Phase separation in dilute LiCl–H$_2$O solution related to the polyamorphism of liquid water

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When an emulsified 4.8 mol % LiCl–H$_2$O solution was cooled under a pressure of 0.35 or 0.45 GPa and decompressed to 0.1 GPa at 142 K, slightly above its glass transition temperature (∼140 K at 0.1 GPa), its volume increased suddenly. This was regarded as an appearance of the low-density amorphous ice in the liquid solution as suggested by x-ray and Raman measurements, and this appearance corresponded to the high-to-low-density polyamorphic transition of pure H$_2$O. Hysteresis was considered to accompany this volumetric change. The hysteresis of the liquid transition proves its first-order nature and, as for the solution, this suggests that the transition is a polyamorphic phase separation. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2743434]

I. INTRODUCTION

Polyamorphism in solvent liquid may be important for understanding the phase behavior of solutions.[1,2] Here, the polyamorphic viewpoint of liquid water was used to interpret the phase behavior of the aqueous solution.

According to the second-critical-point hypothesis of water,[3] liquid water separates into low-density (LDL) and high-density (HDL) liquid phases under a high-pressure and low-temperature condition, and these two liquids become low-density (LDA) and high-density (HDA) amorphous ices at much lower temperatures. Accumulation of experimental and theoretical studies seems to support this hypothesis, but there exists no direct proof of the hypothesis due to the crystallization of the supercooled liquid water.[4]

The crystallization of liquid water has also prevented to prove the supposed liquid-liquid immiscibility in the dilute electrolyte aqueous solutions at low temperatures. Angell and Sare discussed this immiscibility nearly 40 years ago.[5] Recently, Chatterjee and Debenedetti reported a theoretical possibility that, when solvent exhibits polyamorphism, an addition of solute in the solvent induces the liquid-liquid phase separation of the solution.[2] Experiments on this kind of the phase separation have been done mainly on the glassy state of dilute aqueous solution.[6–8] Although the experimental results were consistent with the occurrence of the LDA-HDA phase separation in the glassy solution,[7,8] thermodynamic verification was difficult because of the nonergodic nature of the glasses.

We can regard the high-pressure dilute LiCl aqueous solution as LiCl dissolves in the HDL state of water (written as HDL:LiCl in this paper).[8,9] When cooled at a pressure higher than ∼0.2 GPa, this HDL:LiCl vitrifies below its glass transition temperature T_g and becomes a HDA:LiCl glass, although its structural relation to pure HDA is not established.[10] In our previous experiment,[8] the emulsified LiCl solution was cooled under a pressure and decompressed at different low temperatures while the temperature of the solution was measured. Then, it was claimed that the crystalline ice I_c suddenly appeared in the solution during the decompression above T_g, and that the LDA-like form replaced ice I_c below T_g. In the present experiment, I measured also the volume of the solution during the decompression and found that the sudden volumetric change occurred in the *liquid* solution just above the T_g. I argue that the LDA-like form appeared in the liquid and that the expected polyamorphic phase separation in the solution was realized.

II. EXPERIMENT AND RESULTS

The emulsified 4.8 mol % LiCl–H$_2$O solution (1–10 μm in droplet size) was used in order to hinder the crystallization. The emulsion sample was made by stirring the LiCl aqueous solution (1 ml), an oil matrix (methylcyclohexane, 0.75 ml, and methylcyclopentane, 0.75 ml), and a surfactant (sorbitan tristerate, 50 mg) together, and about 1.4 cm^3 of the sample in an indium cup was compressed in a steel piston-cylinder apparatus with a bore diameter of 15 mm. The emulsion is known to provide nearly the same results about the phase transitions as those of the pure bulk sample[8,9] (except the heterogeneous nucleation of crystalline ices), while the emulsion matrix gives an insignificant monotonous background of the volumetric and thermal responses. After being compressed to 0.35 or 0.45 GPa at room temperature, the sample was cooled under pressure and then decompressed at different low temperatures. The decompression rate was kept strictly constant (∼0.002 GPa/s) by decreasing the press load automatically, while the cylinder temperature was kept constant (±∼0.1 K) by using the cold nitrogen gas and the heater wound around the cylinder. The sample temperature (absolute error: ±∼0.5 K) and the piston displacement (which corresponds to the change of the solution volume) were measured simultaneously to ±∼0.02 K and ±∼1 μm in relative error, respectively. The chromel-alumel thermocouple was brought into the sample through a small hole of the piston. Two digital-linear gages were located at opposite sides of the piston and the average of their values was taken.
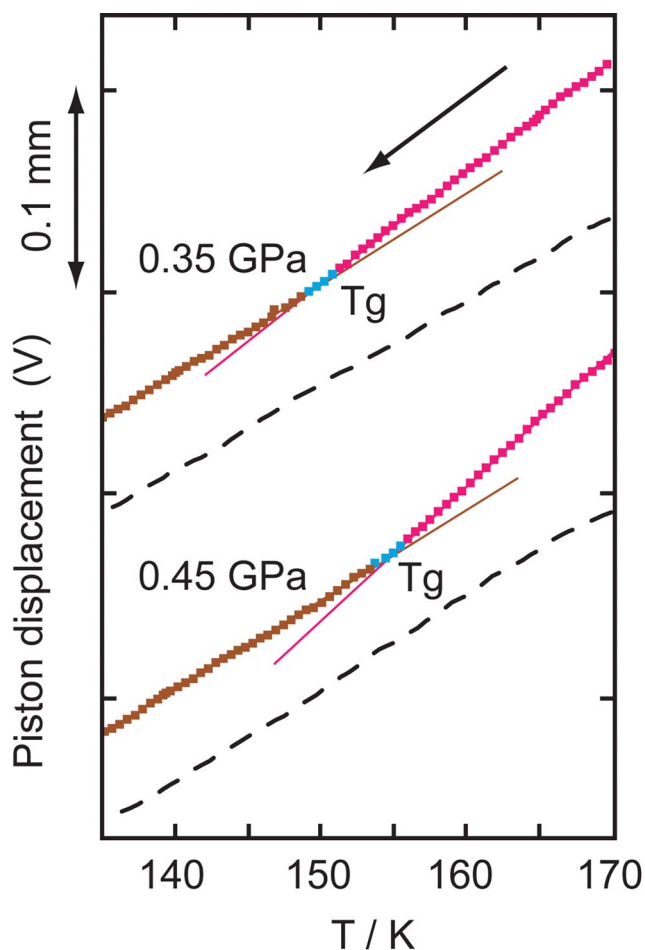
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FIG. 1. (Color online) Piston displacement during cooling of the emulsified 4.8 mol % LiCl–H$_2$O solutions at high pressures. The broken reference lines are the results of emulsion matrix without the LiCl solution. The lines were shifted vertically.

The piston displacement during the high-pressure cooling at ~2.7 K/min is shown in Fig. 1. The volume-temperature curve bended around the expected T_g of the solution,[9] which demonstrated the existence of the glass transition clearly. The sample recovered at ambient pressure and 77 K showed a halo x-ray-diffraction picture without any noticeable crystalline diffraction line nor spot. When the vitrified solution after the high-pressure cooling was decompressed around 140–150 K [the brown lines of Fig. 2(a)], the volume of the glass started to increase more rapidly [the pink line in Fig. 2(b)] at the pressure of the expected T_g [the wide light-blue line of Fig. 2(a)][6,9] or at a slightly higher pressure than that (the blue line of the figure). On further decompression below this pressure, the volume increased at the same rate as that of the liquid solution locating at slightly higher temperatures [the pink lines of Fig. 2(b)]. This was the typical volumetric behavior of devitrification at T_g; the compressibility of the glass changed to that of the liquid. Thus, the glassy solution became liquid during the decompression.

When this liquid solution was decompressed further, its volume increased suddenly and rapidly at the pressure of the red broken line of Fig. 2. The volume increase is shown by the black lines of Fig. 2(b), and by process 2 of Figs. 2(c)

and 2(d). During this volume expansion, the temperature of the solution was almost constant or changed slightly [the black lines of Fig. 2(a)]. This slight change of the temperature probably resulted from a balance of the heat evolution due to the phase transition and the heat absorption due to the quasiadiabatic quick volume expansion. After the rapid volume increase ceased, the temperature of the solution started to increase rapidly as reported in the previous paper[8] [the green lines and the blue lines of Fig. 2(a), and process 3 of Fig. 2(c) and processes 3 and 4 of Fig. 2(d)]. As discussed in the previous paper[8] and as will be described later, the large increase in temperature at higher temperatures corresponded to the crystallization [the green lines and process 3 of Figs. 2(c) and 2(d)], and the small increases at lower temperatures corresponded to the appearance of the LDA-like form [the blue lines with or without the arrow in Fig. 2 and the lines of process 4 of Fig. 2(d)]. At the intermediate temperatures, two exothermic events were observed [the # line of Figs. 2(a) and 2(d)], which suggested that the LDA-like structure appeared first (the blue line), and then the crystallization occurred (the green line). The volume change at the second exothermic event appeared small, if any [Fig. 2(b)]. On decompression below 140 K, the volume of the HDA:LiCl glass gradually started to expand more rapidly around the red broken line, or the T_g line, of Fig. 2(d). The difference between the onset pressure of the volume expansion and the onset pressure of the temperature increase was large and unclear [the low-temperature lines of Fig. 2(d)]. The gradual volume expansion between the two onset pressures (namely, between the red and green dotted lines) at these low temperatures might be caused by the relaxation of the HDA:LiCl glass and/or by the scattered values of the volume-increase pressure of each emulsion particle even if the individual particle might transform much more quickly.

The temperature of the decompression, the decompression rate, the salt concentration, and the pressure of the cooling were changed, and the experiments were repeated (not shown because the results were essentially the same as those of the previous paper[8]). The decompression-induced rapid volume expansion was, then, found to occur on the locus of the smoothly extrapolated line of the decompression-induced homogeneous nucleation of ice I_h and/or ice I_c, as shown by the red broken line in Fig. 3 that continues from the high-temperature T_H line. The similar continuity of the onset pressure of the rapid increase in temperature was also observed, as reported in the previous paper[8] (the green broken line in the figure).

After the samples were decompressed to ambient pressure (samples A, B, C, and D of Fig. 3), they were identified by x-ray and Raman measurements at 77 and 27 K, respectively [Fig. 4(a) and the left panel of Fig. 4(b)]. The x-ray photos indicated that samples A and B were amorphous, and C and D were ice I_c and I_h, respectively. The coupled O–H Raman profiles were used as an indirect probe of the amorphous structures (LDA and HDA) and were compared with those of the pure HDA emulsion made by pressure-induced amorphization of the ice I_h emulsion at 77 K [the center panel of Fig. 4(b)]. They are also compared with those of the pure HDA emulsion made in this study by rapid cooling of
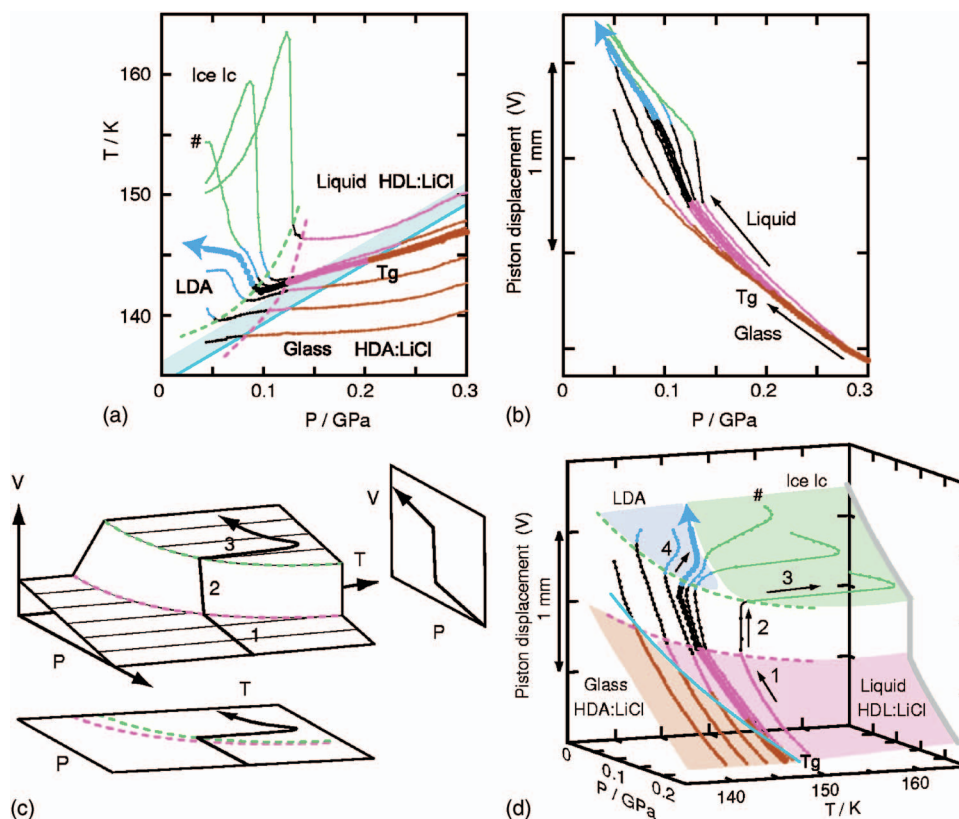
FIG. 2. (Color) Typical results of the pressure P–sample temperature T–piston displacement V relation obtained during decompression of an emulsified 4.8 mol % LiCl–H₂O solution around 140–150 K. The reference experiments using only the emulsion matrix without solution showed only a monotonous P-T-V relation. (a) T-P curve. The wide light-blue line: the reported T_g (Refs. 6 and 9). The straight blue line: T_g corresponding to the change in compressibility during decompression [see graph (b)]. The red and green broken lines: the onset pressures of rapid increase in volume and rapid increase in sample temperature, respectively. The sample temperature increased in two stages on the decompression of #. (b) V-P curve. The raw data of each piston-displacement curve was shifted vertically in order to take the same value at 0.30–0.35 GPa. The right-to-left curves correspond to the upper-to-lower curves in graph (a). (c) A schematic illustration of the P-V-T relation that is constructed by using the V-P and T-P graphs. When the sample decompressed (process 1), its volume increased (process 2), and then the temperature increased (process 3). (d) The obtained P-V-T relation which may be read in conjunction with the illustration of (c). Pink and brown regions are liquid and glassy LiCl–H₂O solution, respectively. Crystalline ice and LDA-like structure appeared in green and blue regions, respectively. The colors of the lines correspond to those of the graphs (a) and (b).

the liquid-water emulsion at ≈0.3 GPa [the right panel of Fig. 4(b)].[11] The Raman profiles and the x-ray photos showed the essentially same phase behavior between the "HDA family," the "LDA family," ice I_c, and ice I_h that resembled the behavior of pure bulk H₂O; LDA appeared in HDA, and then the LDA-to-ice I_c crystallization occurred.[4,7,10]

It was previously mentioned that, as the LiCl concentration goes to zero, the T_H line of LiCl–H₂O solution continues smoothly to that of pure H₂O at high temperatures, whereas at low temperatures the appearance of the LDA-like structure on decompression of the solution resembles the decompression-induced HDA-to-LDA transition of pure H₂O.[8] This similarity of the low-temperature phase behavior between the solution and pure water was confirmed by the Raman measurements in this work (Fig. 4).

III. DISCUSSION

In the present decompression experiment, the sudden rapid increase in volume just above T_g corresponded to the appearance of the LDA-like form in the liquid solution (the thick line with the arrow in Figs. 2 and 3). This sudden volumetric change must be the first-order transition, as dis-

cussed below. The slope of the line of this volumetric change in the pressure-temperature diagram [dT/dP of the red broken line of Figs. 2(a) and 3] is apparently positive around the T_g of 140 K at 0.1 GPa. This indicates that the occurrence of the sudden expansion near T_g "delayed" as the temperature decreased. On the other hand, the slope of the hypothesized LDL↔HDL equilibrium-phase-separation boundary is considered to be negative like that of the ice I_h↔HDL melting boundary. (The proposed location of the LDL-HDL boundary for the solution[8] is shown by the black broken line with the arrow in Fig. 3.) This is because the LDA structure resembles the ice I_h structure and the HDA structure resembles the high-pressure liquid structure.[4] Then, the observed "delay" just above T_g indicates that the high-pressure liquid state (HDL:LiCl) is thermodynamically metastable in the LDA region. The metastability of an ergodic liquid state means that the volumetric change is the first-order transition, and as for the solution this first-order nature means the occurrence of the polyamorphic phase separation. This is because LDL (LDA) and HDL (HDA) are thought to have different LiCl solubilities at low temperatures. In principle, the volume of the solution would increase gradually as the pressure decreases below the LDL-HDL equilibrium-phase-separation
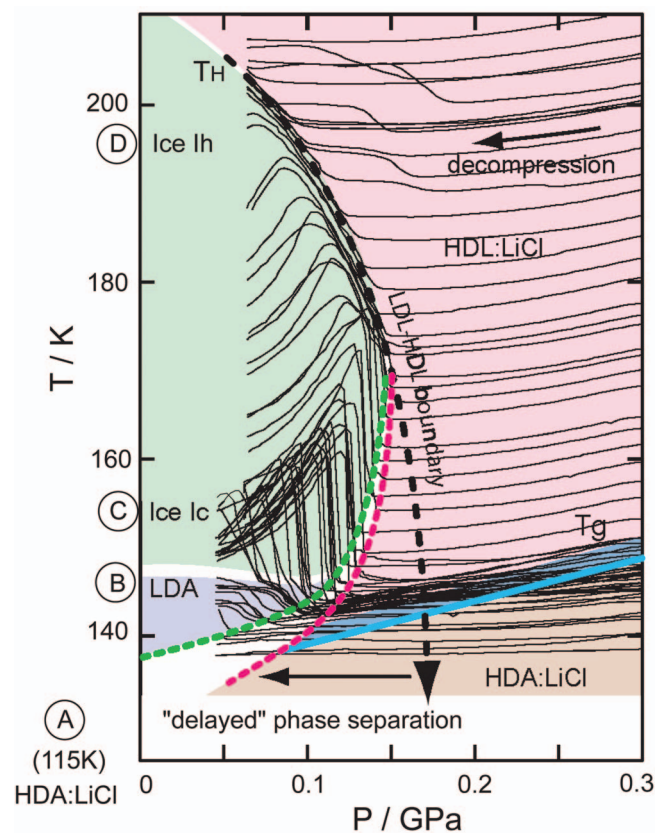
FIG. 3. (Color) Sample temperatures during decompression of the emulsified 4.8 mol % LiCl–H_2O solutions. The colors correspond to those of Fig. 2. The hypothesized LDL-HDL equilibrium-phase-separation boundary (Ref. 8) is shown by the black broken line with an arrow. The volumetric change "delayed" and occurred at the red broken line. The solution samples recovered at 115 K (A) was HDA:LiCl. The x-ray and Raman measurements indicated the existence of LDA-like form, I_c, and I_h in the sample recovered at 148 K (B), 153 K (C), and 195 K (D), respectively. On decompression above ~170 K, the sample volume and the sample temperature gradually increased simultaneously along the T_H line.
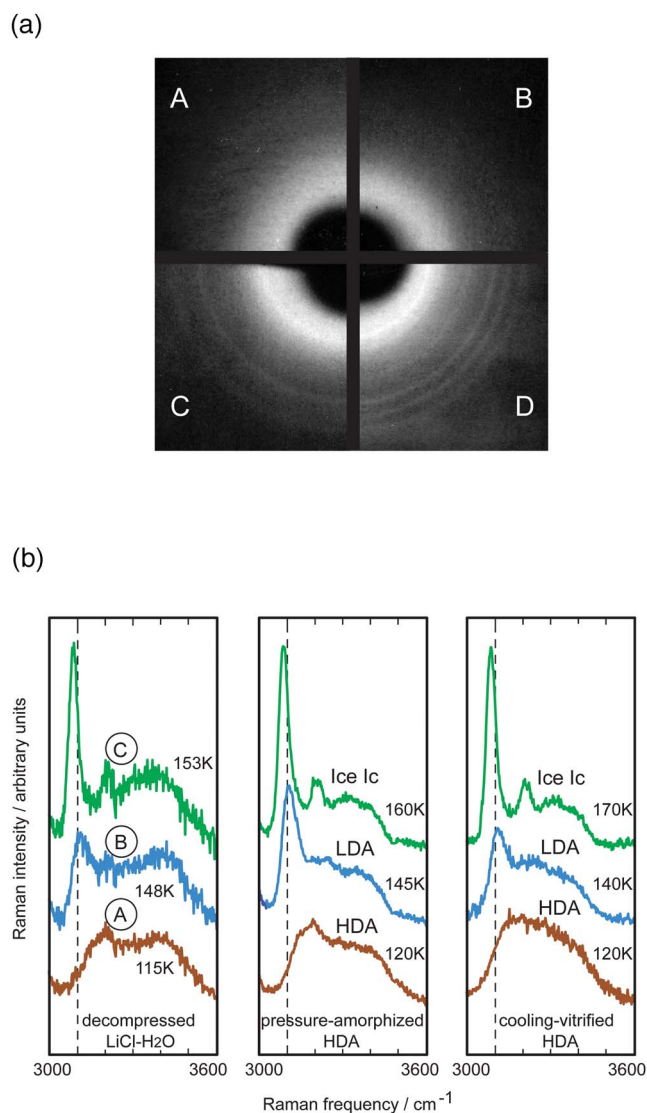

FIG. 4. (Color online) Identification of the solution samples A, B, C, and D of Fig. 3. (a) The x-ray photos taken at 77 K. The samples were placed in a special liquid-nitrogen glass-vacuum flask and exposed to Zr-filtered Mo characteristic x rays (Ref. 9). A Polaroid film was exposed to the x rays diffracted from not only the solution sample but also the liquid nitrogen, thin glass walls of the flask, and emulsion-matrix materials. Although it was difficult to distinguish HDA and LDA precisely, it was possible to find whether ice crystals exist in the sample and to suppose the ice phase. Samples A and B show halo patterns, and C and D show the diffraction lines of ice I_c and ice I_h, respectively. (b) The Raman spectra of the emulsified LiCl–H_2O solutions and the emulsified pure H_2O. The spectra were measured at 27 K with an argon-ion laser (wavelength, 488.0 nm) (Refs. 7, 9, and 11); the laser power in a spot (~20 μm in diameter) on the sample is ~10 mW. The emulsion matrix showed notable peaks below ~3000 cm^{-1}. Left: the spectra of the samples A, B, and C of Fig. 3. When sample A was heated, its spectrum changed to the B-like spectrum between 130 and 140 K, and it further changed to the C-like spectrum between 150 and 160 K (not shown). When sample B was heated, its spectrum changed to the C-like spectrum between 150 and 160 K (not shown). Center: the spectra of the emulsified HDA made by pressure-induced amorphization of ice I_h at 77 K and heated to 120, 145, and 160 K in vacuum. The HDA-to-LDA and LDA-to-ice I_c transitions occurred between 120 and 130 K and between 150 and 160 K, respectively. Right: the spectra of the emulsified HDA made by rapid cooling of emulsified liquid water at ≈0.3 GPa and heated to 120, 140, and 170 K in vacuum. The HDA-to-LDA and LDA-to-ice I_c transitions occurred between 120 and 130 K and between 160 and 170 K, respectively. The results of all the three successful cooling runs were the same and agreed with the previous results (Ref. 11). The slightly higher crystallization temperature suggested the existence of various LDA states.

pressure and as the amount of LDA increases gradually. The "delay" of the low-temperature phase separation explains why the volumetric increase occurred suddenly and rapidly.

Detailed x-ray measurements that show the phase separation have not been done yet. However, the Raman profile of the decompressed LiCl solution [B of the left panel of Fig. 4(b)] could be regarded as a mixture of the LDA spectra and the spectra of the concentrated HDA:LiCl glass that has a broad peak around 3400 cm^{-1}. This is because the Raman profile of the decompressed solution [spectrum B of the left panel of Fig. 4(b)] resembled the spectra of the glassy solution that was made by rapid cooling of the ~4.8 mol % solution near ambient pressure.[7] The spectra of this hyperquenched solution could be regarded as a mixture of LDA and HDA:LiCl.[7–9]

The present study on the thermodynamic phase separation of the dilute LiCl–H_2O solution does not prove the first-order nature of the LDL-HDL transition of pure water because of the crystallization. However, as for the pure water, the smooth connectivity between the T_H line and the HDL-to-LDL transition line is easily expected from the obvious analogy of the phase behavior between the LiCl–H_2O solution and pure water. Then, it is natural to think of the hys-

teresis of the decompression-induced HDL-to-LDL transition of pure water. Indeed, a large hysteresis of the reversible LDA↔HDA transition was observed around 130−135 K,[12–14] just below the expected T_g of pure HDL (~140 K at 0.1−0.3 GPa),[9] which strongly argues the first-order nature of the LDL↔HDL transition of pure water.

In conclusion, the observed decompression-induced volumetric change of dilute LiCl aqueous solution can be interpreted by the polyamorphic viewpoint about the solvent water and can be regarded as the expected polyamorphic phase separation.

ACKNOWLEDGMENT

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