Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 457 (2007) 20–26
thermochimica acta
www.elsevier.com/locate/tca

Thermodynamic investigation of several natural polyols (I): Heat capacities and thermodynamic properties of xylitol

Bo Tong [a,c], Zhi-Cheng Tan [a,b,*], Quan Shi [a,c], Yan-Sheng Li [b], Dan-Ting Yue [a], Shao-Xu Wang [b]

[a] *Thermochemistry Laboratory, Dalian Institute of Chemical physics, Chinese Academy of Sciences, Dalian 116023, China*
[b] *College of Environmental Science and Engineering, Dalian Jiaotong University, Dalian 116028, China*
[c] *Graduate School of the Chinese Academy of Sciences, Beijing 100049, China*

Received 7 July 2006; received in revised form 27 February 2007; accepted 27 February 2007
Available online 3 March 2007

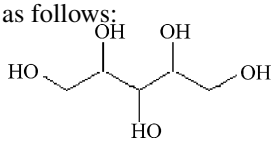
Abstract

The low-temperature heat capacity $C^0_{p,m}$ of xylitol was precisely measured in the temperature range from 80 to 390 K by means of a small sample automated adiabatic calorimeter. A solid–liquid phase transition was found from the experimental C_p–T curve in the temperature range 360–375 K with the peak heat capacity at 369.04 K. The dependence of heat capacity on the temperature was fitted to the following polynomial equations with least square method. In the temperature range of 80–360 K, $C^0_{p,m}(J\,K^{-1}\,mol^{-1}) = 165.87 + 105.19x + 1.8011x^2 - 41.445x^3 - 41.851x^4 + 65.152x^5 + 66.744x^6$, $x = [T(K) - 220]/140$. In the temperature range of 370–390 K, $C^0_{p,m}(J\,K^{-1}\,mol^{-1}) = 426.19 + 5.6366x$, $x = [T(K) - 380]/10$. The molar enthalpy and entropy of this transition were determined to be 33.26 ± 0.17 kJ mol^{-1} and 90.12 ± 0.45 J K^{-1} mol^{-1}, respectively. The standard thermodynamic functions $(H^0_T - H^0_{298.15})$ and $(S^0_T - S^0_{298.15})$, were derived from the heat capacity data in the temperature range of 80 to 390 K with an interval of 5 K. The standard molar enthalpy of combustion and the standard molar enthalpy of formation of the compound have been determined, $\Delta_c H^0_m$ ($C_5H_{12}O_5$, cr) = (-2463.2 ± 1.2) kJ mol^{-1}and $\Delta_f H^0_m$ ($C_5H_{12}O_5$, cr) = (-1219.3 ± 0.3) kJ mol^{-1}, by means of a precision oxygen bomb combustion calorimeter at $T = 298.15$ K. DSC and TG measurements were performed to study the thermal stability of the compound. The results were in agreement with those obtained from heat capacity measurements.

Keywords: Xylitol; Heat capacity; Phase transition; Thermodynamic properties; Standard molar enthalpy of combustion; Standard molar enthalpy of formation; Adiabatic calorimetry; TG–DTG; DSC

1. Introduction

Xylitol [$(CH_2OH)(CHOH)_3(CH_2OH)$, CAS no. 87-99-0] is an important natural polyol in food and pharmaceutical applications, as it is increasingly used to provide sweetness to various products or replaces sugar in confectionery. Its molecular formula is $C_5H_{12}O_5$ with molar mass of 152.15 g mol^{-1} and structural formula as follows:



Compared with the sucrose, the xylitol has the characteristic sweet taste of sugars but the amount of energy (calories) in the products is reduced [1–3]. Another important advantage is that it does not contribute to the development of dental caries. Moreover, it is suitable for diabetics, because it does not require insulin of glucose in their metabolism [2,4]. In industrial applications, the state and phase transition of the xylitol affects its molecular mobility and physicochemical properties [5]. However, the thermodynamic properties of xylitol were scarcely reported. For the application and theoretical research concerned with the substance, the thermodynamic data of this compound are urgently needed.

Heat capacity is one of the most fundamental thermodynamic properties of substances and it closely related to other physical and chemical properties. Heat capacity determinations of various compounds have attracted many researchers. Adiabatic calorimetry is one of the most accurate method for obtaining the heat capacity, melting point and enthalpy of fusion of substances. In the present paper, low-temperature

* 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 © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2007.02.022

heat capacity measurements were carried out with an adiabatic calorimeter over the temperature range from 80 to 390 K, and thermodynamic properties such as molar enthalpies and entropies of transition as well as chemical purity were determined based on the heat capacity measurements. The standard 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 80–390 K.

2. Experimental

2.1. Sample

The xylitol was purchased from ACROS ORGANICS company with labeled purity >99% mass fraction. The sample was recrystallized and then purified by sublimation. It was handled in a dry N_2 atmosphere to avoid possible contamination by moisture.

2.2. Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimeter described in detail in literature [6,7]. 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. Its working temperature is from 80 to 400 K [8] with liquid nitrogen as cooling medium.

The measurements were 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 2–4 K, and temperature drift was maintained about 10^{-4} K min^{-1} during each equilibrium period. The data were automatically collected through a Data Acquisition/Switch Unit (Model: 34420, Agilent, USA) and processed on line by a personal computer according to the program developed in our thermochemistry laboratory [9].

The sample amount used for the heat capacity measurement is 4.87213 g, which is equivalent to 32.022 m mol based on its molar mass of 152.15 g mol^{-1}.

2.3. DSC and TG analysis

A differential scanning calorimeter (Model: DSC141, SETARAM, France) was used to perform the thermal analysis of xylitol 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 3.48 mg.

The TG measurements of the sample were carried out by a thermogravimetric analyzer (Model: Setaram setsys 16/18, SETARAM, France) 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 8.35 mg.

2.4. Oxygen bomb combustion calorimetry

The constant-volume enthalpy of combustion of the sample was measured by means of a precision oxygen bomb combustion calorimeter, which was an isoperibolic calorimeter with a static oxygen bomb. The calorimeter was set up in our thermochemistry laboratory and the structure and principle of the calorimeter have been described previously in detail [10–12].

The sample of 0.6–0.9 g was pressed into pellets and put in a small sample crucible of about 0.004 dm^3, which was suspended in the bomb of about 0.3 dm^3, and burned under an oxygen pressure of 3.00 MPa ignited by a nickel fuse of about 16 cm. The purity of the oxygen used in the combustion was of research grade, mole fraction 0.99998. The real energy of combustion of the nickel fuse (Q_{Ni}) was calculated from the formula, Q_{Ni} $(J) = 2.929\Delta L$, in which ΔL (cm) was the length of the combusted nickel wire. The energy of formation of the aqueous nitric acid produced by oxidation of a trace of nitrogen, which contained in the oxygen bomb and produced from the combustion reaction, was determined by the neutral titration with a 0.08684 mol dm^{-3} of sodium hydroxide solution by using the phenolphthalein as the indicator. The enthalpy of formation of the aqueous nitric acid in the oxygen bomb can be derived from the equation, Q_{HNO_3} $(J) = 59.8NV$, in which N (mol dm^{-3}) is the concentration of the sodium hydroxide solution and V (dm^3) is the volume of the consumed sodium hydroxide solution; based on the molar enthalpy of formation of HNO_3(aq) from N_2(g), O_2(g) and H_2O(l), $\Delta_f H_m^0 = 59.8$ kJ mol^{-1} for 0.1 mol dm^{-3} of HNO_3(aq) [13,14].

3. Results and discussion

3.1. Heat capacity

Experimental molar heat capacities of xylitol measured by the adiabatic calorimeter over the temperature range from 80 to 390 K are listed in Table 1 and plotted in Fig. 1. From Fig. 1, a phase transition was observed in the range of 360–375 K with the peak heat capacity at 369.04 K. According to its melting point 365.7 K [15], 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:

For the solid phase over the temperature range 80–360 K:

$$C_{p,m}^0(\mathrm{J\,K^{-1}\,mol^{-1}}) = 165.87 + 105.19x + 1.8011x^2 - 41.445x^3 - 41.851x^4 + 65.152x^5 + 66.744x^6 \quad (1)$$

where x is the reduced temperature $x = [T - (T_{max} + T_{min})/2]/[(T_{max} - T_{min})/2]$, T the experimental tempera-