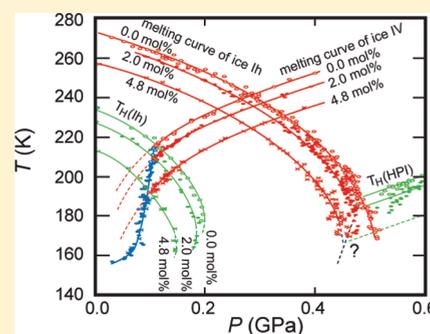


# Melting of the Precipitated Ice IV in LiCl Aqueous Solution and Polyamorphism of Water

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**ABSTRACT:** Melting of the precipitated ice IV in supercooled LiCl–H<sub>2</sub>O solution was studied in the range of 0–0.6 MPa and 160–270 K. Emulsified solution was used to detect this metastable transition. Ice IV was precipitated from the aqueous solution of 2.0 mol % LiCl (or 4.8 mol % LiCl) in each emulsion particle at low-temperature and high-pressure conditions, and the emulsion was decompressed at different temperatures. The melting of ice IV was detected from the temperature change of the emulsified sample during the decompression. There was an apparently sudden change in the slope of the ice IV melting curve (liquidus) in the pressure–temperature diagram. At the high-pressure and high-temperature side of the change, the solute-induced freezing point depression was observed. At the low-pressure and low-temperature side, ice IV transformed into ice Ih on the decompression, and the transition was almost unrelated to the concentration of LiCl. These experimental results were roughly explained by the presumed existence of two kinds of liquid water (low-density liquid water and high-density liquid water), or polyamorphism in water, and by the simple assumption that LiCl dissolved mainly in high-density liquid water.



## 1. INTRODUCTION

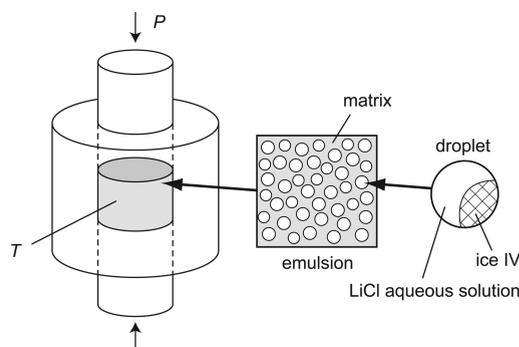
A seemingly discontinuous change in the slope of the metastable melting curve of ice IV was observed in the pressure–temperature diagram of pure H<sub>2</sub>O (and D<sub>2</sub>O), and this implied the existence of the liquid–liquid phase transition (LLT) between low-density liquid water (LDL) and high-density liquid water (HDL).<sup>1,2</sup> This was consistent with, but did not prove, the liquid–liquid critical point (LLCP) hypothesis of water.<sup>3</sup>

If the hypothesis is correct, it would affect strongly the studies of aqueous solutions. There have been the studies of water polyamorphism in solutions with molecular dynamics simulations or theoretical models discussing how the LLCP and, consequently, LDL and HDL regions can be shifted both in hydrophobic solutions<sup>4,5</sup> and in solutions of electrolytes.<sup>6</sup> Experimentally, water anomalies are present in liquid solutions of electrolytes, as well as in their glassy states, and this is possibly related to the existence of water polyamorphism in the solutions.<sup>7,8</sup>

In the present study, the melting curve of the precipitated ice IV in dilute LiCl–H<sub>2</sub>O solution was measured, and the consistency of the results with the polyamorphic viewpoint was examined.

## 2. EXPERIMENT AND RESULTS

The experimental method was the same as that of the pure water.<sup>1,2</sup> About 1.1 cm<sup>3</sup> of emulsion of LiCl–H<sub>2</sub>O solution, made by stirring the 2 cm<sup>3</sup> of aqueous solution of 2.0 mol % LiCl (or 4.8 mol % LiCl) and a matrix (1 cm<sup>3</sup> of methylcyclohexane, 1 cm<sup>3</sup> of methylcyclopentane, and 100 mg of sorbitan triesterate), was placed in an indium container and compressed to 0.8 GPa at



**Figure 1.** The experimental setup. The temperature of the emulsified sample (small LiCl–H<sub>2</sub>O droplets in an oil matrix) is measured while the pressure is changed. Ice IV was precipitated from the LiCl aqueous solution in each droplet, and the pressure-induced melting of the ice was studied.

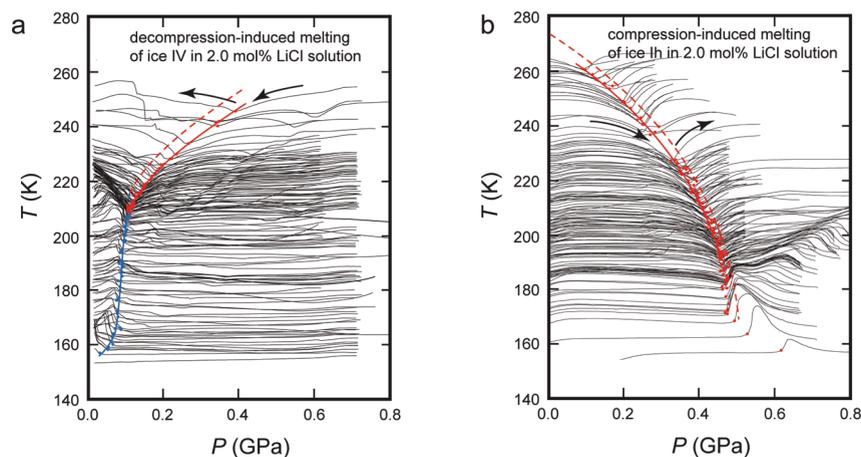
180 K by using a piston-cylinder apparatus (the piston diameter, 15 mm). (Figure 1) The sample was then decompressed to 0.6 GPa and heated to 200 K. In these procedures, ice IV precipitated from the solution in each droplet of 1–10 μm in size; accordingly, the concentration of LiCl in the liquid solution should be changed along the liquidus surface of ice IV in the pressure–temperature–concentration phase diagram. This emulsified sample

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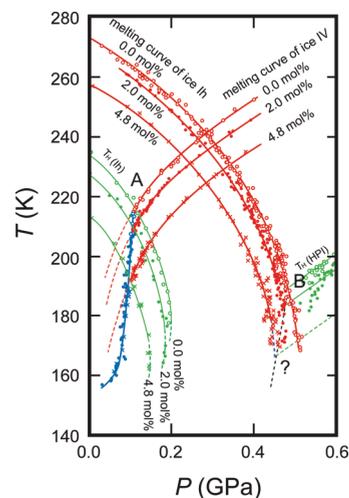


**Figure 2.** Melting (liquidus) curves of ice IV and ice Ih in the emulsified 2.0 mol % LiCl–H<sub>2</sub>O solution. (a) The decompression-induced melting of ice IV; (red solid line) the locus of the melting points, (red broken line) the melting curve of ice IV in pure water, and (blue line) the ice IV-to-ice Ih transition. Some other phase transitions, as recognized by the temperature changes at around 0.4 GPa and 220 K were also observed; they were not identified in this work. (b) The compression-induced melting of ice Ih; (red solid line) the locus of the melting points and (red broken line) the melting curve of ice Ih in pure water. The homogeneous nucleation to the high-pressure ices is observed at  $>\sim 0.5$  GPa and  $>\sim 185$  K, and the melting is thought to become the amorphization gradually at  $>\sim 0.5$  GPa and  $<\sim 165$  K.<sup>12</sup>

was decompressed at a rate of  $\sim 0.2$  GPa/min at different cylinder temperatures. During decompression, the temperature of the sample was measured with the thermocouple, which was brought into the sample through a small hole in the piston.

Melting of ice IV was detected by the change in the temperature of the emulsified LiCl–H<sub>2</sub>O sample, as shown in Figure 2a. Regarding the experiment of this figure, the initial emulsified sample was made by using the 2.0 mol % LiCl aqueous solution. At high temperatures, the sample temperature decreased during decompression and then increased (the arrows in Figure 2a). The locus of the turning points (the red solid line) parallels the known melting curve of ice IV in the emulsified pure liquid water (the red dashed lines).<sup>1</sup> From this resemblance, the red solid line was identified as the melting curve (liquidus) of ice IV in the solution. As a reference, melting of ice Ih in the solution is shown in Figure 2b. In this case, the emulsified sample of the initial concentration of 2.0 mol % LiCl was set at  $\sim 220$  K and atmospheric pressure, and ice Ih precipitated from the solution. When this sample was compressed at different cylinder temperatures, the sample temperature decreased and then increased (the arrows in Figure 2b); the similar melting behavior was observed. It is considered that as the pressure approached the melting curve (liquidus), the sample temperature decreased gradually due to the latent heat of the gradual melting of the ice. The melting occurred gradually because the concentration of LiCl in the liquid solution changed as the ice melted. After the ice (ice IV or ice Ih) melted completely, the concentration of the LiCl in the liquid became the initial 2.0 mol %, and the sample temperature increased toward the temperature of the cylinder.

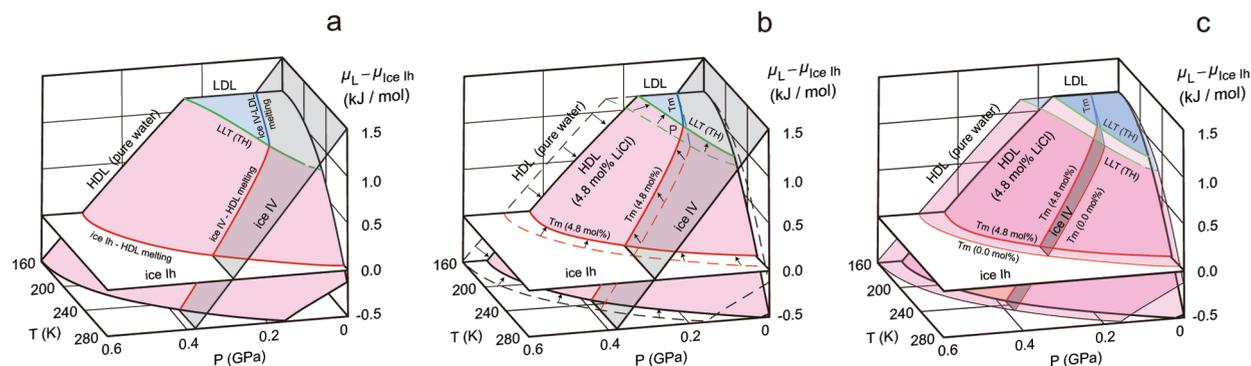
As shown in Figure 2a, the slope of the melting curve (liquidus) of ice IV in the LiCl solution seemed to change suddenly at  $\sim 0.1$  GPa and  $\sim 210$  K like that of ice IV in the pure liquid water at  $\sim 0.1$  GPa and  $\sim 215$  K.<sup>1</sup> On the low-temperature and low-pressure side of the change, ice IV transformed into another phase on the blue line of the figure. This accompanied the heat evolution as recognized by the increase in the sample temperature during the decompression. The phase after the transition



**Figure 3.** The dependence of the initial concentration of LiCl on the melting curves of ice IV and ice Ih. The ice IV-to-ice Ih transition line and the homogeneous nucleation lines are also shown by the blue and green lines, respectively. The  $T_H$ (Ih) data were taken from ref 6;  $\circ$ : 0.0 mol % LiCl,  $\bullet$ : 2.0 mol % LiCl, and  $\times$ : 4.8 mol % LiCl; (red dotted lines) the melting curves of ice IV extrapolated to low pressures.

was identified as ice Ih because, when compressed, it melted on the melting curve of ice Ih in the solution.

The dependence of the initial concentration of LiCl on the melting curve of ice IV and that of ice Ih are shown by the red lines of Figure 3. The freezing point depression was observed; the melting temperature decreased as the concentration of LiCl increased. This suggested that LiCl dissolved in liquid water than ice IV and ice Ih and that the molar fraction of water in the liquid solution decreased. That is, as the ice precipitates from the liquid solution, the concentration of LiCl in the liquid becomes higher than the initial concentration, and the concentration decreases as the ice melts gradually. On the other hand, the initial concentration of LiCl hardly affected the decompression-induced



**Figure 4.** The supposed difference between the chemical potential of liquid water  $\mu_L$  and that of ice Ih  $\mu_{\text{ice Ih}}$ . The hypothetical LDL surface and the LLT line are drawn by assuming that the LLT line locates near the  $T_{\text{H}}(\text{Ih})$  line; (blue) the LDL potential surface, (pink) the HDL potential surface, (white) the basic ice Ih potential surface, and (gray) the ice IV potential surface drawn by assuming the entropy of ice IV is the same with that of ice Ih. The slope of the ice IV surface along the pressure axis corresponds to the difference in volume between ice IV and ice Ih (see ref 1); (a) the chemical potential surface of pure water, (b) the chemical potential surface of water in the 4.8 mol % LiCl aqueous solution, and (c) comparison of the chemical potential of water between the 0.0 and 4.8 mol % solutions.

transition of ice IV to ice Ih (the blue  $\circ$  (0.0 mol %),  $\bullet$  (2.0 mol %), and  $\times$  (4.8 mol %) points near the blue line).

In Figure 3, it is difficult to affirm the discontinuity of the slope between any red melting curve of ice IV and the blue line at the intersection of these lines. However, the crossing of the blue line between the nearly parallel red lines hints that the slope changes discontinuously.

In Figure 3 are also shown the homogeneous nucleation lines (the green  $T_{\text{H}}(\text{Ih})$  and  $T_{\text{H}}(\text{HPI})$  lines), which are the locus of the pressure and temperature where ice crystals start to nucleate spontaneously in the liquid solution.<sup>1,9–11</sup> Ice Ih and another high-pressure ice appear on the  $T_{\text{H}}(\text{Ih})$  line and the  $T_{\text{H}}(\text{HPI})$  line, respectively.

It is known that as the concentration of LiCl in the solution increases, the  $T_{\text{H}}(\text{Ih})$  line shifts toward the low-pressure and low-temperature side, as shown by the green  $T_{\text{H}}(\text{Ih})$  curves in Figure 3.<sup>10,11</sup> It is also known that the slope of the melting curve of ice IV in pure liquid water changes sharply around the intersection with the  $T_{\text{H}}(\text{Ih})$  line of the pure water at  $\sim 0.1$  GPa and  $\sim 215$  K (A in Figure 3).<sup>1</sup> On the other hand, the compression-induced melting curve of ice Ih in pure liquid water is known to continue smoothly over the  $T_{\text{H}}(\text{HPI})$  line, showing no sign of the change in the slope (B in Figure 3).<sup>1,12</sup>

In the present study, it was found that when the initial LiCl concentration of the starting sample was 2.0 mol %, the melting curve of ice IV in the solution did bend sharply around the intersection with the  $T_{\text{H}}(\text{Ih})$  line of the 2.0 mol % solution at  $\sim 0.1$  GPa and  $\sim 210$  K. When the concentration was 4.8 mol %, the intersection was found to be at  $\sim 0.1$  GPa and  $\sim 190$  K. As to the melting curve of ice Ih in the solution, it was difficult to judge whether the slope of the melting curve changed at the intersection with the  $T_{\text{H}}(\text{HPI})$  line or not (the black dotted line in Figure 3). This is because of the experimental uncertainty of the present study.

### 3. DISCUSSION

We suppose the existence of LDL and HDL and discuss a possible reason why the decompression-induced transition of ice IV into ice Ih in the solution (the blue  $\circ$ ,  $\bullet$ , and  $\times$  points in Figure 3) occurred near the seemingly LiCl-unrelated fixed line (the blue line in Figure 3).

LiCl is thought to dissolve better in HDL than in LDL.<sup>8,11,13,14</sup> It is also considered from the observed freezing point depression that LiCl dissolves better in liquid water (HDL) than in ice IV and ice Ih. Therefore, in the following rough and qualitative argument, LiCl is simply assumed to dissolve easily in HDL and to be hardly soluble in ice IV, ice Ih, and the low-temperature LDL; it is supposed that only the chemical potential of HDL lowers significantly by the addition of LiCl.

The chemical potential of pure water in the pressure–temperature diagram has already been estimated, as shown in Figure 4a, and it was consistent with the existence of LDL and HDL.<sup>1</sup> As to the chemical potential of  $\text{H}_2\text{O}$  in the LiCl solution, the potential surface of HDL is lowered; in other words, the HDL potential surface is shifted toward the low-temperature and low-pressure side (Figure 4b). Then, the line of intersection between the HDL surface and the ice Ih surface (melting curve of ice Ih) shifts toward the low-pressure and low-temperature side, and the line of intersection between the HDL surface and the ice IV surface (melting curve of ice IV) shifts toward the low-temperature side. The shifts of these melting lines correspond to the observed freezing point depression.

The line of the intersection between the HDL surface and the LDL surface shifts toward the low-pressure and low-temperature side (the green LLT line of Figure 4b). This shift may correspond to the above-mentioned shift of the  $T_{\text{H}}(\text{Ih})$  line where ice Ih appears (the green  $T_{\text{H}}(\text{Ih})$  lines of Figure 3). This is because LDL probably crystallizes into ice Ih readily due to the structural resemblance, and the HDL  $\rightarrow$  LDL  $\rightarrow$  ice Ih transition (LLT) is thought to become the simultaneous HDL  $\rightarrow$  LDL  $\rightarrow$  ice Ih transition or the appearance of ice Ih in HDL.<sup>11</sup>

Three phases, ice IV, LDL, and HDL, coexist at the point P in Figure 4b, where the potential surfaces of these phases intersect. Three phenomena occur at this point simultaneously, namely, the HDL  $\rightarrow$  LDL transition (the green LLT line), the melting of ice IV into LDL (the blue line), and the melting of ice IV into HDL (the red line). In the present experiment of the decompression of ice IV in the solution of some LiCl concentration, LDL appears at the point like P both from ice IV on the blue melting line and from HDL of some LiCl concentration on the green LLT line. Then, the produced LDL is thought to crystallize into ice Ih easily.

The observed exothermic ice IV  $\rightarrow$  ice Ih transition (the blue line in Figures 2a and 3) may be triggered by the endothermic melting of ice IV into LDL (the blue line in Figure 4a–c) followed by the exothermic LDL  $\rightarrow$  ice Ih crystallization. Because LiCl is regarded as hardly soluble in both ice IV and the low-temperature LDL, the chemical potential surfaces of these ice IV and LDL phases are almost unrelated to the concentration of LiCl. Then, the transition between ice IV and LDL (the blue melting line in Figure 4) is unrelated to the concentration. Accordingly, the ice IV  $\rightarrow$  LDL  $\rightarrow$  ice Ih transition is considered to be unrelated to the concentration of LiCl.

On the other hand, the HDL  $\rightarrow$  LDL transition in the solution (the green LLT line in Figure 4), or the HDL  $\rightarrow$  (LDL)  $\rightarrow$  Ih crystallization line, may be less important for the observed ice IV  $\rightarrow$  ice Ih transition (the blue line in Figures 2a and 3). The reason is the following. In the case of 0.0 mol % LiCl, or pure water, if the HDL  $\rightarrow$  LDL transition triggers the ice IV  $\rightarrow$  ice Ih transition during decompression, this ice IV  $\rightarrow$  ice Ih transition must occur after HDL is produced by the melting of ice IV into HDL on the red line. However, ice Ih actually produced on the blue line (the blue  $\circ$  points in Figure 3) before ice IV melted into HDL on the extrapolated red dotted line of 0.0 mol % LiCl in Figure 3 (ref 1); there is inconsistency in the case of the 0.0 mol % LiCl. Therefore, the appearance of LDL (or ice Ih) is likely related to the melting of ice IV into LDL (the blue line).

Although the sharp change in the slope of the ice IV melting curve suggests the location of LLT, it does not give much information about the location of LLCP by itself; it gives only a rough estimation of the LLCP location. The line of the ice IV  $\rightarrow$  (LDL)  $\rightarrow$  ice Ih transition (the blue line in Figure 3) continued smoothly down to  $\sim 160$  K, showing a slightly positive slope in the pressure–temperature diagram. This implies that the LDL state continues smoothly along the supposed ice IV  $\rightarrow$  LDL melting curve. Below  $\sim 160$  K, the line started to turn to the low-pressure side. From the analogy of the change of the slope of the melting curve of ice Ih in HDL (ref 12), it is implied that LDL becomes noticeably viscous below  $\sim 160$  K.

#### 4. CONCLUSION

The effect of LiCl on the melting curves of ice IV and ice Ih was roughly explained by the change in the chemical potential surface of H<sub>2</sub>O and by the polyamorphic viewpoint.

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