



Thermal properties and solubility of methyl α -D-glucopyranoside in methanol at different temperatures



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ARTICLE INFO

Article history:

Received 24 September 2015
Received in revised form
30 October 2015
Accepted 31 October 2015
Available online 10 November 2015

Keywords:

Methyl α -D-glucopyranoside
Heat capacity
Thermal decomposition
Solubility
Gibbs energy

ABSTRACT

Heat capacity of methyl α -D-glucopyranoside (α -MeG) was measured by differential scanning calorimetry at the temperatures ranging from 298.15 to 513.15 K. Melting point, enthalpy and entropy of fusion, enthalpy $H_T - H_{298.15\text{ K}}$, and entropy $S_T - S_{298.15\text{ K}}$ were determined. Thermal decomposition of α -MeG was investigated using thermogravimetric analysis under pure nitrogen atmosphere. Ozawa-Flynn-Wall and ASTM models were used to calculate the activation energy and pre-exponential factor. Solubilities of α -MeG in methanol were measured within the temperature range of 293.15–318.15 K by using a synthetic method under atmospheric pressure. The modified Apelblat, λh , Wilson and NRTL models were applied to correlate the experimental data. The calculated results show good agreement with the experimental data and Wilson model is slightly more accurate than modified Apelblat, λh and NRTL models. The dissolution enthalpy, entropy, and Gibbs free energy were calculated by the Van't Hoff equation. The excess enthalpy of the solution can be evaluated by the λh model.

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1. Introduction

Methyl α -D-glucopyranoside (α -MeG, $\text{C}_7\text{H}_{14}\text{O}_6$; CASRN: 97-30-3; Fig. 1), a white powder, is a well-known industrial chemical which can be used extensively in the preparation of various products, including, for example, alkyd resins, esterified surfactants, adhesives, coatings, cosmetics and detergents, polyether polyols, and more recently as a starting polyol for use in the preparation of urethane foams, with prior oxyalkylation. α -MeG is, moreover, used as a plasticizer for phenolic, amine, and alkyd resins, in the manufacture of tar-oil varnishes, and for many other industrial purposes. Polyether polyols derived from α -MeG are particularly suitable as intermediates for the production of polyurethanes [1–6].

The crystal structure of α -MeG has been determined and the space group is $\text{P}2_12_12_1$, with four molecules in a unit cell [7]. Until now, the lack of investigation on the basic and thermal properties of α -MeG, such as melting point T_m , heat capacity $C_{p,m}$, thermal decomposition temperature T_d , and enthalpy and entropy of phase

transitions, is, however, fairly self-evident. These properties are important to design any process involving α -MeG in an industrial scale and can be measured via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

α -MeG are typically prepared by the alcoholysis reaction of a monosaccharide (e.g. glucose) or a polysaccharide (e.g. starch) with methanol in the presence of a catalytic amount of *p*-toluene sulfonic acid or sulfuric acid at elevated temperature and pressure in a batch process [5,6,8]. The alcoholysis reaction yields a mixture of products, which mixture includes α -MeG and β -MeG as predominant isomers. The methanol can be evaporated and exchanged with coolant to obtain a dark solution which can be decolorized with a whitening agent (e.g. activated carbon). These species have different temperatures of crystallization, which facilitates the separation and recovery of α -MeG therefrom. Pure α -MeG is obtained by recrystallization from the mixture of α -MeG and methanol, and the solubility of α -MeG in methanol at different temperatures is of paramount importance for the optimization of the solid–liquid crystallization isolation process. It can also, furthermore, provide the thermodynamic properties of the α -MeG solution, such as dissolution enthalpy, dissolution entropy, and excess enthalpy. Unfortunately, the solubilities of α -MeG in methanol, to the best of our knowledge up to the present time, have not been reported in the literature.

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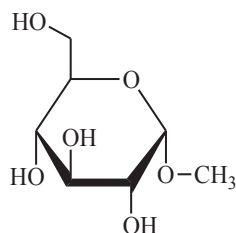


Fig. 1. Chemical structure formula of α -MeG (molar mass, 194.18 g mol⁻¹).

In the present study, the thermal properties of α -MeG were measured by DSC and TGA. Two equations, ASTM method and Ozawa-Flynn-Wall model, were applied to determine the kinetic parameters of thermal decomposition of α -MeG, such as activation energy, pre-exponential factor. Furthermore, this work aims to explore the solubility of α -MeG in methanol at temperatures ranging from 293.15 to 318.15 K by using a synthetic method under atmospheric pressure of 0.1 MPa. The modified Apelblat equation, λh equation, Wilson model and NRTL model were employed to correlate the experimental solubility data. Various thermodynamic parameters for α -MeG dissolution (e.g. enthalpy, entropy, Gibbs free energy, and excess enthalpy) were also calculated based on solubility data of α -MeG at various temperatures. The solubility and thermodynamic data of this study can be helpful in the separation and recovery of α -MeG.

2. Experimental

2.1. Materials

High-grade methanol purchased from Aladdin Industrial Inc. was HPLC grade and used as received, and value of the mass fraction purity was higher than 0.999. α -MeG (mass fraction purity > 0.98) also supplied by Aladdin Industrial Inc. was purified by recrystallization with methanol at least thrice before using to obtain the mass fraction purity of 0.995 and stored under nitrogen (Table 1).

2.2. Measurement of heat capacity

To date, DSC is probably the most common method used to determine the heat capacity of α -MeG. The heat capacity ($C_{p,m}$) of α -MeG in this study was measured by DSC (Q100, TA Instruments). To verify the reliability of the DSC results, the molar heat capacities of synthetic sapphire (α -Al₂O₃) were measured. The deviations of the results from the recommended values by NIST 27 were within $\pm 0.1\%$ in the temperature range of 298.15 K–513.15 K. The DSC experiments were operated with the 'tau lag' correction disabled. Regular performance checks were carried out over the 1-month period of the work to ensure consistency in the results. The DSC conditions were described as follows: sample mass, ~ 7.0 mg; temperature range, 298.15 K–513.15 K; and heating rate, 10 K min⁻¹.

Table 1
Sample information.

Chemical name	Molecular formula	CASRN	Source	Mass fraction
α -MeG	C ₇ H ₁₄ O ₆	97-30-3	Aladdin Industrial Inc.	0.9950
methanol	CH ₄ O	67-56-1	Aladdin Industrial Inc.	0.9990

2.3. Measurement of thermal stability

Thermal stability and kinetics of α -MeG were determined using a thermogravimetric analyzer (Diamond TG/DTA, Perkin Elmer instruments). The experiment conditions were as follows: sample mass, ~ 5.0 mg; heating rates: 5, 10, 15, 20, and 25 K min⁻¹; temperature range, 293.15 K–1073.15 K; and highly pure nitrogen, 50 mL min⁻¹.

2.4. Solubility measurement

A synthetic method was employed to measure the solubility of α -MeG in methanol at atmospheric pressure and the experimental setup was similar to that previously described [9,10]. First, A known mass of methanol was added into a 120 mL magnetically stirred, jacketed glass cell which connected to a super thermostatic water-circulator bath to keep the temperature at a constant value (± 0.05 K). A mercury thermometer with an uncertainty within ± 0.05 K was inserted into the inner chamber of the cell for monitoring the real temperature of the solution. High purity nitrogen was fed into methanol to remove the dissolved oxygen. Second, predetermined amounts of α -MeG were weighed and transferred into the cell and heated as slow as possible (less than 1 K h⁻¹). A laser beam was applied to observe the dissolution of the α -MeG. During the solubility measurements, each experiment was conducted thrice at every temperature to check the reproducibility and the average value was the measured solubility. The estimated uncertainty of the mole fraction was less than $\pm 1 \times 10^{-6}$. The saturated mole fraction solubility x_1 in methanol can be obtained by the following expression:

$$x_1 = \frac{w/M_1}{w/M_1 + (1-w)/M_2} \quad (1)$$

where w represents the mass fraction of the α -MeG in the solution, and M_1 and M_2 represent the molar masses of α -MeG and methanol, respectively.

3. Results and discussion

3.1. Heat capacity and thermodynamic functions

The heat capacity curve of α -MeG determined by DSC is shown in Fig. 2. It can be seen that no other thermal anomaly were observed. From the results obtained from Fig. 2, the melting point (T_m) is 442.33 K, phase transition enthalpy ($\Delta_{fus}H_m$) for α -MeG is 28.04 kJ mol⁻¹. The entropy of fusion ($\Delta_{fus}S_m$) for α -MeG calculated by Eq (2) is 63.39 J K⁻¹ mol⁻¹.

$$\Delta_{fus}S_m = \frac{\Delta_{fus}H_m}{T_m} \quad (2)$$

The heat capacity of α -MeG in the temperature range of 298.15 K–513.15 K can be obtained from Fig. 2, and the data within the solid-phase region and liquid-phase region were correspondingly correlated with the following polynomial equation:

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