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Heat capacity and thermodynamic properties of *p*-dimethylaminobenzaldehyde

Shuang He Meng[a], Ping Liang[b], Zhi Cheng Tan[a,*], Yong Ji Song[a], Li Li[a], Lan Wang[a]

[a]Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian 116023, China
[b]State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China

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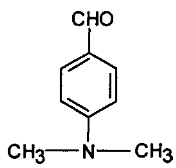
Abstract

The heat capacities of *p*-dimethylaminobenzaldehyde [*p*-DMABD] were measured between 80 and 360 K with a small sample automated adiabatic calorimeter. The thermodynamic parameters of solid–liquid phase transition were also obtained. The melting point, enthalpy and entropy of fusion of this compound were determined to be 346.15 K, 19.07 kJ mol^{-1} and 55.08 J mol^{-1} K^{-1}, respectively. The experiment of purity determination with the adiabatic calorimeter indicated that the sample purity was 99.74% (molar fraction).

Keywords: Adiabatic calorimeter; *p*-dimethylaminobenzaldehyde; Heat capacity; Enthalpy of fusion; Purity determination

1. Introduction

p-dimethylaminobenzaldehyde [*p*-DMABD], also named Ehrlich's reagent, is an important medical and biochemical inspection reagent. Its molecular formula is $C_9H_{11}ON$ and structural formula is



Usually, it is used to inspect amino acid and peptide, to examine hydrogen peroxide, arsphenamine, *o*-aminobenzoic acid, antipyrine, skatole, tryptophan, albumin, ergotin and so on. It is also used to distinguish between scarlet fever and serum sickness.

As an important reagent, the thermodynamic data of *p*-DMABD has not been reported up to now except a few of physical property data which can be found in some reagent manuals. To provide basic thermodynamic data such as heat capacity, melting point, enthalpy and entropy of fusion, calorimetric study was carried out on *p*-DMABD with an adiabatic calorimeter in the temperature range from 80 to 360 K. The purity of the sample was also determined by calorimetric technique. At the same time the differential scanning calorimetric analysis (DSC) was performed on the same sample and the result was compared with that of the adiabatic calorimetric method.

2. Experimental

2.1. Sample

The sample of *p*-DMABD was produced by Tianjin Institute of Chemical Reagent, China with an analy-

*Corresponding author. Fax: +86-411-4691570
E-mail address: tzc@ms.dicp.ac.cn (Z.C. Tan)

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tical grade. Its melting point ranges between 346.15 and 348.15 K [1].

2.2. Calorimetric apparatus

The structure of the adiabatic calorimeter has been described in the literature [2–4]. It includes sample cell, electric heater, thermometer, adiabatic shields, differential thermocouples, vacuum can etc.

The sample cell is a cylindrical container made of thin-walled (0.3 mm thick) gold-plated copper. It is 20 mm long and 20 mm in diameter with an internal volume of 6 cm^3. Four L-shaped 0.10 mm thick radial gold-plated copper vanes are placed in the cell to speed up the thermal equilibrium. A heater made of Karma wire of 0.12 mm in diameter is wound bifilarly on the surface of the cell and fixed by use of cycleweld. At the bottom of the cell an Ω-shape sheath is silver-soldered to insert a miniature platinum resistance thermometer. On the top of the cell, there is a flange, where the sealant would stick. The lid of the cell was made of gold-plated silver. A small amount of cycloweld is used to seal the lid to the main body of the sample cell. No leakage was found when the sealed cell was kept in 1×10^{-3} Pa vacuum in the temperature range of 60–360 K. At the center of the lid, there is an about 5 cm long copper capillary for evacuating the cell, introducing the helium gas and hanging the sample cell. The capillary is pinched off and the resultant fracture is soldered with a little amount of solder to ensure the sealing of the cell after introducing the helium gas.

To measure the temperature of the sample, a miniature platinum resistance thermometer is used (IPRT No. 2, produced by Shanghai Institute of Industrial Automatic Meter, China). The thermometer was calibrated on the basis of ITS-90 by the Station of Low-temperature Metrology and Measurements, Academia Sinica. An integration digital multimeter (Model 5000, Sabstronics, Switzerland) was used to measure the temperature with an accuracy of 0.1 mK.

To verify the accuracy of the adiabatic calorimeter, the molar heat capacities of the standard reference material α-Al_2O_3 were measured from 60 to 360 K. The results indicated that the deviations of the experiment data lie within $\pm$0.2%, while the inaccuracy is within $\pm$0.5% compared with the data of National Bureau of Standards in the whole temperature range.

2.3. Heat capacity measurement

The heat capacity of *p*-DMABD was determined over the temperature range from 80 to 360 K with above adiabatic calorimeter. The melting point and enthalpy of fusion of the sample can be obtained from the heat capacity measurements. The temperatures of initial melting and final melting can be derived from the molar heat capacity vs. temperature curve.

2.4. Purity analysis [5,6]

The purity of the sample is determined during the determining of the melting curve. At the temperature several degrees below the melting point, an enough amount of energy is supplied to the sample cell to melt a small fraction of the sample, say 10%, and the melting temperature is observed until equilibrium is reached. Following the attainment of equilibrium, another amount of energy is supplied to the sample and another portion of sample is melted and a second equilibrium melting temperature is observed. In this way, the values of melting temperatures in the solid–liquid two-phase regions are determined at a series of fractions melted, e.g. 10%, 25%, 50%, 70% and 90%. Then the sample is melted completely, and a final equilibrium temperature a few degrees above the melting point are determined. With the plot of equilibrium temperatures vs. melting fractions, the melting points of the sample and pure substance could be obtained. Then the purity of the sample can be established according to Van't Hoff equation.

3. Results and discussion

3.1. Heat capacity

The heat capacity of *p*-DMABD was determined in the temperature range from 78 to 360 K. The data (total 74 points) are shown in Table 1 and Fig. 1. The result indicates that *p*-DMABD is in solid state in the temperature range 78–337 K and in liquid state in the temperature range 348–360 K. The heat capacity curve vs. temperature is smooth in all of the two temperatures ranges, which means that this compound is stable in the experimental temperature region and there is no phase transition in solid and liquid state.

Table 1
Molar heat capacities of *p*-DMABD

T (K)	C_P ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	C_P ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
79.330	73.4300	245.566	193.222
83.420	75.4653	249.695	193.611
87.340	82.4762	253.826	192.812
91.541	86.7797	257.929	198.868
96.026	87.9796	261.982	202.507
100.350	89.8567	265.996	205.707
104.526	91.8954	269.955	208.602
108.585	93.9204	273.850	211.945
112.541	95.9364	278.040	216.358
116.936	98.8957	282.525	220.278
121.763	101.620	286.951	224.796
126.457	104.268	291.324	229.246
131.030	106.049	295.654	232.133
135.516	109.207	299.946	234.536
139.920	111.834	304.196	237.392
144.232	114.605	308.397	241.191
148.462	117.856	312.968	244.582
152.631	119.714	317.905	249.656
156.720	123.466	322.783	254.726
160.729	124.016	327.602	259.168
164.691	125.974	332.340	268.446
168.601	128.457	336.939	285.819
172.458	130.007	341.163	358.825
176.919	132.638	344.133	909.715
181.972	136.653	345.429	3432.81
186.959	140.076	345.839	7738.50
191.880	144.018	346.010	14223.8
196.735	148.106	346.094	22384.2
201.530	152.339	346.146	28920.2
206.259	157.074	346.150	38111.4
210.915	162.106	346.154	45619.2
215.495	168.153	346.498	3174.92
220.000	171.685	348.968	299.975
224.422	176.030	353.280	302.933
228.745	183.554	357.542	306.660
233.008	182.501	361.710	310.886
237.242	187.283		
241.423	192.542		

The following polynomial expression is obtained by least square curve fitting. In the temperature range of 78–337 K(solid):

$$C_p = -289.2063 + 10.5044T - 0.1155T^2 + 6.3087\times10^{-4}T^3 - 1.6194\times10^{-6}T^4 + 1.5858\times10^{-9}T^5\ (\mathrm{J\,K^{-1}\,mol^{-1}}),$$

its correlation coefficient is 0.9993.

In the temperature range of 348–360 K (liquid):

$$C_p = 2438.1145 - 12.8660T + 1.9311\times10^{-2}T^2\ \left(\mathrm{J\,K^{-1}\,mol^{-1}}\right),$$

its correlation coefficient is 0.9999.

3.2. Melting point and enthalpy of fusion

The melting point can be obtained with step-by-step heating based on the following equation:

$$T_\mathrm{m} = T'_\mathrm{i} + \frac{Q' - \bar{H}_0(T_\mathrm{f} - T'_\mathrm{i}) - nC_{p(\mathrm{S+L})}(T_\mathrm{f} - T_\mathrm{m})}{nC_{p(\mathrm{S+L})}},$$

where, T_m is the melting point of the sample, T'_i the equilibrium temperature in the melting region, T_f the temperature a few degrees above the melting point, Q the total heat energy introduced into the sample cell from T'_i to T_f, H_0 the average heat capacity of sample cell from T'_i to T_f, $C_{p(\mathrm{L})}$ the liquid heat capacity of the sample at $(T_\mathrm{f} + T_\mathrm{m})/2$, $C_{p(\mathrm{S+L})}$ the heat capacity of solid–liquid two phase mixture at $(T_\mathrm{f} + T_\mathrm{m})/2$, and n the molar numbers of the sample.

The melting region of heat capacity curve is shown in Fig. 2. With 19 times heating, the melting point of the sample, $T_\mathrm{m} = 346.154$ K, was obtained.

The initial melting temperature of the sample is 336.939 K and the final melting temperature is 348.968 K. The sample exists in two-phase state in the temperature range of 336.939–348.968 K. The enthalpy of the sample can be obtained based on the following equation:

$$\Delta H_\mathrm{m} = \frac{\left[Q - n\int_{T_\mathrm{i}}^{T_\mathrm{f}} \frac{m_{(\mathrm{S})}}{m} C_{p(\mathrm{S})}\mathrm{d}T - n\int_{T_\mathrm{i}}^{T_\mathrm{f}} \frac{m_{(\mathrm{L})}}{m} C_{p(\mathrm{L})}\mathrm{d}T - \int_{T_\mathrm{i}}^{T_\mathrm{f}} H_0\mathrm{d}T\right]}{n},$$

where T_i is the temperature a few degrees lower than the initial melting temperature, Q the total energy introduced into the sample cell from T_i to T_f, m the total mass of the sample, $m_{(\mathrm{S})}$ the mass of the sample in solid phase, and $m_{(\mathrm{L})}$ the mass of the sample in liquid phase.

In fact, the following equation was used to calculate the enthalpy of fusion.

$$\Delta H_\mathrm{m} = \frac{\left[Q - n\int_{T_\mathrm{i}}^{T_\mathrm{m}} C_{p(\mathrm{S})}\mathrm{d}T - n\int_{T_\mathrm{m}}^{T_\mathrm{f}} C_{p(\mathrm{L})}\mathrm{d}T - \int_{T_\mathrm{i}}^{T_\mathrm{f}} H_0\mathrm{d}T\right]}{n}.$$

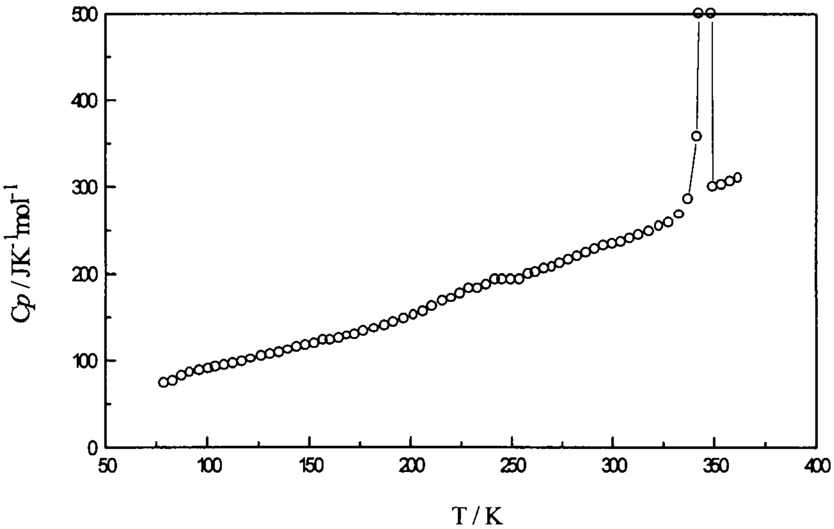

Fig. 1. Molar heat capacity as a function of temperature for *p*-DMABD.

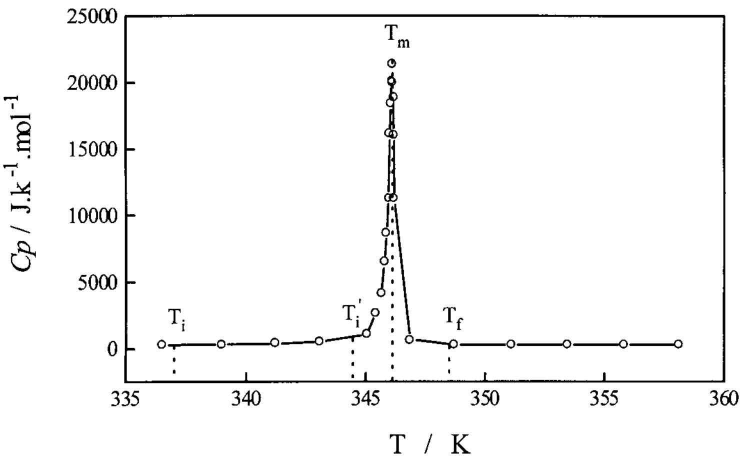

Fig. 2. Melting peak of *p*-DMABD.

Finally, the molar enthalpy and entropy of fusion of the sample are determined to be 19.07 kJ mol^{-1} and 55.08 J K^{-1} mol^{-1}, respectively.

3.3. DSC result

A differential scanning calorimeter (DSC, Model: TA Instrument DSC 910s) was used to perform the thermal analysis of *p*-DMABD. The heating rate was 5 K min^{-1} and the atmosphere was nitrogen gas. The melting peak is observed at 347.02 K and the enthalpy of fusion of the sample is determined to be 18.35 kJ mol^{-1} (123.0 J g^{-1}).

3.4. Purity of the sample

With the experimental heat capacity data a series of temperatures (T) at different melting fraction (F) of the sample are obtained during melting process [7]. The data are shown in Table 2 and the plot of T vs. $1/F$

Table 2
The experimental results of melting fractions and equilibrium temperatures of *p*-DMABD $[F = q/(\Delta H_m \cdot n)]$

q (J)	54.49	75.40	97.11	119.22	141.62	164.16	186.79	209.49	232.19
F	0.15799	0.21859	0.28153	0.34565	0.41059	0.47593	0.54154	0.60736	0.67318
$1/F$	6.3295	4.5748	3.5520	2.8931	2.4355	2.1011	1.8466	1.6465	1.4855
T (K)	345.434	345.654	345.790	345.884	345.951	346.002	346.042	346.073	346.099

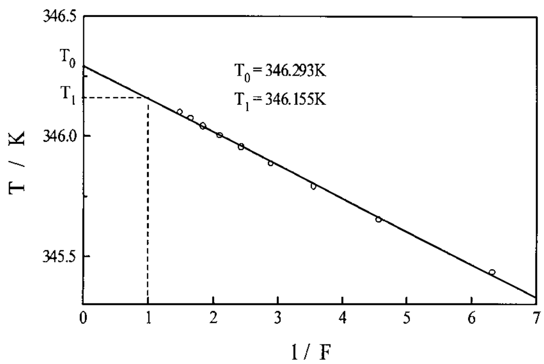

Fig. 3. Melting curve of *p*-DMABD.

is shown in Fig. 3, which is a straight line. The melting points of pure *p*-DMABD and the sample can be obtained at $1/F = 0$ and $1/F = 1$, respectively. The results are that the melting point of pure *p*-DMABD is 346.293 K and that of the sample is 346.155 K. Finally, the purity of the sample is determined to be 99.74% (molar percent) according to the Van't Hoff equation.

Acknowledgements

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