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Heat capacities of some sugar alcohols as phase change materials for thermal energy storage applications

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ABSTRACT

In recent years, sugar alcohols have attracted much attention due to their remarkable phase change properties for thermal energy storage applications. The thermodynamic properties especially the heat capacities would play a crucial role in theoretically and technically investigating the energy storage performance for sugar alcohols. However, as far as we known, the heat capacities of sugar alcohols have never been studied in a wide temperature region. In this study, we have measured the heat capacities of six sugar alcohols of D-mannitol, Myo-Inositol, xylitol, D-arabinitol, L-arabinitol and erythritol in the temperature range from $T = (1.9$ to $550)$ K for the first time using a combination of Physical Property Measurement System and differential scanning calorimeter. Based on the heat capacity curve fitting, the standard molar heat capacity, entropy and enthalpy at 298.15 K and 0.1 MPa, and melting temperature and transition enthalpy in the solid–liquid phase transition region were consequently obtained for these sugar alcohols. Moreover, the heat capacity and phase transition properties obtained in this work were also compared with previous results reported in literature.

1. Introduction

As fossil resources continuously consuming nowadays in the earth, the effective exploitation and management of energy resources becomes more and more urgent for constructing energy-saving societies. Among the emerging techniques at present, the thermal energy storage technique using phase change materials (PCMs) has attracted much attention in related application fields [1–3]. The function of this technique can be achieved by taking advantage of storing or releasing latent heats when the phase transition of PCMs taking place at constant temperatures [4,5]. The densities of thermal energy stored in PCMs are much larger than those of sensible heat of materials, and therefore the studies of PCMs for this objective have become a hot topic for developing energy-saving facilities [6–10].

Most recently, sugar alcohols (SAs) have intrigued a great deal of interests as promising PCMs in the thermal energy storage fields due to its high thermal storage density, low cost, non-flammability, non-toxicity and non-corrosivity [11–17]. Based on the computational analysis and design, Inagaki et al. predicted that the non-natural SAs have potential ability to achieve thermal storage densities up to about (450–500) $kJ \cdot kg^{-1}$, which is significantly larger than the maximum density of thermal energy storage for the present known organic PCMs [18,19]. Consequently, the basic thermodynamic properties of SAs would be theoretically crucial for providing further insight into their molecular mechanism of thermal energy storage, and also be technically important for their practical energy-saving applications.

Heat capacity is a fundamental thermodynamic property of a substance, and using the heat capacity data the related thermodynamic functions, such as entropy and enthalpy, can be derived based on the corresponding thermodynamic relationships. These thermodynamic properties are prerequisite for investigating the related thermal properties of PCMs for energy storage applications. Palomo del Barrio et al. measured heat capacities of five SAs (xylitol, adonitol, L-arabitol, erythritol, D-mannitol) and three eutectic blends (erythritol/xylitol, L-arabitol/erythritol, L-arabitol/xylitol) for thermal energy storage applications in the temperature range from 293 K to about 374 K using a differential scanning calorimeter [20]. Lebrun et al. studied the calorimetric fragility and thermodynamic property of D-maltitol by measuring its heat

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capacities from 100 K to 425 K using an adiabatic calorimeter [21,22]. Tong et al. performed heat capacity measurements on D-mannitol, xylitol and erythritol using an adiabatic calorimeter from 80 K to 390 K [23–25]. Spaght et al. measured heat capacities of erythritol and D-mannitol from room temperature up through the melting transition using a radiation calorimeter [26]. Parks, Anderson and Huffman also studied the heat capacities of D-mannitol, erythritol and dulcitol from 87 K to 295 K using an aneroid calorimeter with Nernst method [27,28]. However, as far as we known, the heat capacity studies on SAs in a wide temperature region especially below 80 K have never been reported, and therefore the thermodynamic properties in this temperature region are urgently needed for further theoretically and technically studying the thermal properties of SAs.

In this study, the heat capacities of six SA samples of D-mannitol, Myo-inositol, xylitol, D-arabinitol, L-arabinitol and erythritol were measured over the temperature region from T = (1.9 to 300) K using a relaxation calorimetric method performed on a Quantum Design Physical Property Measurement System (PPMS), and T = (180 to 550) K including the solid-liquid transition region using a differential scanning calorimeter (DSC). The heat capacity data were fitted to a series of theoretical and empirical models, and the corresponding thermodynamic functions, such as the third low entropy and enthalpy, and phase transition enthalpy and melting temperature have been derived using the fitting parameters. In addition, the heat capacity differences between these SA samples were further discussed in terms of their molecular structures. The heat capacities data and thermodynamic properties reported in this work would provide a thermodynamic basis for these SAs used as PCMs for thermal energy storage applications.

2. Experimental

The SA samples of D-mannitol, xylitol, and erythritol were commercially provided by J&K Scientific Ltd., Shanghai Macklin Biochem. Co., Ltd., and Dalian Meilun Bio. Tech. Co., Ltd., respectively, and Myo-inositol, D-arabinitol, L-arabinitol were provided by Aladdin Industrial Corp. The sample purities of SA samples in mass percent claimed by these providers are 99% or better than 99%. The sample information and molecular structures of these six SA samples are listed in Table 1 and shown in Fig. 1, respectively. It can be seen from their molecular structures that D-mannitol, Myo-inositol have six carbon atoms, xylitol, D-arabinitol, and L-arabinitol have five carbon atoms, erythritol has four carbon atoms, and each carbon atom in these samples are bonded by a hydroxyl group. Additionally, Myo-inositol is cyclic and the other five SAs are acyclic, and xylitol, D-arabinitol and L-arabinitol are isomers with the same molecular formula of $C_5H_{12}O_5$. These interesting molecular structures may result in entirely different thermodynamic properties for these SA samples as discussed in the following sections.

The HPLC technique was applied to further confirm the sample purity using a HPAEC system consisting of a Dionex Bio-LC gradient pump with GM-3 (4 mm) gradient mixer, CarboPac PA-10 column (4 × 250 mm), and an electrochemical detector using AgCl as reference electrode. The waveform was carbohydrates (standard Quad) and the following pulse potentials were used for the detection: t = 0 s, E = 0.10 v; t = 0.20 s, E = 0.10 v; t = 0.40 s, E = 0.10 v; t = 0.41 s, E = −2.00 v; t = 0.42 s, E = −2.00 v; t = 0.43 s, E = 0.60 v; t = 0.44 s, E = −0.10 v; t = 0.50 s, E = −0.10 v. The sample injection volume was 20 μL with the column oven temperature maintained at 30 °C, while the reference standards were resolved by 18 mM NaOH isocratic elution at a flow rate of 0.5 ml·min^{-1} over a 40 min time interval. The HPLC results presented in Table 1 confirms that these SA samples studied in this work possess a mass percent purity better than 99%. Moreover, the phase purity was further verified using a powder X-ray diffraction technique with a Cu Ka radiation (0.15418 nm) (PANalytical Co. X'pert PRO, Netherlands) operated under a voltage of 40 kV and a current of 40 mA. The XRD results showed in Fig. 2 illuminate that the main diffraction peaks of these SA samples are in well agreement with the standard patterns from PDF cards as well as early reported data [30], indicating that these samples used in our calorimetric study are phase pure and behave a good crystallinity.

The low temperature heat capacities of SA samples were measured using a Quantum Design PPMS based on a relaxation calorimetric method in the temperature range from T = (1.9 to 300) K. The standard uncertainty of the PPMS heat capacity measurement was estimated, by measuring the heat capacities of a high purity copper pellet, α-Al_2O_3 (SRM720) and benzoic acid (SRM39 j), and comparing the measured data to the corresponding literature values, to be ±3% in the temperature region from (1.9 to 20) K and ±1% from (20 to 300) K [31]. To meet the measurement requirement, powdered SA samples were prepared into a pellet with a diameter in 3 mm and height in (1–2) mm, by compressing the mixture of powders and copper stripes in a copper cup together using a method developed by Shi et al. The detailed sample preparation process and measurement procedure can be found in previous publications [32,33]. The heat capacity data were collected staring at 1.9 K and ending at 300 K with a logarithmic temperature interval in temperature region from T = (1.9 to 100) K and a 10 K interval from T = (100 to 300) K. The sample coupling in the relaxation process was found to be better than 95%, suggesting a good thermal contact achieved between the sample and the platform. The sample amounts used in the measurements were 6.50 mg, 14.30 mg, 10.12 mg, 6.61 mg, 5.44 mg and 7.88 mg for D-mannitol, Myo-inositol, xylitol, D-arabinitol, L-arabinitol and erythritol, respectively.

Table 1
Sample information of SA samples studied in this work.

Sample	Source	CAS No.	Formula	M_r[a]	X[b]	X_e[c]
D-Mannitol	J&K Scientific Ltd.	69-65-8	$C_6H_{14}O_6$	182.17165	0.99	0.9967
Myo-Inositol	Aladdin Industrial Corp.	87-89-8	$C_6H_{12}O_6$	180.1557	0.99	0.9987
Xylitol	Shanghai Macklin Biochem. Co., Ltd.	87-99-0	$C_5H_{12}O_5$	152.1457	0.99	0.9904
D-Arabinitol	Aladdin Industrial Corp.	488-82-4	$C_5H_{12}O_5$	152.1457	0.99	0.9988
L-Arabinitol	Aladdin Industrial Corp.	7643-75-6	$C_5H_{12}O_5$	152.1457	0.99	0.9929
Erythritol	Dalian Meilun Bio. Tech. Co., Ltd.	149-32-6	$C_4H_{10}O_4$	122.11975	≥0.99	0.9997

[a] The value of M_r is based on the most recent set of relative atomic masses recommended by IUPAC [29]. According to the recommendation of atomic weights (hydrogen [1.00784, 1.00811], carbon [12.0096, 12.0116], and oxygen [15.99903, 15.99977]), each atom has a range of weight; hence, each molecule has a range of weight, $C_6H_{14}O_6$ [182.1615, 182.1818], $C_6H_{12}O_6$ [180.1459, 180.1655], $C_5H_{12}O_5$ [152.1372, 152.1542], and $C_4H_{10}O_4$ [122.1129, 122.1266]. We choose the mean values in these ranges to be 182.17165, 180.1557, 152.1457 and 122.11975 for $C_6H_{14}O_6$, $C_6H_{12}O_6$, $C_5H_{12}O_5$ and $C_4H_{10}O_4$, respectively.
[b] The mass fraction purity provided by the suppliers.
[c] The mass fraction purity measured by HPLC.