

## Measurement of Latent Heat of Melting of Thermal Storage Materials for Dynamic Ice Thermal Storage

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The latent heats of ice slurries with various aqueous solutions were measured by using an adiabatic calorimeter. Ice slurries were made from each aqueous solution of ethanol, ethylene glycol and silane coupling agent. Samples of ice slurries were made by two methods, one was by mixing ice particles made from tap water with each aqueous solution, and the other was by freezing each aqueous solution with stirring in a vessel. We confirmed that the freezing point depression reduces the latent heat. In case of using ethanol and ethylene glycol as the solute, the latent heats at the same freezing point depression are nearly equal to each other. And the measured values are nearly equal to the estimated values derived from the enthalpy difference between ice and water. In case of using silane coupling agent as the solute, however, the latent heat is smaller than the reference values measured by DSC or those for ethanol and ethylene glycol aqueous solutions. There is no difference between the latent heats of slurries made by each method.

### 1. Introduction

Ice slurry is available as secondary refrigerant of thermal storage system. Aqueous solution is often substituted for water with the aims to prevent pipe blockage during ice formation and impede binding of ice particles in a storage tank. Ethanol and ethylene glycol are mostly used as the solute because of economic and environmental considerations. Moreover, silane coupling agent is expected to be more effective than the above materials. Addition of solute to water, however, depresses latent heat of the slurry, and thereby reduces the efficiency of the system. For design and performance evaluation of a thermal storage system, it is necessary to measure latent heat of melting of ice slurry produced from aqueous solution.

So far, some studies have measured latent heat of melting of those aqueous solutions by Differential Scanning Calorimetry (DSC) [1]. Samples for DSC measurements have to be frozen completely. In this procedure, eutectic phase must be produced, and as consequence, latent heat measured by DSC tends to be undervalued. Furthermore, smallness (about 10 mg) and nonuniformity of the samples reduce the accuracy of the measurement value.

An adiabatic calorimeter was designed and manufactured for measurement of latent heat of

melting of ice slurry under practical condition of thermal storage systems. We investigate aqueous solutions of ethanol, ethylene glycol and silane coupling agent (abbreviated as ET, EG and SCA respectively) with concentration from 3 to 20 wt%. We used gamma-Aminopropyltriethoxysilane as SCA. Additionally, ice slurries were made by two methods. In one method, ice particles made from water were mixed with each aqueous solution. In the other method, ice slurry was made by freezing aqueous solutions with stirring in a vessel. By comparison between the results of each method, we discuss effects of ice formation methods on latent heat.

### 2. Experimental Methods

#### 2.1. Experimental Apparatus

Figure 1 shows schematic of the adiabatic calorimetry. The system comprises of essentially five components; dewar vessel, adiabatic enclosure, thermometer unit, heater unit and magnetic stirrer. The dewar vessel made of glass is 115 mm in internal diameter and 240 mm in height. Output power of the heater (about 100 W) was measured by ammeter and voltmeter with an accuracy of 0.1 %. Temperature of slurry is measured at 20, 50 and 90 mm from the top of the vessel by platinum resistance thermometers (Pt-100).

**2.2. Making Ice Slurry for sample**

We make ice slurry by two methods as follows.

**2.2.1. Mixture sample of ice particles and aqueous solution** First, shaved ice, which was 0.5 or 5 mm in average diameter, was made from tap water. We froze the ice (its total mass is  $m_{ice}^{before} = 200$  g) completely at temperature,  $T_{ice} = -20.0$  °C.

Then, aqueous solution was a mixture of tap water and each solute, masses of which were  $m_w^{before}$  and  $m_s^{before}$ , respectively ( $m_w^{before} + m_s^{before} = 500$  g). The solution with the stirrer bar was pored into the dewar vessel and remained at temperature,  $T_{sl}$  (slightly above the freezing point of the solution).

The ice particles and the solution in the dewar vessel were mixed. Equilibrium temperature of the ice slurry,  $T_0$  became uniform by the magnetic stirrer. Because  $T_{ice}$  and  $T_{sl}$  were not equal to the freezing point of the solution, we need to understand final mass of the ice particles,  $m_{ice}$ . Ignoring heat of mixing and change of latent heat, we can use equations of the energy for  $m_{ice}$  as follows,

$$Q_1 + Q_2 + Q_3 + Q_4 + Q_5 = 0, \quad (1)$$

$$Q_1 = (m_{ice}^{before} - m_{ice})L_{pi}, \quad (2)$$

$$Q_2 = \frac{1}{2}(m_{ice}^{before} + m_{ice})c_{ice}(T_0 - T_{ice}), \quad (3)$$

$$Q_3 = \frac{1}{2}(m_{ice}^{before} - m_{ice})c_w(T_0 - T_{ice}), \quad (4)$$

$$Q_4 = (m_w^{before}c_w + m_s^{before}c_s)(T_0 - T_{sl}), \quad (5)$$

$$Q_5 = c_{others}(T_0 - T_{sl}), \quad (6)$$

where  $L_{pi}$  is latent heat of the pure ice,  $c_{ice}$ ,  $c_w$  and  $c_s$  are specific heats of ice, water and solute respectively. The specific heat of SCA solution was measured by the adiabatic calorimeter (4.09 kJ/kgv K), at 0°C for SCA 20wt %). The sources of the other property values are from Ref. [2].  $c_{others}$ , which is specific heat of the heater, inner wall of the vessel and the others, is 0.231kJ/K obtained by a measurement of the well-known specific heat of water. Thus, mass composition of the sample after of the mixing are ice:  $m_{ice}$ , water:  $m_w = m_w^{before} + m_{ice}^{before} - m_{ice}$  and solute:  $m_s = m_s^{before}$ .

**2.2.2. Ice-formation sample from aqueous solution**

Figure 2 shows schematic of the apparatus for making ice-formation sample. Solution ( $m_w^i + m_s^i = 800$  g) was poured into the stainless-steel vessel, the inner wall of which was coated with Perfluoroalkoxy (PFA) in order to minimize

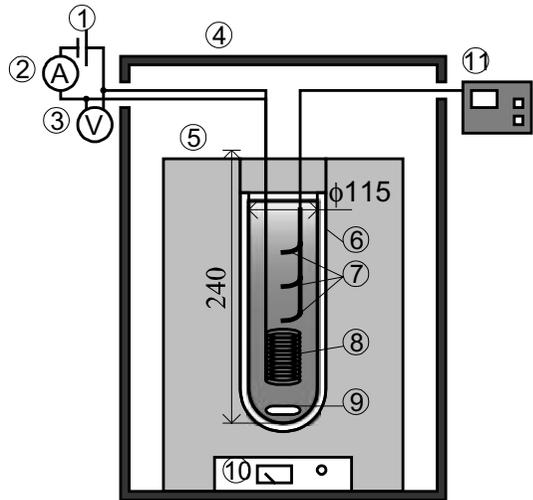


Fig. 1. Schematic of the adiabatic calorimeter.

DC Power Supply	Platinum Resistance
Ammeter	Thermometer
Voltmeter	Heater
Thermostatic box	Stirrer Bar
Insulating Foam	Magnetic Stirrer
Dewar vessel	Data logger

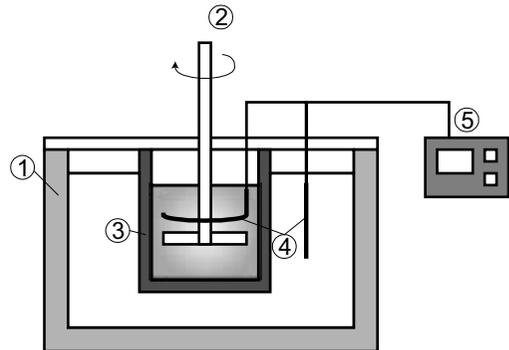


Fig. 2. Schematic of the apparatus for ice formation.

Thermostatic bath	Platinum
Stirrer (150 rpm)	Resistance
	Thermometer
SUS vessel (136	Data logger
mm diameter)	

adherence of ice. The concentration of the solution,  $C_s^i = m_s^i / (m_w^i + m_s^i)$  was varied from 3 to 15 wt%. The thermostatic bath cooled the solution through the vessel with stirring the solution. We controlled temperature of brine of the bath to keep it about 1K lower than that of sample,  $T_{sample}$ . Those temperatures were measured by the platinum resistance thermometers. When ice concentration reached about 30 wt%, the ice formation was stopped. The ice concentration was estimated by  $T_{sample}$ ,  $C_s^i$  and degree of freezing point depression (from Ref. [2]). The ice slurry by this method is shown in Fig. 3.

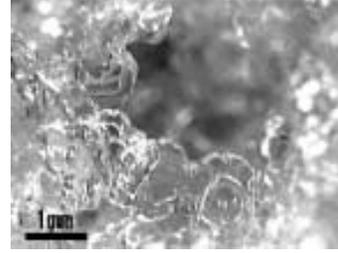


Fig. 3. Ice particles of ice-formation sample made from ET solution,  $C_i = 7.01$  wt%.

Then, by suction filtration, the slurry was divided into two portions; mostly-ice portion and solution portion, which were measured by weight to an accuracy of 0.1 g,  $M_{P1}$  and  $M_{P2}$  respectively. As well as those of Mixture sample, the mostly-ice portion was frozen at  $T_{ice}$  and the solution was at  $T_{sl}$  in the dewar vessel, then they were mixed together.

Masses of water and solute adhering to the ice interface cannot be negligible. Supposing that the ice contains no solute, the mostly-ice portion can be divided into ice, water and solute.

$$M_{P1} = m_{ice}^{before} + m_{wP1} + m_{sP1}, \quad (7)$$

where  $m_{wP1}$  and  $m_{sP1}$  are masses of water and solute of the mostly-ice portion, respectively. Relationships for each solute between  $m_{sP1}$  and  $C_s^i$  were obtained by other experiments, which melted mostly-ice portions and measured concentration of the solution.

$$m_{sP1} = \frac{f(C_s^i)}{100} M_{P1}, \quad (8)$$

$$f_{EA}(C_s^i) = 0.00777C_s^{i2} + 0.332C_s^i, \quad (9)$$

$$f_{EG}(C_s^i) = 0.0140C_s^{i2} + 0.249C_s^i, \quad (10)$$

$$f_{SCA}(C_s^i) = 0.0140C_s^{i2} + 0.338C_s^i. \quad (11)$$

Using the relationship between degree of freezing point depression and concentration,  $m_{w1}$  is determined by  $m_{s1}$ .

$$m_{wP1} = \left( \frac{100}{C_{T_{ice}}} \right) m_{sP1}, \quad (12)$$

where  $C_{T_{ice}}$  is concentration of solute, freezing point of which corresponds  $T_{ice}$ . In the solution portion, masses of water and solute are obtained as follows:

$$m_{sP2} = m_s^i - m_{sP1}, \quad (13)$$

$$m_{wP2} = m_w^i - m_{ice}^{before} - m_{wP1}. \quad (14)$$

In case of the ice-formation sample, equations of the energy are as follows:

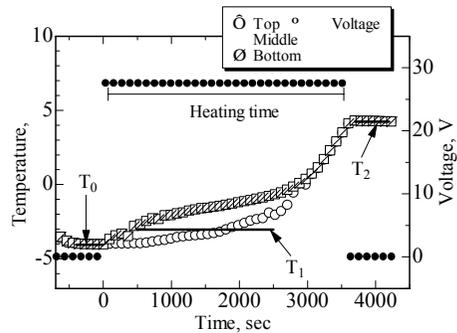


Fig. 4. Temperature and voltage with time during measuring latent heat of mixing sample for ethanol solution ( $C_{s0} = 9.41$  wt%,  $C_{s1} = 7.06$  wt %).

$$Q_1 + Q_2 + Q_3 + Q_4' + Q_5 + Q_6 = 0, \quad (15)$$

$$Q_4' = (m_{wP2}c_w + m_{sP2}c_s)(T_0 - T_{sl}), \quad (16)$$

$$Q_6 = (m_{wP1}c_w + m_{sP1}c_s)(T_0 - T_{ice}). \quad (17)$$

**2.3. Measurement of latent heat by heating** The sample in the dewar vessel was heated by the heater input at Voltage,  $V$  and current,  $I$  for heating time,  $\Delta t$ . Heat quantity,  $Q_{heater}$  is as follows,

$$Q_{heater} = VI\Delta t. \quad (18)$$

Assuming that latent heat,  $L$  is constant, we can obtain  $L$  by solving the following equations,

$$Q_{heater} = Q_{lat} + Q_{ice} + Q_{m-i} + Q_{liq} + Q_{others}, \quad (19)$$

$$Q_{lat} = m_{ice}L, \quad (20)$$

$$Q_{ice} = \frac{1}{2}m_{ice}c_{ice}(T_1 - T_0), \quad (21)$$

$$Q_{m-i} = \left[ \frac{1}{2}(T_1 - T_0) + (T_2 - T_1) \right] m_{ice} c_w, \quad (22)$$

$$Q_{liq} = (m_w c_w + m_s c_s)(T_2 - T_0), \quad (23)$$

$$Q_{others} = c_{others}(T_2 - T_0), \quad (24)$$

where  $T_1$  is freezing point at  $C_{s1} = m_s / (m_{ice} + m_w + m_s)$ ,  $T_2$  is temperature of sample after heating. Figure 4 shows temperature at each point of the mixing sample and voltage of the heater. Although the distribution of temperature in the sample was observed during melting of the ice, it was, however, uniform (within 0.01 K) after a few minutes of heating.

### 3. Results

Figure 5 (a - c) show a relation between latent heat and freezing-point depression,  $\Delta T = (T_0 + T_1)/2$  for each solution. Using method of least squares, we have fitted experimental equals for each solution as follows:

for ethanol

$$L_{M-EA} = -0.121\Delta T^2 - 3.29\Delta T + 334, \quad (25)$$

$$L_{I-EA} = -0.135\Delta T^2 - 3.43\Delta T + 334, \quad (26)$$

for ethylene glycol

$$L_{M-EG} = 0.0557\Delta T^2 - 5.11\Delta T + 334, \quad (27)$$

$$L_{I-EG} = -3.42\Delta T + 334, \quad (28)$$

for silane coupling agent

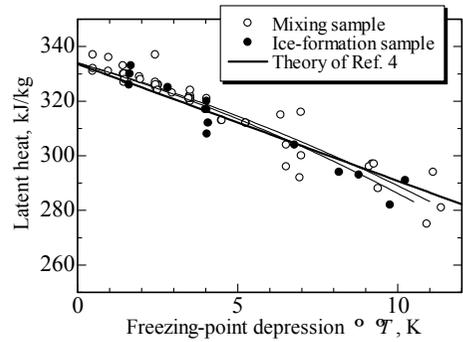
$$L_{M-SCA} = -0.270\Delta T^2 - 4.08\Delta T + 334, \quad (29)$$

$$L_{I-SCA} = -0.105\Delta T^2 - 2.45\Delta T + 334. \quad (30)$$

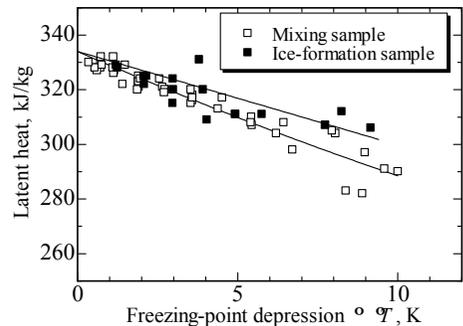
The latent heat for all solutions reduces as  $\Delta T$  increases and is not changed by the size of ice particles. The latent heat of ethanol and ethylene glycol solutions has nearly identical latent heat of melting at same freezing point. For the ice-formation of these solutions, there is a little difference of latent heat between the mixing sample and the ice-formation sample. Of SCA solution, latent heat is, however, smaller than those of the other solution. Moreover, the latent heat of the ice-formation sample for SCA reduces further than that of the mixing sample.

### 4. Discussion

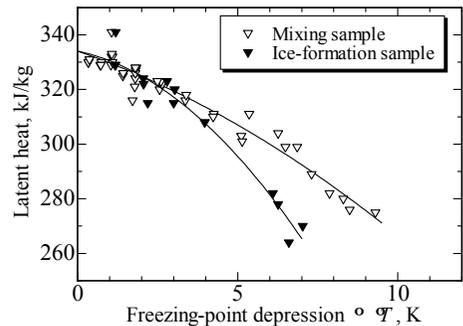
The dependence of latent heat of pure ice for temperature of freezing (or melting) was reported [3, 4]. The latent heat was estimated with difference of enthalpy between ice and liquid at freezing point. This theoretical result agrees with our experimental data of ethanol and ethylene glycol, shown in Fig.7.



(a) Ethanol



(b) Ethylene glycol



(c) Silane coupling agent

Fig. 5. Latent heat of ice particles in ice slurries made from each aqueous solution.

This fact provides evidence that surface energy and other have little effect on latent heat of ice slurry of those solutions. However, in case of SCA solution, latent heat cannot be expressed by the enthalpy

difference theory. We think that one of the reasons is adsorption of SCA to ice interface.

## 5. Conclusions

We carried out the measurement of latent heat of ice slurry for three solutions by the adiabatic calorimeter. The slurry was made by two different methods. The measurement leads us to conclude as follows:

- 1) Ice slurry of ethanol and ethylene glycol solutions have nearly identical latent heat of melting at same freezing point. There is a little difference of latent heat between the mixing sample and the ice-formation sample for both solutions.
- 2) These latent heat for ethanol solutions correspond to the estimation with difference enthalpy between ice and solution at freezing point, from Ref. [4].
- 3) In case of gamma-Aminopropyltriethoxysilane solution, the latent heat of the mixing sample is less

than those of both ethanol and ethylene glycol solution. Additionally, the ice-formation sample of the solution reduces further the latent heat.

## References and Notes

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- [3] C. S. Chen : Systematic calculation of thermodynamic properties of an ice-water system at subfreezing temperatures, *Transactions of the American Society of Agricultural Engineers*, **31**(5), 1602 (1988) <sup>3</sup>/<sub>4</sub>
- [4] Åke Melinder, *Proceedings of the Fourth Workshop on Ice Slurries of the I.I.F./I.I.R.*, 115 (2001) <sup>3</sup>/<sub>4</sub>