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Variation in entropies of fusion driven by mixing in binary glass forming eutectics

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ABSTRACT

Binary eutectic systems are focused to understand the relationship between the glass formation and thermodynamics. Two molecular eutectic systems are studied and the critical cooling rates for glass formation, enthalpy of mixing ΔH_{mix} and entropies of fusion ΔS_m are determined at the eutectic compositions. For the systems with positive ΔH_{mix}, an excess in ΔS_m relative to the linear average of the ΔS_m values of the two pure components is observed, while a deficit in ΔS_m corresponds to negative ΔH_{mix}. Extended studies of binary metallic eutectics shows similar behaviors, finding that for the alloys with positive ΔH_{mix}, the excess in ΔS_m at eutectic points reaches an upper limit defined by the ideal mixing entropy. In addition, the deficit in ΔS_m in the binary eutectics is observed to associate with enhanced glass forming ability. The results suggest that the relative ΔS_m variation in eutectics can address effectively the mixing thermodynamics.

1. Introduction

The understanding of the glass formation has been the focus of attention in search of novel glassy materials with excellent properties for various applications [1,2]. Considerable efforts have been made to account for the glass forming abilities among diverse materials, and various criteria were proposed based on fundamental quantities, involving characteristic temperatures [3], kinetic quantities (such as viscosity [4] and fragility [5,6]), thermodynamic quantities (such as free-energy- [7,8], enthalpy- [9] and entropy-based [10,11] quantities), structural attributes [12] and electron features [13,14]. The criteria have achieved success in interpreting the glass formability for some alloys, however, studies are still needed to explore the basic principles to guide the composition design for glass formation.

Glass formation thermodynamics often emphasizes the Gibbs free energy difference between an undercooled liquid and its equilibrium crystals, known as the thermodynamic driving force for liquid-solid phase transition [15–17], $\Delta G = \Delta H - T\Delta S$, where ΔH and ΔS are the difference in enthalpy and entropy, and small ΔG favors thermodynamically glass formation [7]. When referring to Turnbull's simplification of $\Delta G = \Delta S_m \Delta T$ [18], where ΔS_m is the entropy of fusion and $\Delta T = T_m - T$ is the degree of supercooling relative to the melting point T_m, it is obvious that low ΔS_m should be an advantage for glass formation. Experimental studies indeed indicated that alloys of higher glass forming ability generally have small ΔS_m [11,19–21]. The studies of isomeric molecules reveal that high glass forming ability is always associated with the isomers of low ΔS_m [22,23]. In contrast to the widely-used kinetic criteria for glass formation, the enthalpy- or entropy-based criterion commonly applicable for different types of glass formers has not been successful, partly due to the fundamental challenge that the thermodynamic quantities are numerically related to the number of atoms in a molecule. To solve the problem, we recently proposed to use ΔS_m normalized by the beads number, which defines the degree of freedom of intramolecular motions [24,25], and found a correlation between ΔS_m/beads and melting-point viscosity for molecular and metallic glass forming systems [58].

For binary or multicomponent glass forming systems, the enthalpy of mixing ΔH_{mix} has been a crucial consideration for glass formation, and negative ΔH_{mix} is used as a basic guide for the components [10,26]. Thus, a question arises as to whether the enthalpy of mixing is associated with the liquid - crystal entropy difference, which becomes the entropy of fusion ΔS_m for pure components or alloys at eutectic compositions. To explore the relation between ΔH_{mix} and ΔS_m, binary eutectic systems are

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chosen in this work based on the simplest phase diagram patterns among multi-component systems. Although it was recorded that the best glass forming compositions is somehow off-eutectic [27,28], considering the difficulty to determine the entropy difference at compositions other than the eutectic points, the eutectic compositions are focused. The glass formation and mixing thermodynamics in two binary eutectic systems with negative and positive ΔH_{mix} are studied, and a relation between and ΔH_{mix} and ΔS_m is shown.

2. Experimentals

Benzil (BZL, Alfa Aesar, 98%), *m*-dihydroxybenzene (MDHB, Alfa Aesar, 98%) and *m*-nitroaniline (MNA, Alfa Aesar, 98%) were selected in this study. To guarantee complete mixing, prior to quenching, the BZL - MDHB and BZL - MNA mixtures at various compositions were heated up to temperatures higher than the melting points. A Perkin-Elmer differential scanning calorimeter (Diamond DSC) was used to measure the glass transition and melting behaviors. The molten samples were quenched to low temperatures to attain the glassy states, and then reheating is performed across the glass transition at a fixed heating rate of 20 K/min. The reheating heat capacity C_p curves were recorded. T_gs of pure BZL and MHB were determined by quenching at the highest cooling rate of ~120 K/min due to the easy crystallization. The heat of fusion ΔH_m was determined at eutectic compositions and, accordingly the entropy of fusion ΔS_m was calculated using the definition of $\Delta S_m = \Delta H_m/T_e$, where T_e is the eutectic temperature. The DSC was calibrated using indium and cyclohexane prior to the measurements.

A calvet type microcalorimeter equipped by membrane mixing cells (C80, Setaram) was used to measure the enthalpy of mixing ΔH_{mix} for the mixtures at the two eutectic compositions at 398.15 K to guarantee complete melting of the two components. The reliability of the apparatus was verified by determining the enthalpy of mixing for the diethanolamine - H_2O system under ambient conditions (298.15 K and ambient pressure) [29]. Details of the equipment and measurements have been described [30].

3. Results

The glass transition and melting behaviors of the binary BZL - MDHB mixtures are shown in Fig. 1 across the whole composition range, and the phase diagram (b) is constructed using the composition dependence of liquidus temperature T_l, revealing a typical eutectic fashion with the eutectic temperature T_e = 349 K and eutectic composition of x_{BZL} = 0.50. The composition dependence of T_g is also presented in Fig. 1 (d). ΔH_m of BZL and MDHB are measured to be 108.5 and 186.61 J/g, or 22.81 and 20.55 kJ/mol, respectively, giving ΔS_m to be 61.58 and 53.35 J/mol-K, which are in excellent agreement with the reported results of 61.65 and 53.8 J/mol-K [31,32]. The characteristic temperatures and thermodynamic data of the BZL - MNA (*m*-nitroaniline) system have been measured in our previous studies, showing the eutectic composition to be x_{BZL} = 0.59 [30].

The critical cooling rates for the glass formation in the 50BZL - 50MDHB and 59BZL - 41MNA mixtures are determined. Fig. 2 presents the cooling and the subsequent heating curves. Crystallization is observed in the 59BZL - 41MNA mixture at a cooling rate of 1 K/min, while no crystallization occurs for the 50BZL - 50MDHB mixture, indicative of relatively higher glass formability.

The phase diagram of the BZL - MNA and BZL - MDHB mixtures is compared in Fig. 3(a) and (b). The reduced glass transition temperatures T_{rg} ($=T_g/T_l$), which is often used to serve as an indicator of glass forming ability, are determined to be 0.681 and 0.622 for the 50BZL - 50MDHB and 59BZL - 41MNA mixtures. ΔS_m of pure and eutectic compositions for the two systems is given in Fig. 3(c) and (d). When using a parameter ΔS_m^{ave} to define the linear average of the two pure components' ΔS_m, it can be seen that the ΔS_m value at the eutectic 50BZL - 50MDHB composition is lower than ΔS_m^{ave}, while $\Delta S_m > \Delta S_m^{ave}$ is shown for the 59BZL - 41MNA eutectic. Based on the definition of the excess in the entropy of fusion [33],

$$\Delta S_{m-exc} = \Delta S_m - \Delta S_m^{ave} = \Delta S_m - \left(x_A \Delta S_m^A + x_B \Delta S_m^B\right) \quad (1)$$

$\Delta S_{m\text{-}exc}$ is calculated to be −5.16 and 0.17 J/mol-K for the two eutectics, as shown in Fig. 3(e) and (f). In earlier studies, the ideal mixing entropy $\Delta S_{mix}^{id} = -R[x \ln x + (1-x)\ln(1-x)]$ is emphasized in interpreting the glass formation of multi-component alloys [34,35] and, accordingly, the composition dependences of ΔS_{mix}^{id} is also presented. It is evident that $\Delta S_{m\text{-}exc}$ for the two eutectics is smaller than ΔS_{mix}^{id}.

The isothermal measurements of the enthalpy of mixing are given in Fig. 3(g) and (h) for the two binary systems at the eutectic compositions. The endothermic and exothermic behaviors are observed for the BZL - MNA and BZL - MDHB mixtures, giving ΔH_{mix} to be 23.5 and −16.6 J/g, which corresponds to 4.25 and −2.66 kJ/mol, respectively. Combining Fig. 3(e)–(h), it appears that negative ΔH_{mix} is compatible with the decreased entropy of fusion relative to the averaged value, while the system with positive ΔH_{mix} presents an opposite trend.

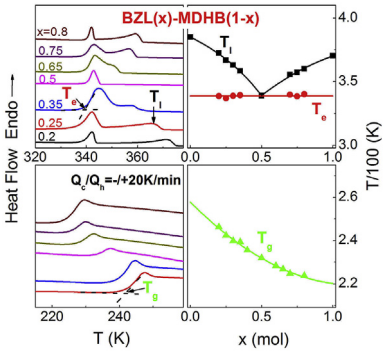

Fig. 1. Calorimetric measurements of the binary mixtures of benzil (BZL) and m-dihydroxybenzene (MDHB) with various compositions, (a) heatflow curves for melting, (b) the phase diagram constructed by the liquidus T_l, and eutectic temperatures T_e, (c) heatflow for the glass formation, (d) composition dependence of the glass transition temperature T_g. *x* is the mole fraction of benzyl. The heating rate is fixed at 20 K/min.

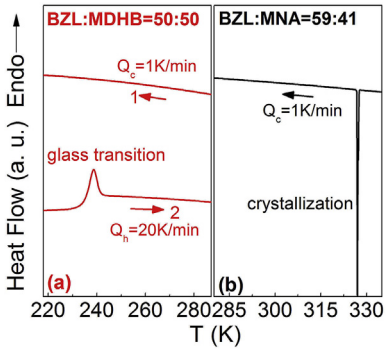

Fig. 2. Critical cooling rates for the glass formation of two eutectic systems in eutectic compositions, (a) benzil (BZL): *m*-dihydroxybenzene (MDHB) = 1:1 (mol/mol), (b) benzil (BZL):*m*-nitroaniline (MNA) = 59:41.