Application of polyamorphism in water to spontaneous crystallization of emulsified LiCl-H$_2$O solution

Osamu Mishima

Advanced Materials Laboratory (AML), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

Aqueous solutions are widely explained by the hydration or the bound water/free water notion. Amorphous polymorphism (polyamorphism) in pure water, which is presently under vigorous discussion, may provide a different view over the solutions. Here, I changed pressure, P, temperature, T, and concentration, C, of emulsified LiCl-H$_2$O solutions and studied their freezing by detecting its heat evolution. It was experimentally indicated that the homogeneous nucleation of low-density crystalline ice I (phase Ih or Ic), in pure water and in solutions, connects to the polyamorphic transition of high-density amorphous ice (HDA) to low-density amorphous ice (LDA). Thus, the polyamorphism of water relates to the phase behavior of aqueous solution. In accordance with the recent simulation result, the nucleation was thought to occur in two stages: the appearance of the LDA-like state and the crystallization. Usefulness of the polyamorphic point of view about the solutions was seen. © *2005 American Institute of Physics.*
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I. INTRODUCTION

When pure liquid water freezes spontaneously at 230 K, molecular-dynamics simulations indicate that LDA-like domains appear in the liquid and that crystallization occurs in the domains.[1] Similar LDA-like domains may also appear in salt water before almost pure ice crystallizes spontaneously and homogeneously. Angell has already proposed the idea of liquid-liquid immiscibility in some dilute aqueous solutions at low temperatures.[2,3] We made the glass of dilute LiCl solution by cooling the liquid extremely rapidly and suggested by Raman spectroscopy that the glass might be a mixture of LDA and another LiCl-rich glass.[4] This LiCl-rich glass is further supposed to be HDA-like because of the broad similarity in structure,[5] in low-frequency Raman profile,[6] and in the suggested glass transition temperature, T_g (Ref. 7). As for pure water, the LDA-HDA transition, as well as the transition between low-density liquid (LDL) and high-density liquid (HDL), has aroused considerable debate,[8] and its discontinuous nature seems to become more and more evident in these past two decades. Particularly, Klotz *et al.* have recently supported the classical first-order nature of the LDA-HDA transition by observing the LDA-HDA coexistence visually in prolonged experiments near the equilibrium condition of LDA and HDA (Ref. 9). The polyamorphism in pure water leads one to expect the phase separation in dilute aqueous solutions. Unfortunately, as in the case of pure water, the liquid-liquid phase separation in the dilute solutions is difficult to be proven directly because of crystallization. Conclusive data of the suggested phase separation in the glassy solution does not exist either. In this context, accumulation of indirect experimental data in the P-T-C diagram and the "consistency" argument would advance the understanding of cold water. In this paper, I indicate in the P-T-C diagram the connection between the homogeneous nucleation in LiCl aqueous solution and the LDA-HDA transition in pure water; then, the polyamorphism of pure water can be consistently applied to the liquid solution.

II. EXPERIMENT AND RESULTS

I used an emulsion of micrometer-sized LiCl-H$_2$O droplets (0-7.7 mol % LiCl) in the oil matrix in order to hinder heterogeneous nucleation of ice crystals.[7,10–13] The employed surfactant, sorbitan tristerate, is known to be insoluble in water, and the size of the emulsion droplets is large enough to show bulk properties. It has already been indicated that the transitions of the emulsified sample occur as if those of the bulk sample occur.[8,10–14] I note that homogeneous nucleation is a phenomenon of bulk water without any special nucleation site. Therefore, most emulsion particles are considered to have no such site; the sites, like dusts, are confined in some particles and the crystallization, induced by the sites, occurs only in these particles. Hence, the results and discussions about the phase relations of the emulsion in this work seem applicable to bulk solution. I omit the term, emulsion, in this paper for simplification.

A solution sample of a certain LiCl concentration, C, was set in a piston-cylinder apparatus as in our previous experiments.[7,14,15] Then, I measured the sample temperature directly by using a thermocouple while I changed pressure, keeping the cylinder temperature nearly constant. In Fig. 1 are shown the temperature changes of the LiCl solutions that are cooled at ~20 K/min under ~0.24 GPa or ~0.32 GPa and decompressed at 0.2 GPa/min at different temperatures. Heat is clearly evolved during the decompression, as shown by the increase in the solution temperature. When C was 0.0 and 2.0 mol %, the crystallization occurred during the cooling under pressure and the decompression-induced heat evolution disappeared below the crystallization temperature
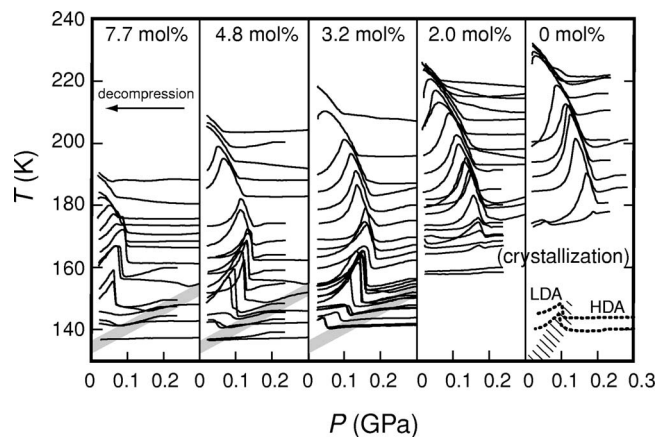
FIG. 1. Some decompression-induced changes in temperature of emulsified LiCl aqueous solution. The emulsion sample ($1-10$ μm in particle size) was made by stirring together a LiCl-H_2O solution (1 cm^3), methylcyclohexane (0.75 cm^3), methylcyclopentane (0.75 cm^3), and sorbitan tristerate (50 mg), and about 1 cm^3 of the sample was confined in an indium cup and compressed in a steel piston-cylinder apparatus. Pressure was changed at 0.2 GPa/min. Errors of absolute pressure and absolute temperature are ± 0.01 GPa and ± 1 K, respectively. Initial concentrations are indicated. The emulsion matrix without the LiCl-H_2O solution was also compressed for the background check, and no heat evolution was observed. The dotted lines and the hatched region of the 0 mol % panel are, respectively, temperature changes of the emulsified HDA made by compression-induced amorphization of ice Ih at 77 K and the location of the known HDA-to-LDA transition of pure bulk water (Ref. 15). Gray lines: the glass transition region of the solutions (Ref. 7). When the 3.2 mol % sample just after the small heat evolution below 150 K was compressed again, it showed heat evolution around 0.3 GPa. On the succeeding decompression below 150 K, the small heat evolution similar to those of the 3.2 mol % panel was observed at a seemingly slightly higher transition pressure. This is consistent with the expected LDA-HDA behavior of LDA separated from the solution.

(Fig. 1). When C was larger than 3.2 mol %, the solution vitrified below T_g (the gray lines[7,16] in Fig. 1) during the high-pressure cooling. No crystalline diffraction line was observed in the x-ray photos of the 3.2 mol % sample that was recovered at 77 K, 1 bar. The heat evolved below $\sim$150 K in the 3.2 and 4.8 mol % panels of Fig. 1 was distinctively small and, in the 7.7 mol % panel, it might be vaguely observed; on further decompression and heating at 1 bar after this small evolution, another sharp heat evolution occurred (not shown). The P-T locus of the large heat evolution above $\sim$150 K continues to the P-T points of the small evolution below $\sim$150 K smoothly. This result was unaffected when the cooled solution was compressed to 1 GPa before the decompression. When the solutions (3.2, 4.8, and 7.7 mol %) were decompressed at 77 K and heated in the cylinder at 20 K/min near 1 bar, they showed a relatively small heat evolution at $\sim$140 K and a large evolution at $\sim$150 K, as already reported;[16] the heat at $\sim$140 K appeared to be smaller as C increases.

The P-T points at which these decompression-induced evolutions begin are plotted in the P-T-C diagram of Fig. 2. As C increased, the onset P of the heat evolution decreased, making a smooth and monotonous P-T-C surface. The decompression-induced heat evolution at high temperatures was regarded as the homogeneous nucleation of the ice I. In Fig. 2 are also shown the published P-T-C data of the homogeneous nucleation of ice I below 0.2 GPa (the thick solid
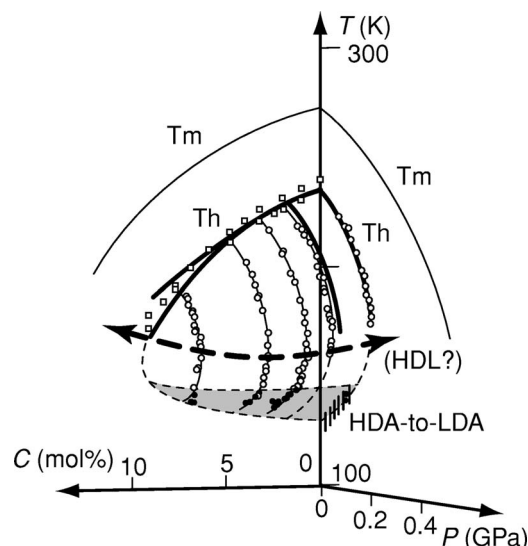

FIG. 2. The P-T-C relation of the homogeneous nucleation and the HDA-to-LDA transition in the LiCl-H_2O solution. Th: the reported homogeneous nucleation lines (Refs. 10–13). Tm: the melting lines (Refs. 12 and 14). Empty and solid circles: the onset points of the large and small heat evolutions of Fig. 1. Open square: the Th points of this work. Short vertical lines at 0 mol %: the region of HDA-to-LDA transition of pure bulk water (Ref. 15). Thin solid and thin broken Th lines (guide to the eye) are drawn by interpolation and extrapolation. The gray region represents the region of the suggested decompression-induced polyamorphic transitions. The broken line with arrows indicates smooth change of liquid states.

lines),[10–13] together with the temperatures at which heat evolution was detected with our differential scanning calorimeter during cooling of the emulsified LiCl solutions at 20 K/min at 1 bar (the open squares in Fig. 2). The locus of the large heat evolution induced by decompression above $\sim$150 K extrapolates smoothly to these homogeneous nucleation points at high temperature, and they are identical at 0 and $\sim$2 mol %.

The P-T region of the known decompression-induced HDA-to-LDA transition of bulk pure water,[15] as well as the temperature change of emulsified pure water at this polyamorphic transition, is also shown in Figs. 1 and 2. The HDA was made by compression-induced amorphization of ice Ih at 77 K. When the presently observed small-heat evolution of solutions below $\sim$150 K is extrapolated to 0 mol %, it appears to correspond to the HDA-to-LDA transition. Then, these heat evolutions at low temperatures are considered to begin by the same mechanism; the appearance of LDA-like ice in an HDA-like glassy solution is suggested. Indeed, by vitrifying the bulk 3.2 mol % solution (as well as the emulsified pure water) during rapid cooling under pressure and by measuring its Raman OH spectra on heating at 1 bar, we have already obtained the result consistent with the appearance of LDA-like ice at $\sim$135 K followed by crystallization at $\sim$155 K (Refs. 17 and 18). This temperature-induced change of the Raman OH profile was reconfirmed in this work on 1-bar heating of the quenched 3.2 mol % emulsion solution in spite of the low quality of the profiles caused by the emulsification. Therefore, by obvious analogy with pure water, the two successive events of the heat evolution, observed in the low-temperature solutions made under pressure, seem to correspond to the two transitions of pure water:
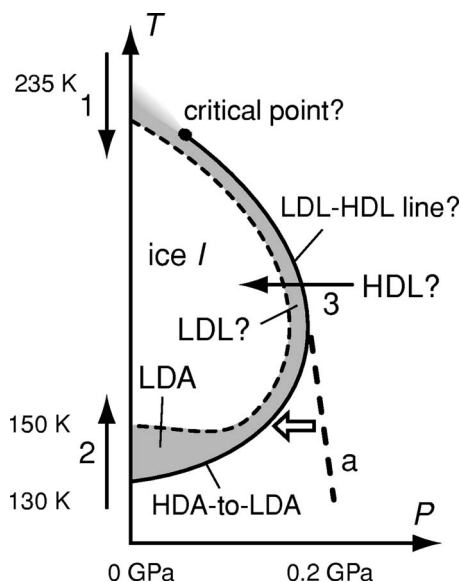
FIG. 3. The illustration of the smooth connection between the homogeneous nucleation and the HDA-to-LDA transition of pure water by applying the LDL-HDL transition hypothesis. Arrow 1: the homogeneous nucleation of ice I in the supercooled pure water, suggested by the simulation (Ref. 1). Arrow 2: the well-known HDA-to-LDA transition and the LDA-to-ice I crystallization. Arrow 3: the hypothesized decompression-induced transition of HDL to LDL, followed by crystallization. LDL, or LDA-like structure, is considered to appear above ~150 K in the gray zone, as LDA appears below ~150 K. Dotted line a: the expected equilibrium LDL-HDL line. The empty arrow shows that the hypothesized equilibrium line shifts to low pressures on decompression at low temperatures. The hypothetical critical point is also plotted; the LDL-like and HDL-like states may fluctuate in the P-T region along the line continuing from the LDL-HDL line extrapolated to higher temperatures above the point.

the HDA-to-LDA transition and the crystallization of LDA. Detailed x-ray characterization of the well-annealed glassy solution would be desirable in order to see if the phase separation of the LDA-like phase occurred, but has not yet been obtained. As noted before, the solvent water of the high-concentration LiCl solution was supposed to be HDA-like. This is consistent with the smooth shift of the state along the smooth P-T-C surface between the expected pure HDL and the concentrated-solution states (the broken line with arrows in Fig. 2).

III. DISCUSSION

As for pure water, the relationship between the homogeneous nucleation and the HDA-to-LDA transition has been unknown due to crystallization. (Fig. 2) The smooth connection between the homogeneous nucleation above ~150 K and the small heat evolution below ~150 K in solutions suggests a similar smooth connection in pure water. Although direct proof is difficult due to crystallization, this connection can be explained by considering polyamorphism. As shown schematically in Fig. 3, the simulations of pure liquid water[1] indicate that LDA-like domains appear before ice I forms (arrow 1). Below ~150 K, experiments of pure water show that the HDA-to-LDA transition occurs first and then the LDA-to-ice I crystallization occurs[8] (arrow 2). Then, at intermediate temperatures, it is natural to suppose that LDL appears in HDL when the sample pressure decreases below

the hypothetical LDL-HDL equilibrium line, and crystallization occurs in the LDL near the line (arrow 3). Since this LDL-to-ice I crystallization is inhibited kinetically below ~150 K, LDL is probably observed as LDA. Although the slope, dT/dP, of the equilibrium LDL-HDL line is likely negative (the broken line, a, in Fig. 3), the positive slope of the decompression-induced HDL-to-LDL line was suggested below ~170 K and above the supposed T_g, that is, ~145 K around 0.2 GPa (Ref. 7). This "delay" of the transition above T_g can be explained by the presence of hysteresis that is accompanying the first-order HDL-to-LDL transition (the empty arrow in Fig. 3). Hence, I propose a hypothesis that the location of the HDL-to-LDL transition is near the homogeneous nucleation line. If the LDL-HDL critical point exists,[8,14,19] the liquid state above and around the critical temperature would fluctuate and the fluctuation would affect the crystallization. The smooth P-T-C surface in Fig. 2 suggests that the LDA-like form would also appear in the liquid solution.

The LDL-HDL line of pure water was previously estimated to locate near its homogeneous nucleation line, and the homogeneous nucleation was, so far, considered to occur before the HDL-to-LDL transition.[14] However, as discussed above, it seems reasonable to think that nucleation occurs after this polyamorphic transition. This interpretation is consistent with the previous suggestion that the homogeneous nucleation in pure water and aqueous solutions is related to a thermodynamic equilibrium process,[20] like this HDL-LDL transition.

In summary, I pointed out the usefulness of the polyamorphic point of view for the consistent explanation of some behaviors of the solution, and this is the purpose of this paper. The application of the polyamorphism to solutions was recently demonstrated by simulation,[21] but experimental data about the immediate application has been almost nonexistent. That is, I experimentally found the connection between the homogeneous nucleation of the LiCl solution and the HDA-to-LDA transition of pure water, and explained it by the polyamorphism of water: that is, the appearance of an LDA-like structure on decompression. Here, I also proposed that the LDA-like structure appears near the homogeneous nucleation condition above ~150 K. A firm experimental proof of the distinct LDA-HDA phase separation in glassy solution does not exist. However, the polyamorphic viewpoint may be promising for easy understanding of the liquid solution, and may have implications in the broad research fields such as cloud formation and cryopreservation. Since the polyamorphism is considered to relate to the properties of pure water near room temperature,[22] such as the density maximum at 4 °C, it may relate to the properties of solution around room temperature. Explanation of the hydrophilic/ hydrophobic or acid/base properties of solutions by polyamorphism is an interesting research direction.[21,23]

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