Solvation and Glass Transition in Supercooled Organic Solutions of Alkaline Perchlorate and Alkaline Tetrafluoroborate

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Abstract. Raman and DSC measurements for binary solutions of polyhydric alcohols and polyamines mixed with alkaline perchlorates and alkaline tetrafluoroborates are presented as a function of temperature and salt concentration. In these systems, the glass transition temperature increases with salt concentration, whereas highly concentrated systems showed an inflection anomaly. This glass transition anomaly is discussed in relation to the solvation of ions surrounded by organic solvents. The solvation structure is interpreted on the basis of the thermal excitation of the hydroxyl and amino groups.

Keywords: Glass Transition, Solvation Structure, Inorganic Salts, Polyhydric Alcohols, Polyamines

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INTRODUCTION

The dynamic properties and glass transition of supercooled liquids have been important research subjects in basic and applied materials science, and chemical technologies [1]. The slow dynamics and glass transition in supercooled liquids are probably controlled by hierarchical dynamics occurring at nanoscale heterogeneities [2–4]. The kinetics of the molecular rearrangement was also discussed in relation to the cooperatively rearranging region from the semi-static viewpoint [5]. These dynamical pictures are expected to interconnect with the variations of the local structures in supercooled glass-forming liquids [6].

On the other hand, in aqueous solutions, characteristic solvation structures should be formed surrounding the solute molecule due to the electrostatic interactions, including hydrogen bonding, between anions and water. The local structure in pure water is expected to be modulated by the solvation interaction. However, dilute aqueous solutions are typically difficult to completely supercool because of the ease of crystallization of water [7]. However, some protic organic solutions are known to form hydrogen bond structures in the neat solvent and are expected to form a solvation structure surrounding the solute molecules. In particular, a special solvation state in alcoholic solutions around ClO$_4^-$ was reported [8].

In the present work, we studied binary systems of alcohols and amines mixed with inorganic salts such as ClO$_4^-$ and BF$_4^-$. In these systems, the local structure is modulated by the moderate interaction between ions and solvents.

Dielectric analysis by Köhler et al. [9] showed the transition from decoupled to coupled dynamics between a solvent and a salt in the LiCl and Gly system. In previous studies of organic–inorganic systems, the concentrations of the solutions were limited. It was possible to investigate a broader concentration range in the present systems, for these systems exhibit relatively high solubility.

EXPERIMENTAL SECTION

Commercially available ethanol (EtOH), 1,2-propanediol (12PDO), glycerol (Gly), and 1,2-propanediamine (12PDA) were dehydrated with metallic Na. The materials 12PDO and Gly were then distilled under vacuum. The materials EtOH and 12PDA were distilled under ambient pressure, and then distilled under vacuum. As purchased, LiClO$_4$, NaClO$_4$, LiBF$_4$, and NaBF$_4$ were used as solute materials. The obtained pure materials were mixed under nitrogen atmosphere and stirred overnight. Mixtures forming uniform solutions were used in the measurements. The concentration of the samples was determined by weighing each component during the mixing process.

Raman scattering measurements were performed using an instrument equipped with a double-monochromator grating system (RAMANOR U1000; Horiba-Jobin-Yvon, Inc.) and a photon counter (Hamamatsu Photonics, Inc.) for the frequency analysis of the scattered light. A liquid nitrogen
cryostat (Optistat DN; Oxford Inst. Co. Ltd.) was used for performing low-temperature measurements. The instability of temperature control was within ±0.1 K. To obtain a uniform vitreous sample, the cell containing a sample of ca. 2 cm$^3$ was immersed in liquid nitrogen. The Raman spectra for each sample were measured at several temperatures to avoid devitrification and phase separation. All the Raman spectra presented were normalized by the integrated intensity in the CH-stretching band.

The DSC measurements were performed using a heat flux type apparatus (DSC10; Seiko Electrical Industry, Inc.) for samples vitrified by the rapid cooling method, i.e., the samples were dropped into the open sample pan that was at liquid nitrogen temperature. The measurement range was 150–300 K and the heating rate was 2 K min$^{-1}$.

RESULTS

Raman Spectra

Figure 1 shows the concentration dependence of the Raman scattering intensity of the OH-stretching region in the (LiClO$_4$)$_x$(EtOH)$_{1-x}$ system. A high wavenumber peak appears and increases with increasing LiClO$_4$ concentration. The spectra exhibited an isosbestic point around 3450 cm$^{-1}$. This is interpreted as an indication of equilibrium between two distinctive OH states, i.e., one OH forming bond with another OH via hydrogen bonding and the other bonding to ClO$_4$$^-$. 

\[ \text{OH} \cdots \text{OH} + \text{ClO}_4^- \rightleftharpoons \text{OH} \cdots \text{ClO}_4^- + \text{OH}^- \quad (1) \]

where the triple dots indicate hydrogen bonding. Furthermore, assigning the higher wavenumber peak for OH groups interacting with ClO$_4^-$, this type of hydrogen bonding is weaker than those formed between the two OH groups [8].

Figure 2 shows decrease in the higher wavenumber peak intensity with decreasing temperature observed in (NaClO$_4$)$_{0.33}$(Gly)$_{0.67}$ for which $T_g = 206$ K. At 220 K and 206 K, the OH interaction with the anion decreases and the interaction between the two OH increases compared to the spectrum at 300 K. The equilibrium described by Eq. (1) moves to the right as the temperature decreases. Similar behavior is observed in the (LiBF$_4$)$_x$(12PDO)$_{1-x}$ system. This is expected to be a common property in alcoholic solutions that include anions with low surface charge density.

Figure 3 shows the Raman spectra of
The vibrational frequency of the OH-stretching band shifts lower with hydrogen-bonding formation because of the lowering of the force constant. On the other hand, it is reported that the solvation of water and alcohols around ClO$_4^-$ or BF$_4^-$ brings about an extra high-frequency peak in the OH-stretching band [8,11]. Hydrogen bonding to anions ClO$_4^-$ and BF$_4^-$ is weaker than those formed with another OH group. Since the stretching of the free OH group is around 3600 cm$^{-1}$, the OH group interacting with anions has an intermediate stability between the free OH and the one interacting with another OH. The higher frequency peak weakens and the lower frequency band increases with decreasing temperature. From the analysis in terms of the van’t Hoff equation, the enthalpy of hydrogen-bond switching in the Gly system is 3.9 and 1.6 kJ mol$^{-1}$ for $x = 0.16$ and 0.33, respectively. The enthalpy of reaction (1) is positive and decreases with increasing $x$.

This implies that the solvation around ClO$_4^-$ and BF$_4^-$ observed at room temperature reflects the entropy effect rather than the preferred structure in enthalpy. In addition, the decrease in the enthalpy change implies that the relative stability between the two states depends on the concentration. This indicates that the switching of bonding is not only controlled by the participating functional group and chemical species directly bonding, but also strongly influenced by the surrounding molecules.

The temperature dependence of the Raman spectra of the 12PDA systems roughly agrees with those of alcoholic systems. A notable behavior observed in (NaClO$_4$)$_x$(12PDA)$_{1−x}$ system is that the enthalpy of the equilibrium between strong and weak hydrogen bonds changes sign for $x > 0.25$, i.e., the two states of NH$_2$ switch their relative stabilities with the concentration [10].

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A phase transition is an abrupt or discontinuous change in thermodynamic parameters such as
temperature or composition. This is because the macroscopic equilibrium phenomena results at the thermodynamic limit. On the other hand, the glass transition, which is controlled by local molecular dynamics, is typically obscure and relatively insensitive to the modulation in molecular interaction. As it has been discussed, the $T_g$ of mixtures with no specific interactions is almost linear or monotonic [12,13]. A system with an anomalous glass transition would be associated with particular molecular arrangements or interactions. The nonlinear concentration dependence of $T_g$ has been observed in several special cases with special intermolecular interactions [14-18].

In Fig. 5, the concentration dependence of $T_g$ is plotted for (NaClO$_4$)$_x$(12PDA)$_{1-x}$ system [10]. $T_g$ is approximately 2/3 of the fusion temperature, $T_{\text{fus}}$, in a broad range of substances. Anhydrous NaClO$_4$ decomposes around 755 K [19] below which the substance is in the crystalline form. Using the decomposition temperature instead of $T_{\text{fus}}$, $T_g$ is estimated to be 503 K. Obviously, the concentration dependence of $T_g$ is accompanied by the inflection point arising from the interaction crossover. In the lower concentration region, the solvent–solvent interaction should be dominant as indicated from the solvent-specific concentration dependence of $T_g$, as shown in Fig. 4. In contrast, in the highest concentration range, including $x > 0.4$, the solvent–ion and ion–ion interactions should be primary. In the intermediate region, these two interactions are competitive and switching of hydrogen bonding also proceeds with increasing concentration. The interaction crossover in $x = 0.2 - 0.25$ is supported by the Raman spectra in Fig. 3. The NH$_2$-stretching modes drastically change their shapes with decreasing temperature in the lower concentration range, $x < 0.2$, whereas the change in the spectrum is minor in the higher concentration range, $x > 0.25$. This suggests that at high concentration the amino groups trapped by the anions at room temperature keep their state even at low temperature, whereas at low concentration the hydrogen-bonded NH$_2$ changes to its counterpart with decreasing temperature. The data support the idea that the dominant interaction changes from hydrogen bonding between NH$_2$ groups to ionic interaction with increasing salt concentration.

CONCLUSION

Solvation is assumed to be the formation of preferred local structure caused by solute–solvent interaction. In the present systems, the solvated state is an intermission of thermal excitation from hydrogen bonding between solvent molecules and free OH. The former is observed at low temperature as approaching the ground state; however, this may help clarify the change in the dominant interaction. At low temperature, the existence of ions avoided by the solvent molecules causes an anomaly in $T_g$ in several systems. Although an obvious anomaly was not observed for other systems because of the limitation of solubility, other systems are also expected to exhibit anomalies once the uniform mixture of higher concentrations is successfully vitrified.

REFERENCES