

**STUDY ON LATENT HEAT OF FUSION OF ICE IN AQUEOUS SOLUTIONS
– EFFECTS OF CONCENTRATION AND TEMPERATURE OF AQUEOUS SOLUTION –**

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ABSTRACT

In dynamic type of ice thermal energy storage system, fluid ice slurry, which has high ability of cold energy transportation, is used as a phase change material. Many types of ice slurries formed from various aqueous solutions are used in practical applications, since each one has its own advantages. The characteristics of ice slurries, such as formation, transportation, melting, and storage, have been investigated by many researchers. Moreover, the thermophysical properties of ice slurries such as latent heat are needed. In this study, the variation of enthalpy per unit mass of ice, generated by melting of ice in aqueous solution, was defined as “effective latent heat” of fusion of ice in aqueous solution. The formulation for calculating the effective latent heat by using thermophysical properties of the aqueous solutions was proposed, considering the effects of freezing-point depression and dilution heat. In the experiment, pure ice was put into ethanol solution, and temperature variations of the solution due to melting of ice were measured. The effective latent heat of fusion was calculated using an energy balance equation. It was confirmed that the

effective latent heat of fusion obtained by the measurements agreed well with that by the calculation. Additionally, the effects of the concentration and the temperature of the aqueous solution on the effective latent heat of ice in aqueous solutions were investigated. As a result, it was clarified that the effective latent heat of ice in aqueous solution is affected by both concentration and temperature of the solution.

NOMENCLATURE

C : heat capacity of experimental apparatus, kJ K^{-1}
 c : specific heat, $\text{kJ kg}^{-1} \text{K}^{-1}$
 L_e : effective latent heat of fusion of ice for a concentration of aqueous solution after ice charging, kJ kg^{-1}
 L_{ice} : latent heat of fusion of ice in pure water, kJ kg^{-1}
 m : mass, kg
 P_{ini} : initial ice packing factor, wt%
 Q_{dil} : heat generated by dilution of solution due to melting of ice per unit mass of the ice, kJ kg^{-1}
 T : temperature of aqueous solution, $^{\circ}\text{C}$

- T_e : freezing temperature of aqueous solution, °C
- x : concentration of aqueous solution, wt%
- x_{ini} : initial concentration of aqueous solution, wt%
- x_{fin} : concentration of aqueous solution after ice melting, wt%
- ΔH : decrement of the enthalpy difference between water and ice caused by the effects of freezing-point depression, kJ kg⁻¹
- ΔP : variation in ice packing factor, wt%
- ΔQ : difference of heat of mixing of aqueous solution between two concentrations per unit mass of solute, kJ kg⁻¹

subscripts

- 1 : before charging ice
- 2 : after charging ice
- i : ice
- sol : aqueous solution
- w : water

INTRODUCTION

In dynamic type of ice thermal energy storage system, fluid ice slurry, which has high ability of cold energy transportation, is used as a phase change material ^[1]. Many types of ice slurries formed from various aqueous solutions are used in practical applications, since each one has its own advantages. The characteristics of ice slurries, such as formation, transportation, melting, and storage, have been investigated by many researchers. Moreover, it is very important to know the latent heat of fusion of ice particles in aqueous solution in designing an ice thermal energy storage system. Teraoka et al. ^[2] attempted to measure the latent heat of fusion of ice slurry, but their study did not account for the dilution heat due to variations in the concentrations of solutions. Using differential scanning calorimetry (DSC), calorimetric analysis has also been carried out ^[3, 4]. However, in the DSC measurement, since the heat of phase change of all aqueous solutions from solid to liquid is measured, the concentration of the solution varies with temperature. Therefore, the latent heat of melting of a solid in aqueous solution at a particular

concentration cannot be measured.

In this study, the variation of enthalpy per unit mass of ice, generated by melting of ice in aqueous solution, was defined as “effective latent heat” of fusion of ice. In our previous study ^[5], it was found the effective latent heat could be calculated by considering the effects of the freezing-point depression and dilution heat in each aqueous solution. Moreover, a calculation method for the latent heat of fusion of ice in aqueous solution with the variation in the IPF (Ice Packing Factor) being infinitesimal was proposed ^[6]. However, the effect of the temperature of the solution has not been investigated.

In this study, the effects of concentration and temperature of solution is investigated by experiment and calculation.

CALCULATION METHOD

Considering the effects of freezing-point depression, and the dilution in the solution, the effective latent heat of fusion of ice can be calculated as follows.

$$L_e = L_{ice} - \Delta H - Q_{dil} \quad (1)$$

The first term on the right side of the equation, L_{ice} , expresses the latent heat of ice in water (333.5 kJ/kg), the second term, ΔH , expresses the decrement of the enthalpy difference between water and ice caused by the effects of freezing-point depression, and the third term, Q_{dil} , expresses heat generated by dilution of the solution due to the melting of ice.

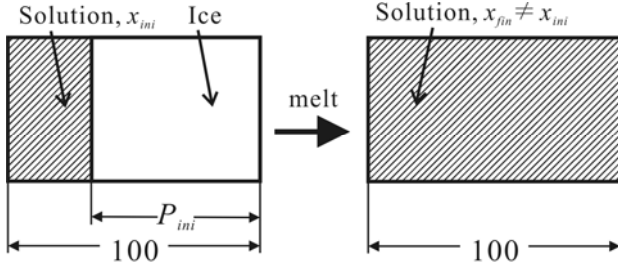
ΔH can be calculated from the specific heats of water and ice, as follows.

$$\Delta H = \int_{T_e}^0 (c_w - c_i) dT \quad (2)$$

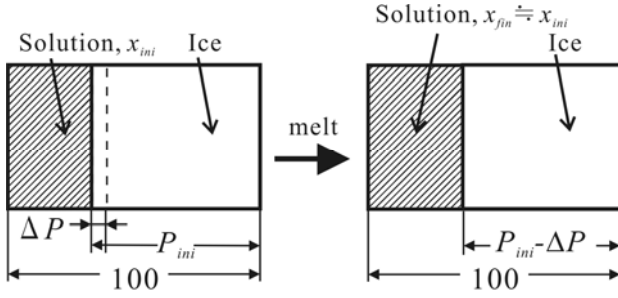
The specific heats of water and ice were given by Angell et al. ^[7] and Dorsey ^[8], as follows.

$$c_i = 2.12 + 7.8 \times 10^{-3} T \quad (3)$$

$$c_w = 4.22 + 5.43 \times 10^{-3} T + 1.48 \times 10^{-3} T^2 + 6.49 \times 10^{-5} T^3 + 1.54 \times 10^{-6} T^4 \quad (4)$$



(a) all ice is melt



(b) infinitesimal mass of ice is melt

Figure 1

Physical Model of the Ice Melting Process

The relationship between the phase equilibrium temperature and concentration for ethanol solution obtained from the literature ^[9] was approximated using a least squares method as follows.

$$T_e = -0.358x - 0.00814x^2 - 0.0000788x^3 \quad (5)$$

From these equations, it was shown that the decrease in enthalpy, ΔH , can be calculated as a function of the concentration of the aqueous solution, x .

When all ice melts in an ice / solution mixture, as shown in Fig. 1 (a), Q_{dil} can be expressed using P_{ini} and x_{ini} as follows.

$$Q_{dil} = \frac{\Delta Q x_{fin}}{P_{ini}} = \frac{\Delta Q x_{ini} \left(1 - \frac{P_{ini}}{100}\right)}{P_{ini}} \quad (6)$$

where, ΔQ is difference of heat of mixing of aqueous solution between two concentrations per unit mass of solute, x_{ini} is the initial concentration of aqueous solution and P_{ini} is the initial IPF, which

is the mass fraction of ice in the ice / solution mixture. When the heat generated from the mixing of solute and water is expressed as a function of concentration after mixing and temperature, $f(x, T)$, Eq. (6) can be expressed as follows.

$$Q_{dil} = \frac{x_{ini} \left(1 - \frac{P_{ini}}{100}\right)}{P_{ini}} \left[f\left(\frac{100 - P_{ini}}{100} x_{ini}, T\right) - f(x_{ini}, T) \right] \quad (6)$$

When the variation of IPF, ΔP , is infinitesimal and much smaller than P_{ini} , as shown in Fig. 1 (b), Q_{dil} can be expressed as follows.

$$\begin{aligned} Q_{dil} &= \lim_{\Delta P \rightarrow 0} \frac{x \left(1 - \frac{P_{ini}}{100}\right)}{\Delta P} \\ &\times \left[f\left(\frac{100 - P_{ini}}{100 - P_{ini} + \Delta P} x, T\right) - f(x, T) \right] \quad (7) \\ &= -\frac{x^2}{100} \frac{\partial f(x, T)}{\partial x} \end{aligned}$$

Here, it is considered the concentration and temperature of the aqueous solution does not vary before and after the melting of ice, because the variation in IPF is infinitesimal.

$f(x, T)$ for ethanol solution at 12.5, 25, 35, 50 and 65 °C were given by Friese ^[10, 11], and approximated as follows.

$$f(x, 12.5) = 2.70 \times 10^2 - 2.11x - 1.28 \times 10^{-1}x^2 + 2.29 \times 10^{-3}x^3 - 1.07 \times 10^{-5}x^4 \quad (8)$$

$$f(x, 25) = 2.35 \times 10^2 - 3.00x - 6.41 \times 10^{-2}x^2 + 1.35 \times 10^{-3}x^3 - 6.44 \times 10^{-6}x^4 \quad (9)$$

$$f(x, 35) = 2.12 \times 10^2 - 3.75x - 2.41 \times 10^{-2}x^2 + 8.37x^{-4} - 4.33 \times 10^{-6}x^4 \quad (10)$$

$$f(x, 50) = 1.74 \times 10^2 - 4.83x + 4.31 \times 10^{-2}x^2 - 1.20 \times 10^{-4}x^3 \quad (11)$$

$$f(x, 65) = 1.17 \times 10^2 - 3.39x + 2.78 \times 10^{-2}x^2 - 5.34 \times 10^{-5}x^3 \quad (12)$$

Therefore, the heat generated by dilution due to the

melting of ice can be calculated from the concentration and the differential coefficient of the function of the heat generated by mixing, which is depends on the temperature of the aqueous solution.

As a result, the effective latent heat of fusion of ice in an aqueous solution can be expressed as a function of the concentration and temperature of the aqueous solution.

$$L_e = L_{ice} - \Delta H(x) - \frac{x^2}{100} \frac{\partial f(x, T)}{\partial x} \quad (13)$$

EXPERIMENT

Measurement of the effective latent heat of fusion of ice in ethanol solution was carried out, in order to compare with that obtained by the formulation.

Figure 2 shows the experimental apparatus. An ethanol solution (600-900 g) was placed into a Dewar vessel, and the solution was stirred to maintain a uniform temperature. Then, ice particles (30-100 g) maintained at a uniform temperature of -5°C were put into the solution. The ice particles were made from distilled water. The temperature of the solution was measured before and after ice melting, using T-type thermocouples.

Using the following energy balance equation, the effective latent heat of fusion of ice in the solution could be calculated.

$$m_i L_e + m_i c_i (T_e - T_i) + m_w c_w (T_2 - T_e) = m_{sol} c_{sol} (T_1 - T_2) + C (T_1 - T_2) \quad (14)$$

In this equation, C is the heat capacity of the experimental apparatus. In preliminary experiments, the temperature variation due to the melting of ice in pure water was measured, and C was calculated from the latent heat of pure ice. We confirmed the accuracy of C did not influence measurements of latent heat, since heat capacity of the experimental apparatus was about 3% of that of the aqueous solution.

Effect of concentration of solution: The measurements were carried out on the condition of various initial concentrations of the solution, in order to investigate the effect of the concentration

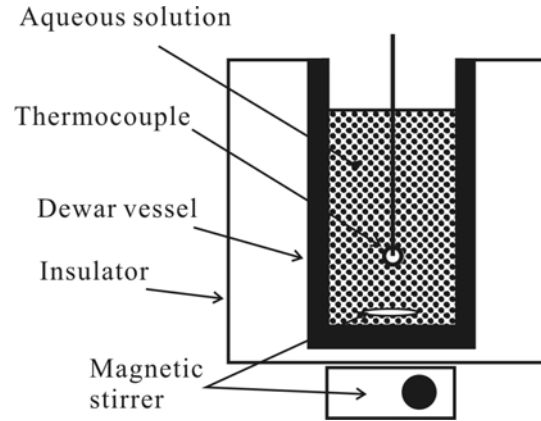


Figure 2
Experimental Apparatus

on the effective latent heat. The initial concentrations of the solution were varied from 5 to 30 wt%. The initial temperature of the solution was kept between 20 and 25°C , which is ambient temperature.

Effect of temperature of solution: The measurements on the condition of various initial temperatures of the solution were also carried out, in order to investigate the effect of the temperature. The initial temperatures of the solution were varied from 2 to 65°C . In this case, 30wt% ethanol solution was used, because the effect of the temperature appears more significant as the concentration of the solution increases.

RESULTS AND DISCUSSION

Effect of concentration of solution: The results of the experiment and the calculation are shown in Fig. 3. The abscissa is the initial concentration of the solution, and the ordinate is the effective latent heat. The black dots represent experimental results and the solid line represents the result of the calculations. The initial temperatures of the solution were between 20 and 25°C in the experiment, and 25°C in the calculation. Measurements were carried out several times under the same conditions.

The results of the measurement and the calculation agreed well with each other. It can be

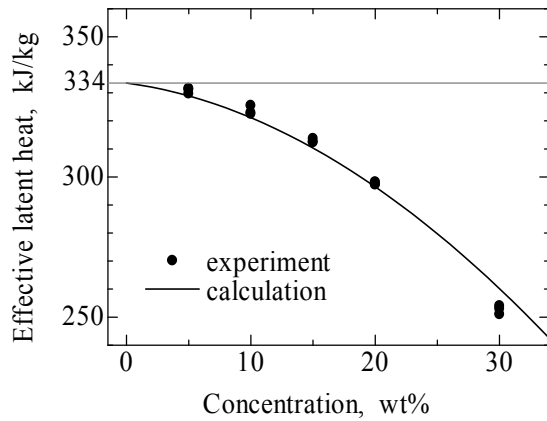


Figure 3

Effect of Concentration of the Ethanol Solution on the Effective Latent Heat of Ice in the Solution (Initial temperature of the solution is about 25 °C.)

said that the latent heat of fusion calculated in this study is appropriate.

It was found that the effective latent heat decreases with an increase in the concentration of the solution. The reason of this can be explained using Eq.(1). The decrement of the enthalpy difference between water and ice, ΔH , increases with an increase in the concentration of the solution, because the melting point decreases. The heat generated by dilution due to the melting of ice, Q_{dil} , increases with an increase in the concentration of the solution, because the generated heat increases with an increase in the variation of concentration due to the melting of ice.

Effect of temperature of solution: The results of the experiment and the calculation are shown in Fig. 4. The abscissa is the temperature of solution, which is defined as the average temperature of the solution before and after ice melting in the experiment. The ordinate is the effective latent heat. The black dots represent experimental results and the white circles represent the result of the calculations. The approximation of the value of the calculation is shown as broken line in the figure. The initial concentration of the solution was 30 wt% in all of the results.

The results of the measurement and the

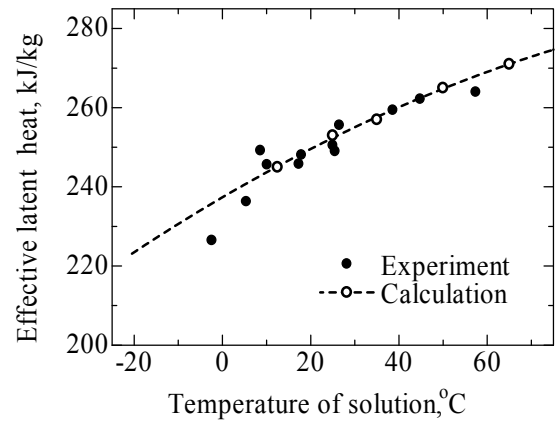


Figure 4

Effect of Temperature of the Ethanol Solution on the Effective Latent Heat of Ice in the Solution (Initial concentration of the solution is 30 wt%.)

calculation agreed well with each other. It can be said that the latent heat of fusion calculated in this study is appropriate.

It was found that the effective latent heat increases with an increase in the concentration of the solution. Differentiating $f(x, T)$ in Eqs. (8)-(12), it was found that the deferential coefficient of heat of mixing, $\partial f / \partial x$, decreases with an increase of temperature, in the case of ethanol solution. The effective latent heat was increased due to the effect of the decrease in $\partial f / \partial x$, as shown in Eq. (7).

Additionally, it was found that the variation of the effective latent heat due to the temperature of the solution was significant.

CONCLUSION

In this study, a calculation method of effective latent heat of fusion in aqueous solution was proposed. In the calculation, the effects of the freezing-point depression and dilution of solution was considered. Moreover, the effective latent heat was measured in the experiments of adding ice to ethanol solution. As a result, the values of effective latent heat in ethanol solution obtained from the calculation and the experiment agreed well with each other, and it was found that the calculation method of the latent heat of fusion in aqueous solutions was valid. It was clarified that the

effective latent heat of ice in aqueous solution is significantly affected by both concentration and temperature of the solution.

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