
131.604	448.58	295.492	914.07	348.726	46594
135.213	460.75	299.108	926.52	348.775	54665
138.758	466.65	302.684	945.30	348.811	61077
142.254	472.85	306.219	961.54	348.838	68733
145.706	478.54	309.717	982.42	348.86	77937
149.12	484.04	313.785	991.90	348.876	94998
152.495	490.65	316.62	1011.9	348.889	116748
155.826	500.18	320.017	1062.5	348.900	137287
159.115	506.96	323.377	1052.2	348.91	128272
162.371	511.29	326.693	1076.2	348.919	139189
165.593	519.85	329.583	1093.5	348.927	148941
169.196	526.61	332.051	1121.7	348.934	171610
173.175	535.70	334.478	1146.8	348.939	185200
177.108	543.33	336.852	1197.2	348.943	215664
181.001	550.68	339.164	1244.1	348.947	240791
184.845	562.78	341.162	1334.9	348.951	167193
188.636	572.61	342.804	1529.8	348.966	37248
192.384	582.06	344.183	2106.1	349.138	8024.6
196.093	590.58	345.04	4514.7	350.213	1182.1
199.764	599.08	345.575	7225.6	352.056	1230.4
203.398	607.78	345.827	7090.2	353.902	1234.5
206.995	617.64	346.137	5674.4	355.738	1244.1
210.559	625.24	346.374	3911.3	358.148	1252.6
214.087	636.85	346.52	7536.5	361.138	1250.2
217.579	645.58	346.6	14743	364.117	1259.8
221.039	654.73	346.653	22326	367.074	1269.5
224.465	665.26	346.693	27736	370.016	1273.5

ing temperatures from low to high). Obviously, Cry_{III} has shown lower heat capacities, and the second phase transition has already taken following the first one, as the heat capacities of the compound have not reverted to the normal values. That is, Cry_{III} is a stable structure of *n*-hexatriacontane in the solid phase, while Cry_{II} and Cry_{I} are metastable phases.

Two polynomial equations have also been fitted by the least squares method based on the experimental values of heat capacity.

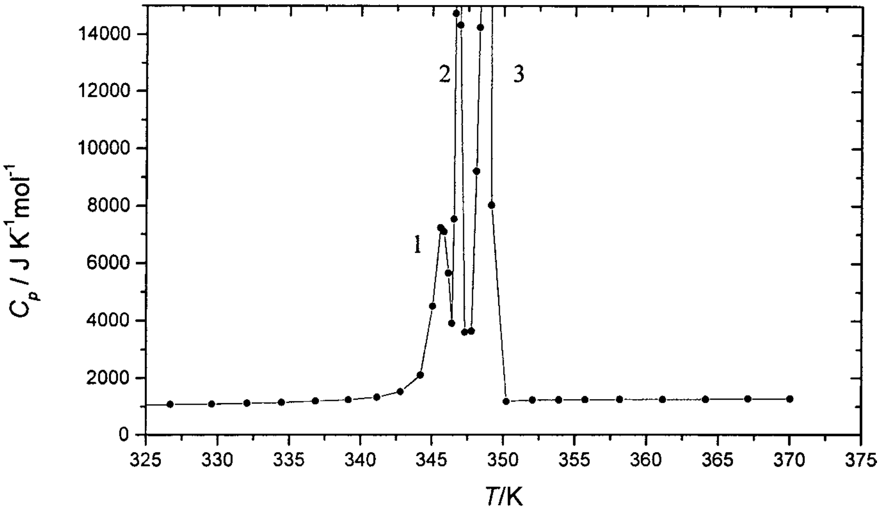

Fig. 2. Heat capacity near the phase transitions and melting of *n*-hexatriacontane.

1. For the solid phase:

$$C_{p,\mathrm{m}}/\mathrm{J\,K\,mol^{-1}} = 626.67 + 317.31X + 83.662X^2 + 112.75X^3 + 39.567X^4,$$

in which $X = \{(T/\mathrm{K}) - 210.0\}/130$. The equation is valid from 80 to 340 K with an accuracy of ±0.2%.

2. For the liquid phase:

$$C_{p,\mathrm{m}}/\mathrm{J\,K\,mol^{-1}} = 1251.04 + 25.547X - 3.2608X^2,$$

in which $X = \{(T/\mathrm{K}) - 359.5\} - 10.5$. The equation is valid from 349 to 370 K with an accuracy of ±0.5%.

3.2. Enthalpy and entropy of transitions

Enthalpies of transitions in the solid region are calculated based on the following equation:

$$\Delta_{\mathrm{trs}}H_{\mathrm{m}} = \frac{\left[Q - n\int_{T_\mathrm{i}}^{T_\mathrm{f}} C_{p(\mathrm{s})}\mathrm{d}T - \int_{T_\mathrm{i}}^{T_\mathrm{f}} H_0\mathrm{d}T\right]}{n} \quad (\mathrm{kJ\,mol^{-1}}). \qquad (1)$$

Enthalpy of fusion is calculated from the following equation:

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = \frac{\left[Q - n\int_{T_\mathrm{i}}^{T_\mathrm{m}} C_{p(\mathrm{s})}\mathrm{d}T - n\int_{T_\mathrm{m}}^{T_\mathrm{f}} C_{p(\mathrm{L})}\mathrm{d}T - \int_{T_\mathrm{i}}^{T_\mathrm{f}} H_0\mathrm{d}t\right]}{n} \quad (\mathrm{kJ\ mol^{-1}}), \qquad (2)$$

where T_i in Eqs. (1) and (2) is a temperature point slightly below the starting transition temperature, T_f the temperature slightly higher than the finishing transition temperature, Q the total heat introduced to heat the sample and container from temperature of T_i–T_f, T_m the melting point of the sample measured, n the number of moles of sample, H_0 the heat capacity of the empty cell, $C_{p(\mathrm{s})}$ the heat capacity of the solid and $C_{p(\mathrm{L})}$ the heat capacity of the liquid. The sample and cell were heated step by step to approach the transition temperatures. In the region of melting, a heating step was within 0.01 K, which means that the deviation of the experimental melting point from the actual melting point is no higher than 0.01 K. Supposing the experimental melting point was used to calculate $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ instead of actual melting point, the calculated deviation could be neglected within the measurement precision. Based on the heat capacity measurements, the $\Delta_{\mathrm{trs}}H_{\mathrm{CryIII\text{–}CryII}}$, $\Delta_{\mathrm{trs}}H_{\mathrm{CryII\text{–}CryI}}$ and $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ are determined to be 10.098, 32.126 and 87.495 kJ mol^{-1}, respectively. $\Delta_{\mathrm{trn}}S_{\mathrm{CryIII\text{–}CryII}}$, $\Delta_{\mathrm{trn}}S_{\mathrm{CryII\text{–}CryI}}$ and $\Delta_{\mathrm{fus}}S$ calculated from $\Delta S_{\mathrm{m}} = \Delta H_{\mathrm{m}}/T_{\mathrm{m}}$ are 29.236, 92.626, and 250.637 J mol^{-1} K^{-1}, respectively.

Comparisons of our work with Mazee [1], Schaaer et al. [2], and Compamy [3] are listed in Table 2. The temperatures of transitions and the enthalpy for $\mathrm{Cry_{III\text{–}II}}$ and fusion agree well within the given uncertainties. The discrepancy of $\Delta_{\mathrm{trs}}H_{\mathrm{CryII\text{–}CryI}}$

Table 2
Transition temperatures and enthalpies of transitions of *n*-hexatriacontane

	T/K			ΔH/kJ mol^{-1}		
	Cry$_{\text{III–II}}$	Cry$_{\text{II–I}}$	Fusion	Cry$_{\text{III–II}}$	Cry$_{\text{II–I}}$	Fusion
Mazee [1]	–	346.65 ± 0.10	348.980 ± 0.05	–	30.1 ± 0.9	118 ± 6[a]
Schaaer [2]	345.25 ± 0.50	346.95 ± 0.50	349.05 ± 0.50	9.92 ± 0.21	30.54 ± 0.25	88.83 ± 0.25
Compamy [3]	345.35 ± 0.50	347.05 ± 0.40	349.5 ± 0.30	9.92 ± 0.29	30.5 ± 0.6	88.8 ± 0.6
Present work	345.394 ± 0.250	346.836 ± 0.020	348.947 ± 0.005	10.098 ± 0.050	32.126 ± 0.161	87.495 ± 0.437

[a] Total enthalpy of fusion and Cry$_{\text{II–I.}}$

is probably caused by the using of different measurements.

3.3. Melting point and purity

The purity of the sample is evaluated from a set of equilibrium melting temperatures and melting fractions corresponding to these temperatures [6]. According to the ideal solution law, the relation between the mole fraction N ($N \ll 1$)of a small amount of impurities in the sample and its melting-point can be expressed as:

$$N = \frac{\Delta_{\text{fus}}H(T_0 - T_1)}{RT_0^2}, \tag{3}$$

where T_0 is the melting point of an absolutely pure substance, T_1 the melting point of the given sample (strictly speaking, under the experimental adiabatic condition $T_{0,}$ and T_1 should be the triple points), $\Delta_{\text{fus}}H_{\text{m}}$ the enthalpy of fusion, and R the molar gas constant. As for the liquid solution formed by a part of the sample melted, given that N' is the mole fraction of the impurities and T the melting point of the solution, then

$$N' = \frac{\Delta_{\text{fus}}H(T_0 - T)}{RT_0^2}. \tag{4}$$

Assuming that the impurities are solid-insoluble, i.e., no solid-solution will be formed, and all of the impurities can transfer completely into the liquid phase when the melting started, the relative amount of the sample in the liquid phase will increase in the process of the melting. On the other hand, since the total amount of the impurities is constant, the mole fraction of the impurities in the liquid phase will gradually decrease. Given that F is the ratio of the sample in the liquid phase to the total amount, then

$$F = \frac{q}{Q}, \tag{5}$$

where F is also designated as the melting fraction, and its value is the ratio of the partial heat (q) required to melt a part of the sample to the total heat (Q) required to melt the whole sample. Obviously, F is inversely proportional to the mole fraction of the impurities in the liquid phase, that is,

$$N' = \frac{1}{F}N. \tag{6}$$

Substituting Eqs. (4) and (5) into Eq. (6), the following equation is obtained.

$$T_0 - T = \frac{1}{F}(T_0 - T_1). \tag{7}$$

Eq. (7) suggests that the relationship between the equilibrium melting temperature T and $1/F$ is linear. Plotting T vs $1/F$, and extrapolating the straight line to $1/F = 1$ and $1/F = 0$, T_1 and T_0 can be derived. The results of observation are tabulated in Table 3 and plotted in Fig. 3. $T_0 = 349.023$ K and $T_1 = 348.952$ K

Table 3
Mole fractions and experimental equilibrium temperatures of *n*-hexatriacontane

q/J	$F = q/\Delta_{\text{fus}}H$	$1/F$	T/K
104.408	0.2581	3.8745	348.775
122.29	0.30233	3.30769	348.811
158.574	0.39203	2.55084	348.86
195.274	0.48276	2.07143	348.889
324.687	0.80269	1.24581	348.943

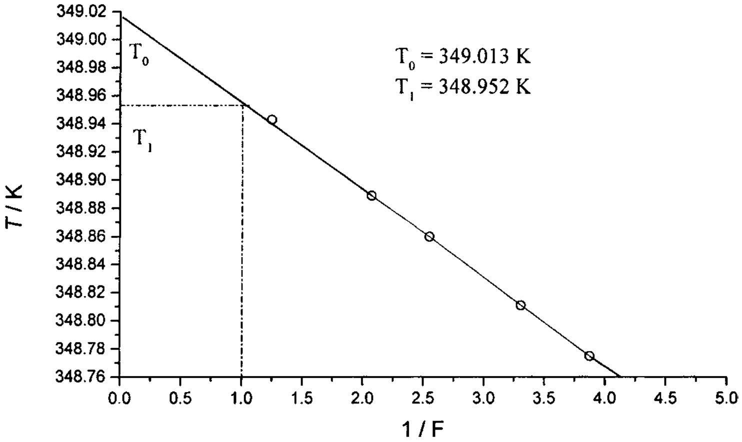

Fig. 3. Melting fractions and equilibrium temperatures of *n*-hexatriacontane in the melting region.

are obtained from the figure. According to Eq. (3), $N = 5.53 \times 10^{-3}$ mol is evaluated. The purity of the sample is $1 - N = 99.45$ mol%.

3.4. Themogravimetric analysis

Thermal stability of *n*-hexatriacontane was investigated with a TG system, which is equipped with a JF-2 thermobalance, a platinum wire furnace, and two sets of platinum–rhodium thermocouples. The measurements were carried out in a nitrogen atmosphere with the flowing rate of 25 ml min^{-1} and heating rate of 10 K/min, and a sample mass of 9.5 mg was employed. The experimental results of TG and DTG are shown in Fig. 4. It suggests that only one mass-lost step was discovered, which may be caused by the thermal decomposition of *n*-hexatriacontane. According to the TG curve, the initial and final decomposition temperatures of the substance are 483 and 632 K, respectively. The largest mass-loss

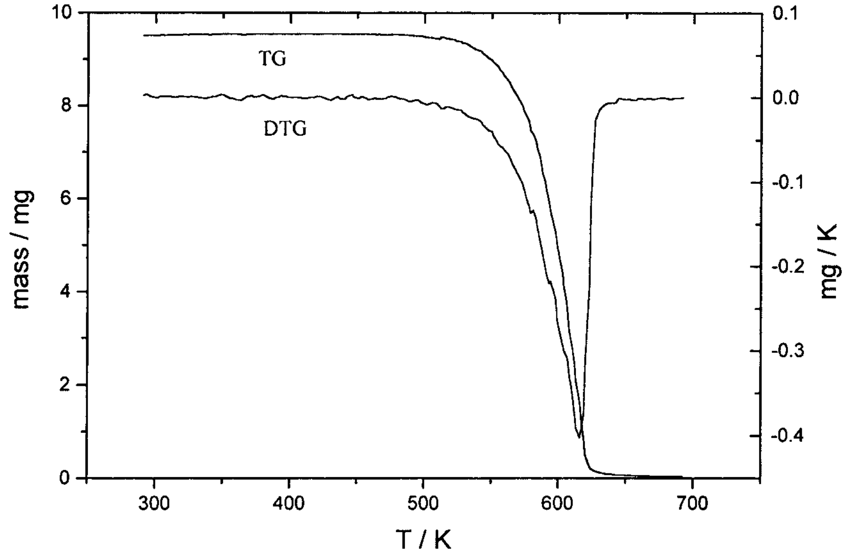

Fig. 4. TG and DTG curves of *n*-hexatriacontane.

took place at the temperature of 616 K, based on the observation of the peak of DTG.

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