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HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF 1-HEXADECANOL

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The low-temperature heat capacities of 1-hexadecanol have been measured with an automatic adiabatic calorimeter over the temperature range from 80 to 370 K. A solid–liquid phase transition was observed at T_m=322.225±0.002 K and the molar enthalpy and entropy of fusion were determined to be 57.743±0.008 kJ mol^{-1} and 179.19±0.04 J K^{-1} mol^{-1}, respectively. The purity, the real melting point (T_1) and the ideal melting point without any impurity or absolutely purity (T_0) of the sample under investigation were determined to be 99.162 mol%, 322.21 and 322.34 K, respectively, by fractional melting method. According to the polynomial equation of heat capacity and thermodynamic relationship, the thermodynamic functions of the compound relative to the reference temperature 298.15 K were calculated in the temperature ranges of 80 to 370 K with an interval of 5 K. In addition, further researches of thermal properties for this compound were carried out by means of TG/DTG.

Keywords: *adiabatic calorimetry, 1-hexadecanol, low-temperature heat capacity, purity determination, TG/DTG, thermodynamical functions*

Introduction

1-hexadecanol can be prepared from palm oil by grease exchange and catalytic hydrogenation under high pressure, or obtained from cotton oil. 1-hexadecanol is one of the main raw materials in the production of many detergents, surfactants, perfumes, chemicals used for industry, agriculture and daily life. In recent years, it was considered as an energy storage material in aircraft and industrial purpose due to its large enthalpy of fusion, non-toxicity, thermal stability in its melting process. In order to develop new application field of this compound and carry out some theoretical studies concerned with it, the thermodynamic properties of the compound were urgently needed. Mosselman *et al.* determined the melting point and the enthalpy of the melting to be 322.2 K and 58.38 kJ mol^{-1} of 1-hexadecanol with adiabatic calorimetry in 1973 [1]. However, owing to the limited precision and performance of the calorimeter used, the measured heat capacity data cannot satisfy the requirement of practical application. So, in the present study, we determined low-temperature heat capacity of 1-hexadecanol from T=80 to 370 K with an automatic precision adiabatic calorimeter. The equations of the heat capacity with the reduced temperatures in solid phase and liquid phase were fitted by means of the least square fitting, and the melting point, the molar enthalpy and entropy of fusion of the 1-hexadecanol were obtained from the experimental heat capacity data. According to the polynomial equations of heat capacity, the thermodynamic functions of the sample relative to the reference temperature 298.15 K were calculated with an interval of 5 K.

Experimental

Sample

The sample used for the calorimetric study is of a chromatogram purity and was purchased from Shanghai Reagent Company, the formula: $C_{16}H_{34}O$, the molar mass: 242.45 g mol^{-1}, melting point range: 48–50°C, labeled purity: >99.5%, in accordance with the standards of Q/GHSA 829-94.

Methods

Calorimetric experiment

A precision adiabatic calorimeter was applied to measure the heat capacities over the temperature range of 80 to 370 K. The apparatus was described elsewhere [2, 3] in detail. The sample vessel was made of gold-plated copper with a wall thickness of 0.3 mm. The vessel is 20 mm in diameter and height with a

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volume of ca. 6 cm^3. The electric heating wires were evenly and bifilarly wound and fixed on the outer surface of the vessel body. A copper sheath was soldered at the bottom of the vessel for inserting a miniature platinum resistance thermometer to measure the temperature of the vessel. The lid of the vessel was sealed with a small amount of silicone thermally conductive sealant (type HT916, produced by Shanghai Huitian New Chemical Material Co., Ltd.) after the sample was loaded. The air in the vessel was evacuated and a small amount of helium gas (0.1 MPa) was introduced through a copper capillary on the lid to enhance the heat transfer within the cell. The capillary was then pinched off and soldered at its end.

Liquid N_2 was used as the refrigerant and the heat capacity measurement started when the sample was cooled down to 78 K. The heating duration was 10 min and the temperature increment was 3–4 K for each experimental temperature point.

The heat capacity was intermittently measured. The programmed heating and the acquisition of the temperature and electrical energy data were performed by means of a personal computer. The reliability of the calorimeter was verified by the heat-capacity measurements of Standard Reference Material 720 (α-Al_2O_3) . The relative deviations of the experimental heat-capacity values from those given by NIST [4] were ±0.1% in the temperature range from 80 to 400 K.

Thermogravimetric experiment

Thermogravimetric experiment was carried out by using the thermal balance, (Model DT-20B made in Japan) with the experiment condition: flow rate of N_2: 25 mL min^{-1}, heating rate 10 K min^{-1}.

Results and discussion

Heat capacity

The measured heat capacities of 1-hexadecanol in the temperature range of 80 to 370 K were listed in Table 1 and shown in Fig. 1. It can be seen that the sample was in solid phase between 80 and 316 K, and in liquid phase between 324 and 370 K. The heat capacity curve is smooth, no matter how the sample is in solid or liquid phase, which means that the structure of 1-hexadecanol is stable. No other phase change occurred in solid phase and no aggregation or decomposition took place in liquid phase. The heat capacity values were fitted by the least square method, and the polynomial equations of heat capacity of 1-hexadecanol as a function of temperature were obtained for solid and liquid phase sections, respectively.

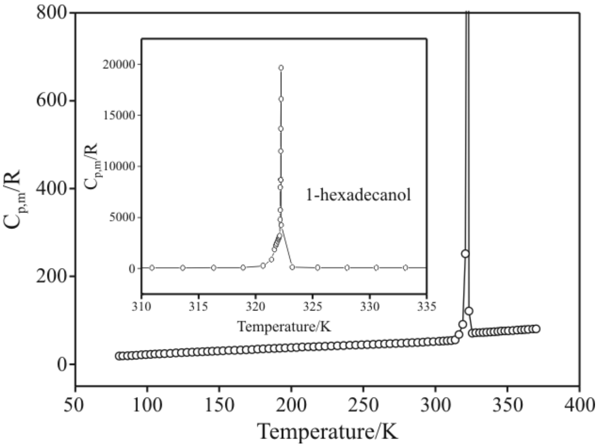

Fig. 1 The curve of experimental molar heat capacities ($C_{p,m}/R$) of the 1-hexadecanol as a function of temperature (T)

For solid phase temperature range (80~316 K):

$$C_{p,\,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})=300.67+150.68X-30.004X^2+4.6578X^3+21.822X^4+10.316X^5 \quad (1)$$

where X is the reduced temperature, $X=(T/\mathrm{K}-187)/127$, the correlation coefficient of the fitting: $R^2=0.9998$.

For liquid phase temperature range (324~370 K):

$$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})=631.41+40.930X+0.1429X^2-1.2982X^3 \quad (2)$$

where $X=(T/\mathrm{K}-347)/23$, the correlation coefficient of the fitting: $R^2=0.9997$.

Melting point, the molar enthalpy and entropy of fusion

The abnormal section of the heat capacity curve is due to the melting of the sample, which is shown in the inset of Fig. 1. The melting point of the sample was determined by stepwise heating and gradually approaching, the result was calculated by formula in literature [4, 5]:

$$T_m=T_i'+\frac{Q'-\overline{C}_{p(0)}(T_f-T_i')-nC_{p(L)}(T_f-T_m)}{nC_{p(S+L)}} \quad (3)$$

where T_m is the melting temperature of the sample; T_i', a certain equilibrium temperature at which solid and liquid phase coexist in the melting region; T_f, a temperature slightly above the melting temperature T_m; Q', the total heat introduced to heat the sample and the sample cell from T_i' up to T_f; $\overline{C}_{p(0)}$, the average heat capacity of the empty sample cell in the temperature range from T_i' to T_f; $C_{p(L)}$, the heat capacity of the sample in the liquid region at temperature $(T_f+T_m)/2$; $C_{p(S+L)}$, the heat capacity of the solid-liquid coexistent system at temperature $(T_m+T_i')/2$; n, the amount of the sample.

The molar enthalpy of fusion of the sample can be calculated by the following formula:

Table 1 Experimental molar heat capacity of 1-hexadecanol (M=242.45 g mol^{-1}, R=8.31451 J K^{-1} mol^{-1})

T/K	$C_{p,m}$/R	T/K	$C_{p,m}$/R	T/K	$C_{p,m}$/R	T/K	$C_{p,m}$/R
80.577	18.675	176.621	34.401	280.102	48.753	322.188	8710.4
83.154	19.041	180.488	35.067	283.841	49.269	322.198	8784.2
86.253	19.659	184.370	35.718	287.579	49.896	322.205	11502
89.260	20.127	188.172	36.265	291.178	50.435	322.213	13695
92.444	20.707	191.910	36.796	294.778	51.113	322.221	16584
95.826	21.477	195.648	37.304	298.378	51.728	322.227	19642
99.090	22.119	199.802	37.987	302.462	52.503	322.252	4239.8
102.274	22.754	203.579	38.551	305.445	53.117	323.202	121.26
105.379	23.436	207.555	39.092	308.208	53.673	325.445	71.047
108.504	24.071	211.570	39.646	310.907	54.307	328.006	71.618
112.025	24.530	215.452	40.164	313.607	55.617	330.577	72.103
115.981	25.181	219.224	40.629	316.323	67.860	333.128	72.785
119.916	25.982	223.338	41.208	318.909	91.072	335.621	73.213
123.734	26.610	227.691	41.712	320.659	251.575	338.172	73.761
127.472	27.118	231.981	42.239	321.401	872.311	340.684	74.237
131.131	27.720	236.202	42.789	321.653	1873.3	343.156	74.856
134.731	28.148	240.437	43.358	321.759	2267.9	345.589	75.356
138.251	28.799	244.584	43.874	321.832	2437.4	348.081	75.991
141.772	29.165	248.674	44.374	321.912	2633.5	350.514	76.546
145.193	29.926	252.749	44.992	321.973	2837.2	353.540	77.180
148.615	30.402	256.843	45.532	322.021	2943.8	356.665	77.879
152.412	30.894	260.858	46.016	322.067	3108.1	359.632	78.451
156.586	31.497	264.794	46.579	322.108	3207.7	361.906	79.093
160.700	32.053	268.334	46.991	322.138	4772.0	364.418	79.585
164.774	32.655	272.488	47.602	322.158	5720.9	367.464	80.219
168.769	33.234	276.364	48.182	322.174	7953.3	369.857	80.672
172.735	33.798						

$$\Delta_{\text{fus}}H_{\text{m}}/(\text{J mol}^{-1})= \left[Q-n\int_{\text{T}_\text{i}}^{\text{T}_\text{m}}C_{\text{p(s)}}\text{d}T-n\int_{\text{T}_\text{m}}^{\text{T}_\text{f}}C_{\text{p(l)}}\text{d}T-\int_{\text{T}_\text{i}}^{\text{T}_\text{f}}C_{\text{p(0)}}\text{d}T\right]/n \tag{4}$$

The molar entropy of fusion can be calculated from the molar enthalpy of fusion and the melting point:

$$\Delta_{\text{fus}}S_{\text{m}}/\text{J K}^{-1}\text{mol}^{-1}=\frac{\Delta_{\text{fus}}H_{\text{m}}}{T_{\text{m}}} \tag{5}$$

In formula (4) , T_{m} is the melting point of the sample; T_{i} is the temperature slightly below the beginning melting temperature; T_{f} is the temperature which is a little higher than the ending melting temperature; Q is the total energy introduced into the sample vessel when heating up from T_{i} to T_{f}; $C_{\text{p(0)}}$ is the heat capacity of the empty vessel between T_{i} and T_{f}; $C_{\text{p(s)}}$ is the heat capacity of solid, $C_{\text{p(l)}}$ is the heat capacity of liquid, and n is the molar amount of the sample.

Through natural cooling (about 0.5 K min^{-1}) and liquid nitrogen fast cooling (about 20 K min^{-1}) , the sample was cooled to about 298 and 78 K, respectively, and the heat capacity of the sample was measured repeatedly in the melting temperature range. The enthalpy of fusion of the sample for the two series of measurements are 57.751 and 57.735 kJ mol^{-1}, respectively, which means the enthalpy of solid-liquid phase transition is not affected by cooling method under the experimental condition. The thermodynamic parameters are listed in Table 2.

Purity determination of the sample

The purity of the sample was estimated by a set of equilibrium melting temperatures and melted fractions corresponding to these temperatures [6, 7]. On the basis of ideal solution theory, the relationship between the molar fraction N of the impurity and the melting point is:

$$N=\frac{\Delta_{\text{fus}}H_{\text{m}}(T_0-T_1)}{RT_0^2} \tag{6}$$

In formula (6), T_0 is the melting point of the absolutely pure substance; T_1 is the melting point of the given sample; $\Delta_{\text{fus}}H_{\text{m}}$ is the enthalpy of fusion of the sample; R is the gas constant. For the liquid solution

Table 2 Thermodynamic parameters of 1-hexadecanol

Thermodynamic parameters	Series 1	Series 2	Mean value
T_m/K	322.227	322.223	322.225±0.002
$\Delta_{fus}H_m$/kJ mol^{-1}	57.751	57.735	57.743±0.008
$\Delta_{fus}S_m$/J K^{-1} mol^{-1}	179.220	179.170	179.190±0.040

formed by a part of the sample melted, if the molar fraction of the impurity is N' and the equilibrium melting temperature is T, we have:

$$N' = \frac{\Delta_{fus}H_m(T_0-T)}{RT_0^2} \tag{7}$$

If it is assumed that the impurities are solid-insoluble, i.e., no solid-solution is formed, and all of the impurities are transferred completely into the liquid phase when the melting started, along with the melting process going on, the relative amount of the sample in the liquid phase is progressively increased. Because the total amount of the impurities remains constant, the molar fraction of the impurities in the liquid phase becomes less and less. If F is the ratio of the amount of the sample in the liquid phase to total amount of the sample, and the value is also equal to the ratio of the heat needed for melting part of the sample to that needed for melting the whole sample ($F=q/Q$) . Obviously, F is in inverse ratio to the molar fraction of the impurities in the liquid phase. That is:

$$N' = \frac{1}{F}N \tag{8}$$

Substituting formula (6) and (7) into formula (8), we have:

$$T_0-T = \frac{1}{F}(T_0-T_1) \tag{9}$$

From formula (9) , the linear relationship can be found between equilibrium melting temperature T and $1/F$. By plotting T *vs.* $1/F$ and extrapolating to $1/F=0$ and $1/F=1$, respectively, T_1 and T_0 are obtained. The results are shown in Fig. 2 and listed in Table 3. From the Fig. 2, T_0=322.34 K and T_1=322.21 K were obtained. Using formula (6), N is calculated to be 0.00338. The purity of the sample is 99.662 mol%.

Table 3 Observed equilibrium temperature (T) and fractions melted (F) of 1-hexadecanol

q/J	$F=q/(n\Delta H_m)$	$1/F$	T/K
49.262	0.0943	10.5981	320.695
85.046	0.1628	6.1424	321.401
135.354	0.2591	3.8588	321.769
183.310	0.3509	2.8496	321.921
274.991	0.5264	1.8997	322.086
360.873	0.6904	1.4485	322.133
452.030	0.8653	1.1556	322.188

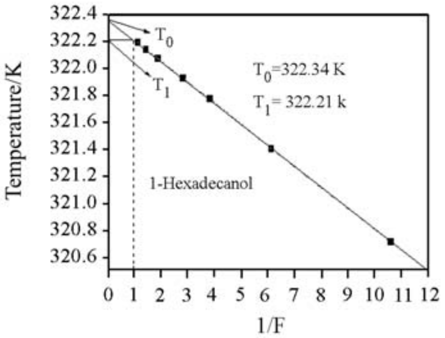

Fig. 2 The melting curve of 1-hexadecanol

Thermodynamical functions

According to the polynomial equation of heat capacity and thermodynamic relationship, the thermodynamic functions of the sample relative to the reference temperature 298.15 K were calculated in the temperature ranges of 80 to 316 and 325 to 370 K with an interval of 5 K. The thermodynamic relationships were listed as follows.

Before the melting of sample,

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,m}(s)\mathrm{d}T \tag{10}$$

$$S_T - S_{298.15} = \int_{298.15}^{T} [C_{p,m}(s)/T]\mathrm{d}T \tag{11}$$

After the melting of sample,

$$H_T - H_{298.15} = \int_{298.15}^{T_i} C_{p,m}(s)\mathrm{d}T + \Delta_{fus}H_m + \int_{T_f}^{T} C_{p,m}(l)\mathrm{d}T \tag{12}$$

$$S_T - S_{298.15} = \int_{298.15}^{T_i} [C_{p,m}(s)/T]\mathrm{d}T + \Delta_{fus}H_m/T_m + \int_{T_f}^{T} [C_{p,m}(l)/T]\mathrm{d}T \tag{13}$$

The values of thermodynamic function H_T–$H_{298.15}$, S_T–$S_{298.15}$ were listed in Table 4, respectively.

Table 4 Thermodynamic functions of 1-hexadecanol

T/K	$C_{p,m}/R$	$[(H_T–H_{298.15\ K})/R$ $K\cdot 10^{-3}$	$[S_T–S_{298.15\ K}]/R$
80	18.766	–7.796	–42.49
85	19.633	–7.700	–41.34
90	20.497	–7.599	–40.20
95	21.356	–7.494	–39.07
100	22.212	–7.385	–37.95
105	23.0639	–7.272	–36.84
110	23.911	–7.155	–35.74
115	24.75325	–7.033	–34.65
120	25.590	–6.907	–33.57
125	26.421	–6.777	–32.51
130	27.245	–6.643	–31.45
135	28.063	–6.505	–30.41
140	28.874	–6.362	–29.36
145	29.675	–6.216	–28.34
150	30.468	–6.065	–27.31
155	31.252	–5.911	–26.31
160	32.026	–5.753	–25.30
165	32.790	–5.591	–24.31
170	33.543	–5.425	–23.32
175	34.286	–5.255	–22.34
180	35.017	–5.082	–21.36
185	35.737	–4.905	–20.40
190	36.446	–4.725	–19.44
195	37.145	–4.541	–18.49
200	37.832	–4.353	–17.55
205	38.509	–4.162	–16.61
210	39.178	–3.968	–15.68
215	39.837	–3.771	–14.75
220	40.489	–3.570	–13.83
225	41.136	–3.366	–12.92
230	41.777	–3.158	–12.01
235	42.416	–2.948	–11.11
240	43.054	–2.734	–10.21
245	43.693	–2.517	–9.31
250	44.337	–2.297	–8.42
255	44.988	–2.074	–7.53
260	45.649	–1.847	–6.64
265	46.324	–1.617	–5.76
270	47.017	–1.384	–4.89
275	47.731	–1.147	–4.01
280	48.472	–0.906	–3.14
285	49.245	–0.621	–2.27
290	50.055	–0.413	–1.41
295	50.908	–0.161	–0.54
298.15	51.470	0	0
300	51.809	0.095	0.32
305	52.767	0.357	1.18
310	53.787	0.623	2.04
315	54.877	0.895	2.90
320	melting region	–	–
325	71.388	7.841	24.46
330	72.379	8.200	25.55
335	73.403	8.564	26.65
340	74.453	8.934	27.74
345	75.517	9.309	28.84
350	76.587	9.689	29.93
355	77.653	10.075	31.03
360	78.705	10.466	32.12
365	79.733	10.862	33.21
370	80.729	11.263	34.31

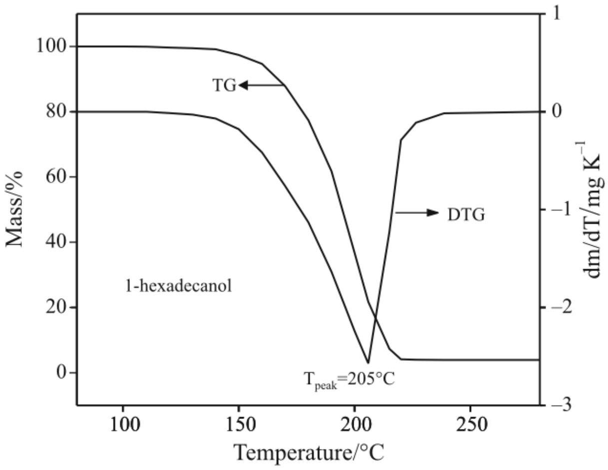

Fig. 3 TG and DTG curves of 1-hexadecanol under the atmosphere of nitrogen

Thermogravimetric analysis

Thermogravimetric result is shown in Fig. 3. It can be seen that no mass loss was observed below 110°C and mass loss of 5% occurred between 110 and 170°C. In the temperature range of 170–220°C, the mass loss rate obviously became faster. From the DTG curve, it was found the largest mass loss rate was at about 205°C.

Acknowledgements

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