Thermochimica Acta 499 (2010) 117–122

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermodynamic investigation of several natural polyols (IV): Heat capacities and thermodynamic properties of adonitol

Bo Tong[a], Ying Yu[b], Zhi-Cheng Tan[c,*], Chang-Gong Meng[a], Li-Jun Cui[a], Guang Xiao[a], Rui-Bin Liu[a]

[a] Department of Chemistry, School of Chemical Engineering, Dalian University of Technology, Dalian 116023, China
[b] PetroChina Dalian Petrochemical Company, Dalian 116032, China
[c] Thermochemistry Laboratory and China Ionic Liquid Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

ARTICLE INFO

Article history:
Received 6 January 2009
Received in revised form
15 November 2009
Accepted 27 November 2009
Available online 3 December 2009

Keywords:
Adonitol
Phase transition
Adiabatic calorimetry
Oxygen-bomb combustion calorimetry
DSC
TGA

ABSTRACT

Adonitol was investigated by adiabatic calorimetry (AC), differential scanning calorimetry (DSC), thermogravity analysis (TGA) and oxygen-bomb combustion calorimetry. The heat capacity was precisely measured in the temperature range from 78 to 400 K by means of a small sample automated adiabatic calorimeter. The melting temperature, the molar enthalpy and entropy of this transition were determined to be $T = 369.08 \pm 0.45$ K, 36.42 ± 0.18 kJ mol^{-1} and 98.68 ± 0.49 J K^{-1} mol^{-1} respectively from the experimental C_p–T curve. The thermodynamic functions $[H_T^0 - H_{298.15}^0]$ and $[S_T^0 - S_{298.15}^0]$, were derived from the heat capacity data with an interval of 5 K. The standard molar enthalpy of combustion and formation of the compound have been determined to be $\Delta_c H_m^0$ ($C_5H_{12}O_5$, cr) = (-2562.4 ± 1.3) kJ mol^{-1} and $\Delta_f H_m^0$ ($C_5H_{12}O_5$, cr) = (-1120.1 ± 1.5) kJ mol^{-1} respectively by means of a precision oxygen-bomb combustion calorimeter at $T = 298.15$ K. The thermostability of the compound was further studied by DSC and TGA measurements.

1. Introduction

Considerable efforts are being expended lately to develop new additives for food and drug from natural polyols because of safe and environmental concerns relating to synthetic industrial additives. Xylitol, sorbitol, erythritol and adonitol are significant natural polyols for food and pharmaceutical industry [1–3]. As natural extracts, they have many advantages such as low cost, no toxic, no erosion and no environmental pollution. Therefore, they are increasingly used to provide sweetness in replace of sugars to various products due to low energy content. Moreover, they reduce the development of dental caries and they do not require insulin or glucose in their metabolism so they are suitable for prevention and treatment of adiposis and diabetics [4–7].

The state and phase transitions of chemicals are very important in chemical engineering and pharmaceutical industry, because they reflect molecular mobility and physicochemical properties. These characteristics have direct effect on the formation of structure, structural changes, time-dependent crystallization and product shelf life [8–10]. It is now recognized that the amorphous solid state offers very interesting possibilities in the control of bioavailability [10–12]. Therefore, heat capacities, phase change data and thermal decomposing temperature that characterize the basic thermophysical properties are an important requirement for safe storage and use of these new chemicals. However, the thermodynamic data especially the heat capacities of adonitol have not been published in literature as far as we know.

As a continuation of our earlier work in obtaining the low-temperature heat capacity and thermodynamic data of xylitol and sorbitol [13,14], in the present study, the heat capacity, phase change behavior and thermostability of adonitol were investigated in detail by adiabatic calorimetry (AC), differential scanning calorimetry (DSC) and thermogravity analysis (TGA) methods. The thermodynamic properties including molar enthalpies and entropies of phase transition were determined based on the heat capacity measurements. The thermodynamic functions, $[H_T^0 - H_{298.15}^0]$ and $[S_T^0 - S_{298.15}^0]$, were calculated from heat capacity data in the temperature range of 78–400 K. The standard molar enthalpy of combustion and the standard molar enthalpy of formation of the compound which reported in literature [15] have been determined by means of a precision oxygen-bomb combustion calorimeter again at $T = 298.15$ K.

2. Experimental

2.1. Sample

The adonitol [CAS No. 488-81-3] was purchased from ACROS ORGANICS company with labeled purity of 99.0% mass fraction and

* Corresponding author. Tel.: +86 411 84379199; fax: +86 411 84691570.
E-mail address: tzc@dicp.ac.cn (Z.-C. Tan).

0040-6031/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.tca.2009.11.011

was handled in a dry N_2 atmosphere to avoid possible contamination by moisture. GC analyses of the samples gave purities >99.0% in agreement with their specifications. The sample was used without additional purification.

2.2. Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimeter described in detail in literature [16–18]. The calorimeter was established by Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences in PR China. It mainly consisted of a sample cell, a miniature platinum resistance thermometer, an electric heater, an inner and outer adiabatic shield, two sets of chromel-copel thermocouples and a high vacuum system. Liquid nitrogen was used as the cooling medium.

The sample amount used for the heat capacity measurement is 2.27977 g, which is equivalent to 14.984 mmol based on its molar mass of 152.15 g mol^{-1}. The measurements were conducted by means of the standard method of intermittently heating the sample and alternately measuring the temperature. Heat capacity of the sample is derived from the total heat capacity subtracting the heat capacity of the calorimeter cell determined in a separate experiment.

To verify the reliability of the adiabatic calorimeter, the molar heat capacities for the reference standard material α-Al_2O_3 were measured. The deviations of our experimental results from the recommended values of the National Bureau of Standards (NBS) [19] were within ±0.2% in the entire temperature range of 80–400 K.

2.3. DSC and TG analysis

A differential scanning calorimeter (Model: DSC822^e, METTLER TOLEDO, Switzerland) was used to perform the thermal analysis of adonitol under high purity nitrogen (99.999%) with a flow rate of 40 ml min^{-1} and heating rate of 10 K min^{-1}. The mass of the sample used in the experiment was 6–8 mg.

The TG measurements of the sample were carried out by a thermogravimetric analyzer (Model: DT-20B, Shimadzu, Japan) under N_2 with a flow rate of 40 ml min^{-1} and heating rate of 10 K min^{-1}. The mass of the sample used in the experiment was 11.72 mg.

2.4. Oxygen-bomb combustion calorimetry

An isoperibolic calorimeter with a static oxygen bomb (IKA-WERKE C2000 control) was used for measuring of the energy of combustion of adonitol. The accuracy of the commercial calorimeter is close to ±0.01% by combustion experiments of benzoic acid [cr, (−3227.0 ± 0.3) kJ mol^{-1}], 3-methoxybenzoic acid [cr, (−3736.2 ± 0.9) kJ mol^{-1}] and nicotinic acid [cr, (−2731.3 ± 0.5) kJ mol^{-1}] [20,21], provided that the weighing procedure is made at the level of 0.00001 g for the samples and 0.01 g for the water amount in the calorimetric system. The sample of 0.6–0.7 g was pressed and transferred into gelatine capsule (IKA, Germany) of 1 cm^3 volume against absorption of air moisture, because the adonitol is easily hygroscopic under high pressure in the bomb. Then, the capsule was placed in the crucible and was burned in oxygen at a pressure 3.04 MPa.

All the necessary weightings for the combustion experiments were made with a precision of ±10^{-5} g in a Mettler Toledo ABS-135 analytical balance. For each combustion experiment, the ignition temperature was T = 298.15 K and the final temperature were also close to this temperature.

The energy equivalent of the oxygen-bomb calorimeter, ε_{calor} = (8958.05 ± 0.78) J K^{-1} was determined from 10 combustion experiments using NIST 39i benzoic acid with a certified mass energy of combustion of $\Delta_c U = -26{,}434 \pm 3$ J g^{-1} under experimental conditions, where the uncertainty quoted is the standard deviation of the mean.

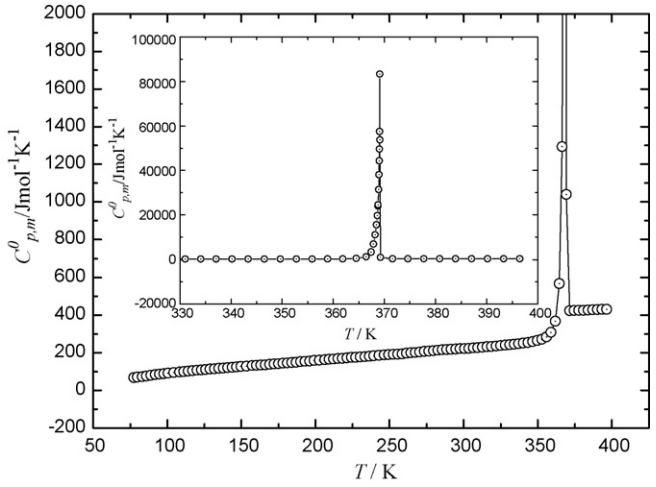

Fig. 1. Experimental molar heat capacity $C^0_{p,m}$ of adonitol as a function of temperature. Outer part: $C^0_{p,m}$ from 78 to 400 K, the whole experiment. Inner part: $C^0_{p,m}$ from 330 to 400 K, the melting process.

The energy of formation of the aqueous nitric acid produced by oxidation of a trace of nitrogen, which contained in the oxygen bomb, was determined by the neutral titration with a 0.1 mol dm^{-3} of sodium hydroxide solution by using the phenolphthalein as the indicator. A summary of the auxiliary values for the combustion experiments is given in Table 4. Washburn Correction [22] was applied to convert the energy of the actual combustion process to that of the isothermal process, and reduce to standard states.

3. Results and discussion

3.1. Heat capacity

Experimental molar heat capacities of adonitol measured by the adiabatic calorimeter over the temperature range from 78 to 400 K are listed in Table 1 and plotted in Fig. 1. From Fig. 1, a phase transition was observed at the peak temperature of 369.08 K. According to its melting point 374.7 K [23], this transition corresponds to a solid–liquid phase change.

The values of experimental heat capacities can be fitted to the following polynomial equations with least square method [24]:

For the solid phase over the temperature range 78–360 K:

$$C^0_{p,m}/\mathrm{J\,K^{-1}\,mol^{-1}} = 170.000 + 98.817x + 23.846x^2 - 56.366x^3 - 92.259x^4 + 71.865x^5 + 82.678x^6 \quad (1)$$

where x is the reduced temperature $x = [T - (T_{max} + T_{min})/2]/[(T_{max} - T_{min})/2]$, T is the experimental temperature, thus, in the solid state (78–360 K), $x = [(T/\mathrm{K}) - 219]/141$, T_{max} is the upper limit (360 K) and T_{min} is the lower limit (78 K) of the above temperature region. The correlation coefficient of the fitting R^2 = 0.9986.

For the liquid phase over the temperature range 375–400 K:

$$C^0_{p,m}/\mathrm{J\,K^{-1}\,mol^{-1}} = 428.460 + 3.821x \quad (2)$$

where x is the reduced temperature, $x = [(T/\mathrm{K}) - 387.5]/12.5$, T is the experimental temperature, 387.5 is obtained from polynomial $(T_{max} + T_{min})/2$, 12.5 is obtained from polynomial $(T_{max} - T_{min})/2$. T_{max} and T_{min} are the upper (400 K) and lower (375 K) limit temperature, respectively. The correlation coefficient of the fitting R^2 = 0.9954.

Table 1
Experimental molar heat capacity of adonitol (M = 152.15 g mol^{-1}).

T/K	$C^0_{p,m}$/J K^{-1} mol^{-1}	T/K	$C^0_{p,m}$/J K^{-1} mol^{-1}	T/K	$C^0_{p,m}$/J K^{-1} mol^{-1}
77.37	68.15	198.99	159.0	321.88	235.5
79.80	70.03	202.62	160.1	324.94	237.9
82.99	73.22	206.24	162.5	328.01	240.6
85.94	76.92	209.20	165.1	331.06	242.8
88.87	79.98	212.15	166.3	334.10	245.2
91.78	83.35	215.14	169.2	337.12	248.7
94.70	86.40	218.19	170.8	340.22	251.5
97.63	89.10	221.21	172.3	343.38	254.6
100.50	91.85	224.19	174.9	346.52	259.5
104.38	94.59	227.15	175.7	349.66	265.5
108.28	97.79	230.23	177.6	352.78	272.2
111.18	100.2	233.30	179.2	355.85	284.5
114.11	102.6	236.35	181.6	358.91	308.1
117.08	104.8	239.36	183.9	361.86	367.7
120.03	107.1	242.92	186.4	364.50	567.4
122.98	109.2	246.43	188.4	366.41	1294
125.92	111.5	249.37	189.9	367.40	3308
128.87	113.3	252.40	191.9	367.84	6797
131.84	115.4	255.42	192.9	368.16	10,958
134.81	117.3	258.42	194.1	368.45	15,481
137.78	119.1	261.40	198.0	368.60	19,618
140.75	120.6	264.36	200.6	368.74	23,979
143.72	122.4	267.31	201.7	368.76	24,488
146.70	124.5	270.32	203.2	368.87	31,362
149.68	126.7	273.41	206.9	368.93	38,018
153.50	128.9	276.48	208.2	368.98	44,286
157.28	131.5	279.54	210.6	369.02	49,539
160.22	133.5	282.58	213.8	369.04	57,525
163.20	134.9	285.60	216.0	369.08	83,380
166.15	136.4	288.58	217.3	369.10	53,727
169.13	138.3	291.56	218.1	369.22	1039
172.13	140.2	294.56	219.3	371.61	423.8
175.11	142.4	297.55	222.2	374.59	424.8
178.06	144.1	300.53	222.4	377.70	425.4
181.04	145.9	303.51	223.6	380.80	426.2
184.05	147.8	306.47	225.5	383.91	427.2
187.03	150.0	309.50	227.4	387.04	428.2
189.99	152.6	312.61	230.0	390.17	429.3
192.98	154.6	315.71	232.1	393.32	430.4
196.00	155.9	318.80	233.7	396.47	431.2

3.2. The temperature, enthalpy and entropy of solid–liquid phase transition

The standard molar enthalpies and entropies of the solid–liquid phase transition $\Delta_{fus}H^0_m$ and $\Delta_{fus}S^0_m$ of the compound were derived according to Eqs. (3) and (4):

$$\Delta_{fus}H^0_m = \frac{Q - n\int_{T_i}^{T_m} C^0_{p,m}(s)\ dT - n\int_{T_m}^{T_f} C^0_{p,m}(l)\,dT - \int_{T_i}^{T_f} H^0\,dT}{n} \quad (3)$$

$$\Delta_{fus}S^0_m = \frac{\Delta_{fus}H^0_m}{T_m} \quad (4)$$

where T_i is the temperature that is somewhat lower than the temperature of the onset of a solid–liquid transition and T_f is the temperature slightly higher than that of the transition completion. Q the total energy introduced into the sample cell from T_i to T_f, H^0 the standard heat capacity of the sample cell from T_i to T_f, $C^0_{p,m}(s)$ the standard heat capacity of the sample in solid phase from T_i to T_m, $C^0_{p,m}(l)$ the standard heat capacity of the sample in liquid phase from T_m to T_f and n is molar amount of the sample. The heat capacity polynomials mentioned above were used to calculate the smoothed heat capacities, and were numerically integrated to obtain the values of the standard thermodynamic functions above T = 298.15 K. The calculated results are listed in Table 2.

3.3. Thermodynamic functions of the compound

The thermodynamic functions of the adonitol relative to the reference temperature 298.15 K were calculated in the temperature range 80–400 K with an interval of 5 K, using the polynomial equation of heat capacity and thermodynamic relationships as follows:

Before melting,

$$H^0_T - H^0_{298.15} = \int_{298.15}^{T} C^0_{p,m}(s)\ dT \quad (5)$$

$$S^0_T - S^0_{298.15} = \int_{298.15}^{T} \frac{C^0_{p,m}(s)}{T}\ dT \quad (6)$$

Table 2
Thermodynamic parameters of adonitol.

Thermodynamic properties	Melting point, T_m (K)	$\Delta_{fus}H^0_m$ (kJ mol^{-1})	$\Delta_{fus}S^0_m$ (J K^{-1} mol^{-1})
Present work			
Adiabatic calorimetry	369.08 ± 0.45	36.42 ± 0.18	98.68 ± 0.49
DSC	373.61 ± 0.55	38.89 ± 1.17	104.09 ± 3.12
Barone. et al. [23]	374.7	37.6	100.3

After melting,

$$H_T^0 - H_{298.15}^0 = \int_{298.15}^{T_i} C_{p,m}^0(s)\ dT + \Delta_{fus}H_m^0 + \int_{T_f}^{T} C_{p,m}^0(l)\ dT \quad (7)$$

$$S_T^0 - S_{298.15}^0 = \int_{298.15}^{T_i} \left[\frac{C_{p,m}^0(s)}{T}\right] dT + \frac{\Delta_{fus}H_m^0}{T_m} + \int_{T_f}^{T} \left[\frac{C_{p,m}^0(l)}{T}\right] dT \quad (8)$$

where T_i is the temperature at which the solid–liquid phase transition started; T_f is the temperature at which the solid–liquid phase transition ended; $\Delta_{fus}H_m^0$ is the standard molar enthalpy of fusion; T_m is the temperature of solid–liquid phase transition.

The standard thermodynamic functions, $H_T^0 - H_{298.15}^0$, $S_T^0 - S_{298.15}^0$, are listed in Table 3.

3.4. Constant-volume combustion energy, standard molar enthalpy of combustion, and standard molar enthalpy of formation

Results of combustion experiments on adonitol are listed in Table 4. The standard molar energy of combustion $\Delta_c U^0 = (-2561.2 \pm 1.3)\,\mathrm{kJ\,mol^{-1}}$ is used to derive the standard molar enthalpy of combustion $\Delta_c H_m^0\ (C_5H_{12}O_5, \mathrm{cr}) = (-2562.4 \pm 1.3)\,\mathrm{kJ\,mol^{-1}}$ and the standard molar enthalpy of formation $\Delta_f H_m^0\ (C_5H_{12}O_5, \mathrm{cr}) = (-1120.1 \pm 1.5)\mathrm{kJ\,mol^{-1}}$ based on the following reaction:

$$C_5H_{12}O_5\,(\mathrm{cr}) + 11/2O_2\,(\mathrm{g}) = 5CO_2\,(\mathrm{g}) + 6H_2O\,(\mathrm{l}) \quad (9)$$

$$\Delta_c H_m^0 = \Delta_c U^0 + \Delta n \cdot RT \quad (10)$$

$$\Delta n = \sum n_i\ (\mathrm{products, g}) - \sum n_i\ (\mathrm{reactants, g}) \quad (11)$$

where $\sum n_i$ was the total molar amount of the gases in products or reactants.

The standard molar enthalpy of formation of the organic compound, $\Delta_f H_m^0$, was calculated by a designed Hess thermochemical cycle according to the reaction (9) as follows:

$$\Delta_f H_m^0\ (C_5H_{12}O_5, \mathrm{cr}) = [5\Delta_f H_m^0\ (CO_2, \mathrm{g}) + 6\Delta_f H_m^0\ (H_2O, \mathrm{l})] - \Delta_c H_m^0\ (C_5H_{12}O_5, \mathrm{cr})$$

In the above formula, the standard molar enthalpies of formation of CO_2 (g) and H_2O (l), recommended by CODATA [25], $\Delta_f H_m^0\ (CO_2, \mathrm{g}) = (-393.51 \pm 0.13)\mathrm{kJ\,mol^{-1}}$, $\Delta_f H_m^0\ (H_2O, \mathrm{l}) = (-285.83 \pm 0.04)\,\mathrm{kJ\,mol^{-1}}$, were employed in the calculation of $\Delta_f H_m^0\ (C_5H_{12}O_5, \mathrm{cr})$ values.

3.5. The result of TG and DSC analysis

From the DSC curve in Fig. 2, a sharply endothermic peak corresponding to melting process was observed, with the melting temperature of $373.61 \pm 0.55\,\mathrm{K}$ and the enthalpy of $38.89 \pm 1.17\,\mathrm{kJ\,mol^{-1}}$, which are slightly higher than the values (369.08 K, $36.42 \pm 0.18\,\mathrm{kJ\,mol^{-1}}$) observed from the adiabatic calorimetric measurements and slightly lower than the values observed from DSC (374.7 K, $37.6\,\mathrm{kJ\,mol^{-1}}$) from Barone et al. [23]. The results were listed in Table 2. The data from DSC are obtained at a $10\,\mathrm{K\,min^{-1}}$ scanning rate, in which the sample could not reach thermal balance. However, the data of adiabatic calorimetry are conducted by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The temperature difference between the sample and adiabatic shield was automatically kept to be about 10^{-3} K during the whole experiment. The temperature increment for a heating period was 3 K, and temperature drift was maintained about $10^{-4}\,\mathrm{K\,min^{-1}}$ during each equilibrium period. Therefore, this process is much more near to "adiabatic" and "balanced" than DSC method. Generally, the phase change temperature obtained from AC is lower than that from DSC.

From the TG–DTG curve in Fig. 3, it can be seen that the mass loss of the sample was completed in a single step. The sample keeps

Table 3
Calculated thermodynamic functions of adonitol.

T (K)	$C_{p,m}^0$ (J K^{-1} mol^{-1})	$H_T^0 - H_{298.15}^0$ (kJ mol^{-1})	$S_T^0 - S_{298.15}^0$ (J K^{-1} mol^{-1})
80	71.61	−32.93	−178.05
85	75.96	−32.56	−173.60
90	80.51	−32.17	−169.11
95	85.14	−31.76	−164.60
100	89.77	−31.32	−160.07
105	94.33	−30.86	−155.55
110	98.76	−30.38	−151.03
115	103.0	−29.87	−146.53
120	107.1	−29.35	−142.06
125	111.0	−28.80	−137.61
130	114.7	−28.24	−133.20
135	118.2	−27.66	−128.82
140	121.5	−27.06	−124.47
145	124.7	−26.44	−120.17
150	127.8	−25.81	−115.91
155	130.8	−25.16	−111.69
160	133.6	−24.50	−107.50
165	136.5	−23.83	−103.36
170	139.3	−23.14	−99.25
175	142.2	−22.43	−95.17
180	145.1	−21.72	−91.12
185	148.0	−20.98	−87.10
190	151.0	−20.24	−83.11
195	154.1	−19.47	−79.14
200	157.2	−18.70	−75.19
205	160.5	−17.90	−71.26
210	163.8	−17.09	−67.34
215	167.2	−16.26	−63.44
220	170.7	−15.42	−59.55
225	174.2	−14.56	−55.66
230	177.8	−13.68	−51.79
235	181.4	−12.78	−47.92
240	185.0	−11.86	−44.06
245	188.6	−10.93	−40.21
250	192.1	−9.976	−36.37
255	195.6	−9.007	−32.53
260	198.9	−8.020	−28.71
265	202.1	−7.018	−24.90
270	205.2	−5.999	−21.10
275	208.2	−4.966	−17.31
280	211.0	−3.917	−13.54
285	213.8	−2.855	−9.784
290	216.4	−1.780	−6.048
295	218.9	−0.692	−2.332
298.15	220.4	0.000	0.000
300	221.4	0.409	1.366
305	223.9	1.522	5.045
310	226.6	2.648	8.709
315	229.5	3.788	12.36
320	232.7	4.943	16.00
325	236.5	6.116	19.64
330	241.0	7.310	23.29
335	246.5	8.528	26.96
340	253.2	9.777	30.67
345	261.3	11.06	34.42
350	271.4	12.39	38.25
355	283.6	13.78	42.18
360	298.6	15.23	46.24
365	Phase change	/	/
370	/	/	/
375	424.6	53.65	150.3
380	426.2	55.78	156.0
385	427.7	57.92	161.5
390	429.2	60.06	167.1
395	430.8	62.21	172.6
400	432.3	64.37	178.0

Table 4
Results of combustion experiments for adonitol at $T = 298.15$ K ($p^0 = 0.1$ MPa)[a].

	1	2	3	4	5	6	7
m (substance)/g[b]	0.61150	0.61151	0.61155	0.61153	0.61147	0.61152	0.61149
m' (cotton)/g[b]	0.00298	0.00300	0.00295	0.00299	0.00302	0.00302	0.00300
m' (bulb)/g[b]	0.11565	0.11559	0.11583	0.11543	0.11548	0.11396	0.11438
n (HNO_3)($\times 10^5$/mol)	11.07	11.29	10.94	11.34	10.90	10.85	10.95
$(T_i - 273.15)$/K	23.57952	23.58089	23.56851	23.56656	23.56796	23.57077	23.58385
$(T_f - 273.15)$/K	25.00036	24.99947	24.99003	24.98795	24.98609	24.98805	25.00012
ε^i/J K^{-1}	16.15	16.15	16.16	16.15	16.15	16.15	16.14
ε^f/J K^{-1}	18.36	18.37	18.36	18.36	18.36	18.36	18.36
ΔT_c/K[c]	1.4144	1.41197	1.41361	1.41249	1.40923	1.41005	1.41004
ΔU (ign)/J[d]	70.00	70.00	70.00	70.00	70.00	70.00	70.00
$-\Delta U_{IBP}$/J	12,622.63	12,601.24	12,615.95	12,605.94	12,576.64	12,584.03	12,583.95
ΔU_Σ/J	69.38	69.37	69.44	69.41	69.41	69.37	69.38
ΔU (HNO_3)/J[d]	6.62	6.75	6.54	6.78	6.52	6.49	6.55
ΔU (cotton)/J[d]	49.67	50.00	49.17	49.83	50.33	50.33	50.00
ΔU (bulb)/J[d]	2188.79	2187.66	2192.20	2184.63	2185.57	2156.81	2164.76
$-\Delta_c U^0$/J g^{-1}	16,859.68	16,825.50	16,841.28	16,837.33	16,788.70	16,846.53	16,834.70
$-\Delta_c U^0$/kJ mol^{-1}	2565.2	2560.0	2562.4	2561.8	2554.4	2563.2	2561.4

Avg $\cdot\ \Delta_c U^0 = (\overline{\Delta_c U^0} \pm \sigma^e) = (-2561.2 \pm 1.3)$ kJ mol^{-1}

[a] The symbols are defined according to Ref. [20] calorimeter: $T_h = 298.15$ K; V (bomb) = 0.2605 dm^3; p^i (gas) = 3.04 MPa; m^i (H_2O) = 1.00 g. The specific energy of combustion of the gelatine capsule and cotton is 18926.00 and 16666.67 J g^{-1} (provided by the supplier), respectively; $\rho_{(adonitol)} = 1.525$ g cm^{-3} calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris (refer to SciFinder Scholar).

[b] Masses obtained from apparent masses.

[c] $\Delta T_c = T_f - T_i - \Delta T_{corr}$.

[d] ΔU (HNO_3), ΔU (cotton), ΔU (bulb), ΔU (ign) is the energy correction of the nitric acid formation, the combustion of the cotton, the combustion of the capsule and the electrical energy of ignition, respectively.

[e] $\sigma = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/n(n-1)}$, in which n is the experimental number ($n = 7$); x_i, a single value of combustion energies; $\bar{x}$, the mean value of combustion energies.

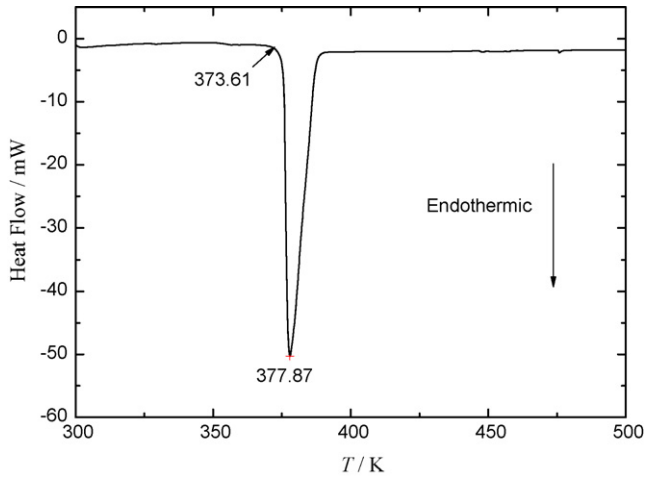

Fig. 2. DSC curve of adonitol under high purity nitrogen with onset temperature 373.61 K and peak temperature 377.87 K.

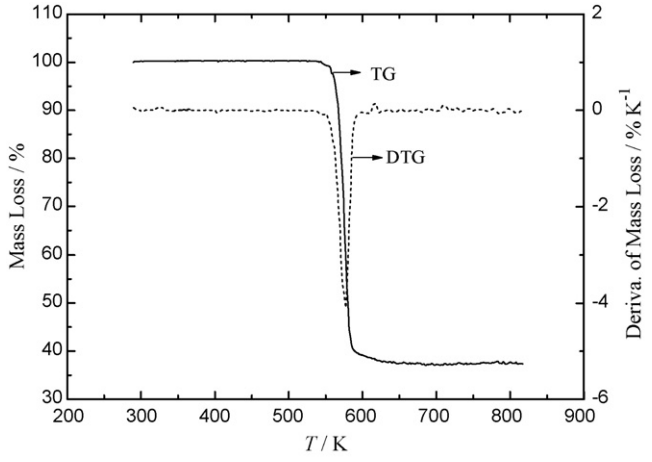

Fig. 3. TG–DTG curve of adonitol under high purity nitrogen.

thermostable below 550 K. It begins to lose weight at 551.55 K, reaches the maximum rate of weight loss at 577.38 K and completely loses its weight when the temperature reaches 601.82 K.

4. Conclusions

The heat capacities of adonitol were measured in the temperature range from 78 to 400 K by a high-precision automated adiabatic calorimeter. From the results of heat capacity experiment, the thermodynamic properties of fusion were completely studied, and the thermodynamic functions $[H_T^0 - H_{298.15}^0]$ and $[S_T^0 - S_{298.15}^0]$, were derived in the range from 78 to 400 K with temperature interval of 5 K. The melting temperature, standard molar enthalpy and entropy of this transition were determined to be 369.08 ± 0.45 K, 36.42 ± 0.18 kJ mol^{-1} and 98.68 ± 0.49 J K^{-1} mol^{-1}, respectively. The values of the standard molar enthalpy of combustion and formation of the compound are $\Delta_c H_m^0$ ($C_5H_{12}O_5$, cr) = (-2562.4 ± 1.3) kJ mol^{-1} and $\Delta_f H_m^0$ ($C_5H_{12}O_5$, cr) = (-1120.1 ± 1.5) kJ mol^{-1} respectively using IKA commercial oxygen-bomb combustion calorimeter.

Acknowledgements

This research was financially supported by the Talented Personnel Funds for Scientific Research of Dalian University of Technology under the grant no. 893110, and the National Nature Science Foundation of China under the grants nos. 20373072 and 20753002.

References

[1] A.G.J. Voragen, Technological aspects of functional food-related carbohydrates, Trends Food Sci. Technol. 9 (1998) 328–335.
[2] D. Glaser, M. Wanner, J.M. Tinti, C. Nofre, Gustatory responses of pigs to various natural and artificial compounds known to be sweet in man, Food Chem. 68 (2000) 375–385.
[3] R.A. Talja, Y.H. Roos, Phase and state transition effects on dielectric, mechanical, and thermal properties of polyols, Thermochim. Acta 38 (2001) 109–121.
[4] N. Marti, L.L. Funes, D. Saura, V. Micol, An update on alternative sweetness, Int. Sugar J. 110 (2008) 425–429.
[5] M. Kroger, K. Meister, R. Kava, Low-calorie sweeteners and other sugar substitutes: a review of the safety issues, Compr. Rev. Food. Sci. F. Food Saf. 5 (2006) 35–47.

[6] F. Bellisle, A. Drewnowski, Intense sweeteners, energy intake and the control of body weight, Eur. J. Clin. Nutr. 61 (2007) 691–700.
[7] V.B. Duffy, M. Sigman-Grant, Position of the American Dietetic Association: use of nutritive and nonnutritive sweeteners, J. Am. Diet. Assoc. 104 (2004) 255–275.
[8] J. Steenwijk, R. Langerock, D.S. van Es, J. van Haveren, J.W. Geus, L.W. Jenneskens, Long-term heat stabilisation by (natural) polyols in heavy metal- and zinc-free poly(vinyl chloride), Polym. Degrad. Stabil. 91 (2006) 52–59.
[9] D.S. van Es, J. Steenwijk, G.E. Frissen, H.C. van der Kolk, J. van Haveren, J.W. Geus, L.W. Jenneskens, The compatibility of (natural) polyols with heavy metal- and zinc-free poly(vinyl chloride): their effect on rheology and implications for plate-out, Polym. Degrad. Stabil. 93 (2008) 50–58.
[10] H.P. Diogo, S.S. Pinto, J.J. Moura Ramos, Slow molecular mobility in the crystalline and amorphous solid states of pentitols: a study by thermally stimulated depolarisation currents and by differential scanning calorimetry, Carbohydr. Res. 342 (2007) 961–969.
[11] B.C. Hancock, G.J. Zografi, The use of solubility parameters in pharmaceutical dosage form design, Pharm. Sci. 86 (1997) 1–12.
[12] D.Q.M. Craig, P.G. Royal, V.L. Kett, M.L. Hopton, Int. J. Pharm. 179 (1999) 179–207.
[13] B. Tong, Z.C. Tan, Q. Shi, Y.S. Li, D.T. Yue, S.X. Wang, Thermodynamic investigation of several natural polyols (I): heat capacities and thermodynamic properties of xylitol, Thermochim. Acta 457 (2007) 20–26.
[14] B. Tong, Z.C. Tan, Q. Shi, Y.S. Li, D.T. Yue, S.X. Wang, Thermodynamic investigation of several natural polyols (II)—heat capacities and thermodynamic properties of sorbitol, J. Therm. Anal. Calorim. 91 (2008) 463–469.
[15] E.S. Domalski, Selected values of the heat of combustion and heats of formation of organic compounds containing the elements hydrogen, oxygen, phosphorus and sulphur, J. Phys. Chem. Ref. Data 1 (1972) 221–277.
[16] Z.C. Tan, G.Y. Sun, Y.J. Sun, An adiabatic low-temperature calorimeter for heat-capacity measurement of small samples, J. Therm. Anal. Calorim. 45 (1995) 59–67.
[17] Z.C. Tan, G.Y. Sun, Y.J. Song, L. Wang, J.R. Han, Y.S. Liu, M. Wang, D.Z. Nie, An adiabatic calorimeter for heat capacity measurements of small samples—the heat capacity of nonlinear optical materials $KTiOPO_4$ and $RbTiOAsO_4$ crystals, Thermochim. Acta 352 (2000) 247–253.
[18] Z.C. Tan, L.X. Sun, S.H. Meng, L. Li, F. Xu, P. Yu, B.P. Liu, J.B. Zhang, Heat capacities and thermodynamic functions of p-chlorobenzoic acid, J. Chem. Thermodyn. 34 (2002) 1417–1429.
[19] D.G. Archer, Thermodynamic properties of synthetic sapphire (α-Al_2O_3), standard reference material 720 and the effect of temperature-scale differences on thermodynamic properties, J. Phys. Chem. Ref. Data 22 (1993) 1411–1453.
[20] M. Colomina, P. Jimenez, M.V. Roux, C. Turrion, Thermochemical properties of benzoic acid derivatives. VII. Enthalpies of combustion and formation of the o-, m-, and p-methoxy-benzoic acids, J. Chem. Thermodyn. 10 (1978) 661–665.
[21] T. Sato-Toshima, A. Kamagughi, K. Nishiyama, M. Sakiyama, S. Seki, Enthalpies of combustion of organic compounds. IV. Acetanilide and nicotinic acid, Bull. Chem. Soc. Jpn. 56 (1983) 51–54.
[22] W.N. Hubbard, D.W. Scott, G. Waddington, in: F.D. Rossini (Ed.), Experimental. Thermochemistry, Interscience, New York, 1956, pp. 75–127.
[23] G. Barone, G.D. Gatta, D. Ferro, V. Piacente, Enthalpies and entropies of sublimation, vaporization and fusion of nine polyhydric alcohols, J. Chem. Soc. Faraday Trans. 86 (1990) 75–79.
[24] S.X. Wang, Z.C. Tan, Y.S. Li, Y. Li, Q. Shi, B. Tong, Heat capacity and thermodynamic properties of benzyl disulfide ($C_{14}H_{14}S_2$), Thermochim. Acta 463 (2007) 21–25.
[25] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.