Two Distinct Raman Profiles of Glassy Dilute LiCl Solution

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We make glass of dilute LiCl aqueous solution by cooling micrometer-sized droplets of the solution extremely quickly and measure the Raman spectra of the glass. It is found that the OH stretching vibration mode of the glass of dilute solution is composed of the OH stretching vibration mode of pure glassy water and that of the glass of solvent water in the highly concentrated solution. This is consistent with the possibility of the existence of two distinct glassy states of water in dilute LiCL solution at low temperature.

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The studies on the local structure of solvent water in the glassy aqueous solution have been carried out not only to understand the physical properties of pure water but also to broaden an application of the glassy solution in cryobiology and so on [1,2]. In particular, these studies would be important in order to clarify the validity of the liquid polymorphism in water [3,4]. If two liquid waters exist at low temperatures as proposed by recent studies [3], this "polyamorphism" should affect the properties and the structure of dilute aqueous solution. However, it had been difficult experimentally to prepare pure glass of dilute aqueous solutions which does not contain any icy crystals [5,6], because a crystallization of water solvent to ice I_h occurs easily at low temperature. Since the early 1980s, the development of a liquid-hyperquenching technique by Mayer *et al.* [7] made it possible to vitrify pure water and dilute aqueous solutions. Although several studies on the glass of dilute aqueous solution have been performed by Mayer and co-workers [8–10], the properties and the structure of the glasses of dilute solution are still unclear.

When liquid water (H_2O) is cooled extremely rapidly at one atmospheric pressure using the liquid-hyperquenching technique, it becomes a low-density amorphous ice (about 0.94 $\mathrm{g\,cm^{-3}}$) called hyperquenched glassy water (HGW) [7,11,12]. The Raman profile of the coupled OH stretching vibration modes of HGW is characterized by a broad and strong band around 3100 $\mathrm{cm^{-1}}$ as shown in Fig. 1. The Raman spectrum of HGW is similar, but not exactly identical, to that of crystalline ice I_c (Fig. 1) [12,13], and it is believed that there is a slightly distorted tetrahedral hydrogen-bonded network in HGW [14,15].

On the other hand, when we cool rapidly at 1 atm the LiCl aqueous solution whose solute concentration is higher than 10 mol % solute (or, $R < 9$, where R is the number of water moles per mole of salt), it forms another glass [5,16]. In the glass of the highly concentrated solution, the solvent water is considered to exist only as the nearest neighbor water molecules around ions [5,17]. The structure of the solvent in the glass differs from the HGW structure [18]. A wide band around 3450 $\mathrm{cm^{-1}}$, shown in Fig. 1, is assigned as the OH stretching vibration of the solvent in the highly concentrated LiCl solution [18].

In the present work, we make glasses of dilute LiCl aqueous solution ($0 \sim 9.1$ mol % solute; $R \geq 10$) using the liquid-hyperquenching technique [7]. Solution droplets at 0 °C (10–30 μm size) suspended as an aerosol in gaseous dry N_2 at ~0 °C are made by means of an ultrasonic nebulizer and allowed to enter a high-vacuum cryostat through a small hole. Once inside of the cryostat, the

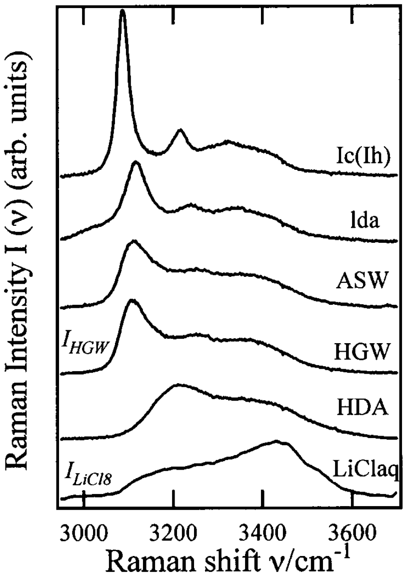

FIG. 1. The coupled OH stretching vibration modes of amorphous and crystalline ices. Raman spectra of three low-density amorphous ices (HGW, ASW, and "lda"), a high-density amorphous ice (HDA), crystalline ice I_c, and a quenched (not hyperquenched) glassy LiCl aqueous solution with $R = 8$(I_{LiCl8}) are shown. HGW, ASW, and lda are made by a liquid-hyperquenching method [7], a vapor deposition method [26,27], and a heating of HDA [28,29], respectively. Although there are slight structural differences between lda and other low-density amorphous ices (HGW and ASW) [12,30], we ignore the differences in this discussion because of the similarity of Raman spectra of these ices. Raman profile of ice I_c is apparently identical with that of ice I_h which is not shown in this figure.

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droplets are deposited on a cold plate held at 85 K to form a glassy state. The glassy solution is further cooled down to 40 K, and a Raman spectrum of the glassy solution is recorded in the region from 2900 to 3700 cm^{-1} with a resolution of about 2.0 cm^{-1} with a microscopic Raman spectrometer system.

Several Raman spectra of the glass of dilute solution are shown in Fig. 2(a). The OH stretching vibration mode around 3100 cm^{-1} which is characterized by the structure of HGW and the OH stretching vibrational mode around 3450 cm^{-1} which is characterized by the solvent structure in the glass of the highly concentrated solution are observed in the Raman spectra of the glass of dilute solutions in the examined concentration region (0 ~ 9.1 mol % solute; $R \geq 10$). Indeed, the Raman profile of these glassy dilute solutions can be expressed by a linear combination of the Raman spectrum of HGW (I_{HGW}) and that of the glass of highly concentrated LiCl aqueous solution with $R = 8$ (I_{LiCl8}) as the following equation. $I_{\mathrm{fit}} = \alpha I_{\mathrm{HGW}} + (1 - \alpha) I_{\mathrm{LiCl8}}$, where I_{fit} is the result of the fit to the experimental data. A coefficient, α, stands for a respective weight of a I_{HGW} component and ranges between 0 and 1. $\alpha = 1$ means that the structure is equal to that of HGW. The value of α decreases continuously and monotonously with an increase in the concentration (Fig. 3).

We note that two "spectra" (I_{HGW} and I_{LiCl8}) are combined in this study; this is different from the simple combination of two peaks in the previous studies on the mixture model of water [19]. The fact that the linear-combination fitting by I_{HGW} and I_{LiCl8} is good quality is consistent with the possibility that only two kinds of glassy water states—a state with HGW structure and a state with highly concentrated glass structure—exists in the glass of the dilute solution, and that there is no intermediate state between these two states. Therefore, the boundary between the two states appears to be discontinuous.

The 3100 cm^{-1} band of HGW is known to be a result of intermolecular coupling. The breakdown of the coupling makes the band position shift toward the higher frequency [20,21]. If the present glassy LiCl solution is a molecular level mixture of hydrated ions and other water, a similar decoupling would occur, and the 3100 cm^{-1} band would move toward the higher frequency with increasing solute concentration. However, this is not observed in the present experiment.

These results appear to show, but do not prove, that a phase separation into the two glassy states with different structures of solvent water occurs in the solution on hyperquenching. This apparent phase separation is not observed in LiCl solution at room temperature because the HGW structure tends to disappear at room temperature [4]. Although the observation of some macroscopic property relating to the phase separation is desirable, the existence of two distinct states in glasses of dilute LiCl solution is plausible from the evolution of α coefficient. The monotonous decrease of α with the increase in solute concentration also suggests a low solubility of electrolyte solute into HGW.

When the Raman spectra of the glass of LiCl aqueous solution with $R = 8 \sim 6$ are used in place of I_{LiCl8}, the result of the fit to the experimental Raman spectra is good. However, using Raman spectra of glass of LiCl aqueous solution with $R < 6$, the error between the fitted spectra

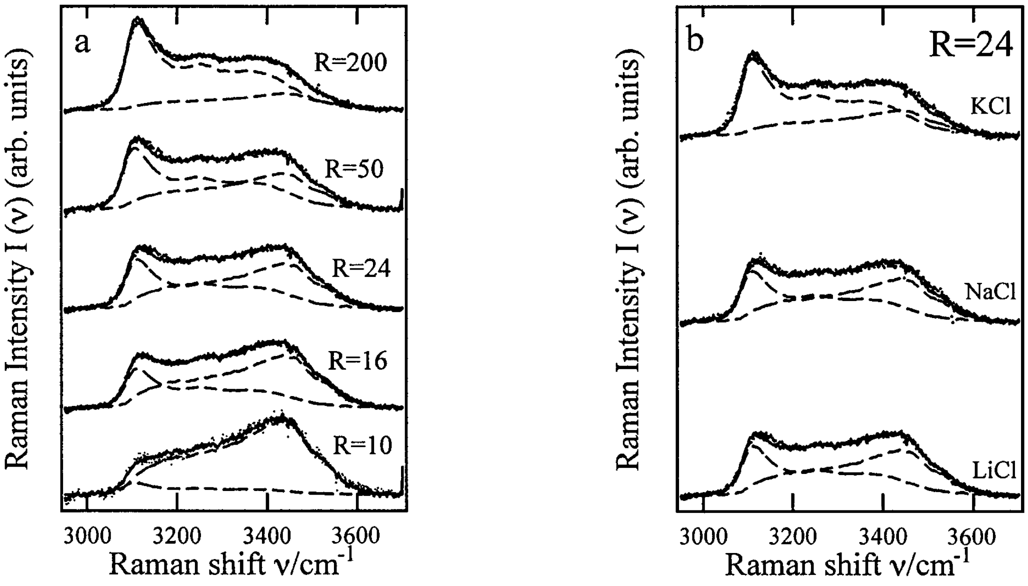

FIG. 2. The coupled OH stretching vibration modes of glasses of electrolyte aqueous solution. (a) The experimental Raman spectra of hyperquenched glassy LiCl aqueous solution with 9.1, 5.9, 4.0, 2.0, and 0.5 mol % solute ($R = 10$, 16, 24, 50, and 200) are displayed by dots. Solid lines represent I_{fit} obtained by fitting to the experimental spectrum. Two broken lines represent αI_{HGW} and $(1 - \alpha) I_{\mathrm{LiCl8}}$. (b) The experimental Raman spectra of hyperquenched glassy LiCl, NaCl, and KCl solutions with 4 mol % solute ($R = 24$) as compared to the result of the fit.

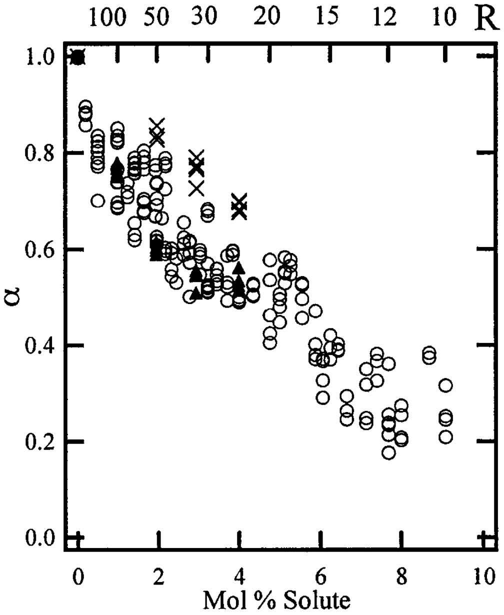

FIG. 3. The concentration dependence of α for glassy solutions of LiCl (○), NaCl (▲), and KCl (×). From the value of α, ~0.2, for LiCl solution with $R = 10$, we estimate that the amount of low-density amorphous ice (ASW) made by the deposition of water vapor in this experiment is less than ≈10% in the sample glass.

and the experimental spectra becomes larger. In addition, it is difficult to analyze the Raman spectra of hyperquenched glassy dilute solution by a linear combination of I_{LiCl8} and the Raman spectrum of crystalline ice I_c in place of I_{HGW}, because the central frequency of the characteristic largest Raman peak of HGW (3100 cm^{-1}) differs from that of I_c (3050 cm^{-1}) (Fig. 1). This indicates that crystalline ice is not nucleated on hyperquenching.

Raman spectra of glasses of dilute NaCl solution and KCl solution are also well expressed by a linear combination of I_{HGW} and I_{LiCl8} as shown in Fig. 2(b). As observed in the glass of LiCl solution, the phase separation might occur in the dilute NaCl solution and the dilute KCl solution. Although the microscopic solvent structure near the metal cation M^+ must vary with M^+ [17], the good result of the linear-combination fit implies that the Raman profile in the glass of highly concentrated NaCl (or KCl) solution is similar to that in the glass of LiCl solution. We believe that a domain of cooperated water molecules probably exists near the cation and the structure of the domain, rather than of the individual water molecules adjacent to the cation, reflects on the Raman profiles of I_{LiCl8}.

This apparent phase separation into two glassy states in dilute LiCl solution at low temperatures may be regarded as a new kind of phase separation. The present phase separation seems to resemble the common segregation behavior into ice I_h crystal and the solute-rich liquid at low temperatures [22]. This is because the structure of HGW is similar to that of ice I_h [4]. Therefore, this phase separation in LiCl solution at low temperatures is a phase separation into two "glassy" phases with different composition (a "HGW-rich" liquid and a solute-rich liquid) and different solvent structure corresponding to I_{HGW} and I_{LiCl8} structure. Contrarily, the usual phase separation in the binary mixture as observed in the water-oil system is the one into a high-temperature "normal-water"-rich liquid and a solute-rich liquid. The HGW structure hardly exists in the high-temperature normal water [4]. For the low-temperature dilute electrolyte aqueous solutions, the latter phase separation to the normal water has been a subject for discussion [9,23] and was thought to be unreasonable to occur because of the negative enthalpy of mixing at ambient temperature [9]. The present phase separation is also different from the phase separation in the $\mathrm{Y_2O_3}$-$\mathrm{Al_2O_3}$ system into two liquids with an apparently "same" composition and a different density [24].

Recent theories on supercooled liquid water suppose the localized formation of low-density structured molecular arrangements; the "HGW structure" in water [25]. Our result that a solubility of electrolyte solute to HGW solvent is low indicates that the formation of HGW would cause the segregation of solute in the low-temperature dilute solution. In this connection, Fleissner *et al.* [9,10] reported the increasing ion paring in the glassy state on cooling. This phenomena may relate to the structure of the separated solvent waters at low temperatures. We think that the present phase separation in the low-temperature dilute aqueous solutions may furnish useful hints to clarify the "liquid-liquid phase-transition hypothesis of water" [4].

In conclusion, we have experimentally observed two distinctly different OH stretching vibrational modes in the glasses of dilute LiCl aqueous solution, as well as in those of NaCl and KCl aqueous solutions, at low temperature. The experimental results are consistent with the possibility of the existence of two distinct glassy states in the dilute LiCl solution.

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