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Fragility and glass transition for binary mixtures of 1,2-propanediol and $LiBF_4$

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ABSTRACT

The fragility and glass transition for binary mixtures of 1,2-propanediol and $LiBF_4$ were investigated by measuring the heating rate dependence of glass transition temperature (T_g) using differential scanning calorimetry. With increasing $LiBF_4$ mole fraction, x, up to 0.25, fragility, m, increased rapidly from 53 to 85, and then remained approximately unchanged for $x > 0.25$. The concentration dependences of T_g and heat capacity jump at T_g also showed anomalies around $x = 0.25$. We suggest this mixture transformed from a moderate to quite fragile liquid at $x = 0.25$ because of a structural change from a hydrogen-bonding- to ionic-interaction-dominant system.

1. Introduction

Amorphous solids and viscous liquids play an important role in various technological applications [1]. The physical properties of an amorphous material depend on its molecular dynamics and structure. Recently, there has been considerable progress in understanding both the glass transition phenomenon and the structural relaxation dynamics of supercooled liquids [2]. The structural relaxation dynamics in a highly viscous regime can be classified into two categories: Arrhenius and non-Arrhenius behavior. Supercooled liquids exhibiting Arrhenius and non-Arrhenius behavior are termed 'strong' and 'fragile' liquids, respectively. Typical 'strong' liquids, such as SiO_2, have a three-dimensional network structure of covalent bonds, while 'fragile' ones, such as *o*-terphenyl (OTP), consist of molecules interacting through nondirectional, noncovalent interactions [3]. The temperature dependence of relaxation time, τ (or viscosity, η), for supercooled liquids is usually described by the Vogel–Fulcher–Tammann (VFT) equation [4]. The degree of deviation from Arrhenius behavior in supercooled liquids is often described by the fragility concept [5,6]. Non-Arrhenius behavior in the glass transition region can be quantified by the fragility parameter, m, which is defined as the slope in the plot of logarithmic mean relaxation time $\langle\tau\rangle$ (or η) versus change in reciprocal temperature at the glass transition temperature, T_g,

$$m \equiv \left.\frac{\mathrm{d}\log\langle\tau\rangle}{\mathrm{d}(T_g/T)}\right|_{T=T_g} \tag{1}$$

The parameter, m, quantifying the rate of the change in structural relaxation dynamics near T_g, is often called dynamic or kinetic fragility. Dynamic fragility is usually obtained from dielectric relaxation [1,7,8] and viscosity [9] measurements, which can assess molecular mobility directly. The fragility can also be estimated with thermal methods using differential scanning calorimetry (DSC) [5,10,11]. Typical strong liquids have a small m value, such as ~20 for SiO_2 [12], while fragile ones have a large m value, such as ~81 for OTP [13].

As compared to strong liquids, fragile liquids are structurally more unstable and their property, changes going from liquid to glass, is more significant. Fragile liquids are expected to have a large configurational heat capacity, resulting from a rapid change in configurational entropy with temperature. The heat capacity change during glass transition is the most commonly considered thermodynamic property. The difference and ratio between the heat capacity of supercooled liquids (C_p^{liquid}) and that of glass (C_p^{glass}) or crystal (C_p^{crystal}) at T_g have been used as thermodynamic measures of fragility. There has been considerable interest in the relation between dynamic and thermodynamic fragility [14–17]. Recently, a correlation between m, ΔC_p ($C_p^{\mathrm{liquid}} - C_p^{\mathrm{glass}}$) at T_g, and entropy of fusion ($\Delta_{\mathrm{fus}}S$), according to the equation $m = 40\Delta C_p/\Delta_{\mathrm{fus}}S$, was noted for many organic small molecules [2].

Most of the investigations of dynamic and thermodynamic fragility have concentrated on pure substances or miscible molecular liquids [1,2,6,10]. In contrast, little attention has been paid to

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the fragility of mixtures of quite different compounds, such as inorganic/alcoholic systems. For such binary mixtures, there is little quantitative data on the composition dependence of fragility and the correlation of dynamic fragility with thermodynamic properties. Since intermolecular interactions can be changed systematically with concentration, fragility data for mixtures can be useful for understanding the physical origin of fragility in supercooled liquids.

In a previous study, we reported the glass transition and solvation structure of several polyalcohol and polyamine solutions of inorganic salts using DSC and Raman measurements [18–20]. Tetrafluoroborate anions were found to exert a large structural breaking effect on the OH hydrogen bonding structure in aqueous [21] and alcoholic [18] solutions, and $LiBF_4$ has a significantly high solubility in 1,2-propanediol. Thus, 1,2-propanediol solution of $LiBF_4$ is expected to indicate a significant structural change with added salts, and we can systematically investigate the dynamic fragility and thermodynamic properties of the glass transition for a wide concentration range. In this Letter, we discuss the structural change in the mixture with salt addition based on the fragility and glass transition data obtained from DSC measurements.

2. Experimental

Commercial 1,2-propanediol (12PDO; Wako Pure Chemical Industries, Ltd., >99%) was dehydrated by adding metallic sodium, and was distilled under vacuum. Lithium tetrafluoroborate ($LiBF_4$; Wako, >97%) was used as received. Pure components were mixed under a dry nitrogen atmosphere, and the mixture was homogenized by stirring in a sealed flask at room temperature for 6 h or more. Homogeneous mixtures of $(LiBF_4)_x(12PDO)_{1-x}$ for $x > 0.50$ could not be obtained, as this exceeded the solubility of $LiBF_4$ in 12PDO at room temperature.

For DSC measurements, a drop of each mixture, about 3–6 mg, was sealed in an aluminum sample pan. The measurements were performed using a power-compensated DSC (DSC8500, Perkin Elmer, Inc.) under a flow of helium gas. To measure the dependence of T_g on heating rate, β, the DSC signal was recorded for $\beta = 2, 5, 10, 20, 50$, and 100 K min^{-1} for a glassy sample that was first prepared by cooling from room temperature to 120 K at a cooling rate of $-\beta$. Each sample was held at 120 K for 3 min before the heating scan to obtain a completely glassy sample. The heat capacity jump at the glass transition was measured at $\beta = 10$ K min^{-1} for samples quenched at a cooling rate of 100 K min^{-1} to ensure the same thermal history with avoidance of phase separation and recrystallization in the samples. Before the measurements, the DSC equipment was calibrated using cyclohexane and indium at each heating rate. Figure 1 shows the DSC curves for different x values.

The onset (T_g) and offset (T_g^{off}) glass transition temperatures following enthalpy recovery were determined at $\beta = 10$ K min^{-1} using the standard method of extrapolation of the baselines, as shown in Figure 1. The heat capacity jump at T_g, which is defined as $\Delta C_p = C_p^{liquid} - C_p^{glass}$, was determined from the difference between the extrapolated baselines below and above T_g.

3. Results and discussion

3.1. Glass transition temperature

A single endothermic baseline shift due to glass transition was observed for each sample, as shown in Figure 1. The DSC heating curves showed a clear overshoot due to enthalpy recovery for each concentration. Other thermal anomalies were not observed during cooling and heating scans in the temperature range of 120–300 K. Figure 2 shows the concentration dependence of T_g and T_g^{off} and the glass transition width. The value of T_g for 12PDO was determined to be 165 K, which almost agreed with previous dielectric and calorimetric results (167–169 K) [6–8]. With increasing x, T_g and T_g^{off}

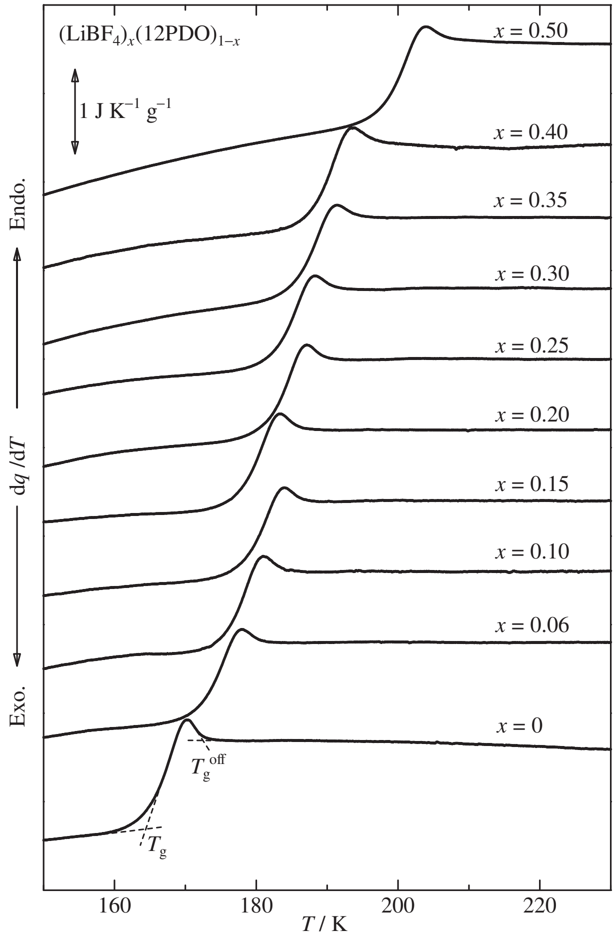

Figure 1. DSC curves for $(LiBF_4)_x(12PDO)_{1-x}$ obtained at a heating rate of 10 K min^{-1}. Each curve is normalized by the sample mass and is offset vertically for clarity.

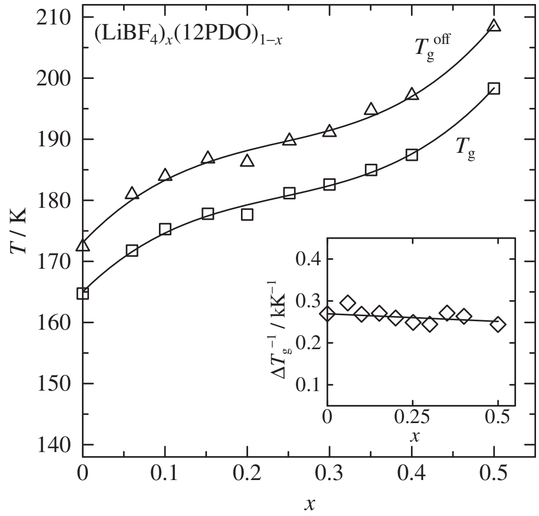

Figure 2. Concentration dependence of the glass transition temperatures for $(LiBF_4)_x(12PDO)_{1-x}$. Squares and triangles represent T_g and T_g^{off}, respectively. The reciprocal glass transition width is represented by diamonds in the inset. Solid lines are guides for eyes.