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# Measurements of Thermophysical Properties of Sodium Acetate Hydrate

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Methods to measure the thermal conductivity, the specific heat capacity, and the heat of fusion of sodium acetate hydrate have been developed and the measured results have been reported for various concentrations and especially for various supercooling temperatures. Thermal conductivity was measured by using a probe method with a thermistor. The sensor element is very small, with a diameter of 0.5 mm and a length of 1.5 mm. Data for both the ordinary liquid and the supercooled liquid are smoothly connected to each other.

**KEY WORDS:** heat of fusion; sodium acetate hydrate; specific heat capacity; supercooled liquid; thermal conductivity; thermistor.

## 1. INTRODUCTION

Sodium acetate hydrate has attracted attention as a heat storage medium for low-temperature applications, because of its high heat of fusion and its considerable supercooling. In any design of a storage system, the thermophysical properties, such as thermal conductivity, specific heat capacity, and heat of fusion, are of prime importance. However, the thermophysical property data of sodium acetate hydrate over a wide range of temperature and concentration have not been reported except for the trihydrate.

The purpose of this research is to measure the thermal conductivity, the specific heat capacity, and the heat of fusion of sodium acetate hydrate for various concentrations and, especially, for various supercooling temperatures. It is also intended to develop the proper method to measure the

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thermal conductivity of the supercooled liquid, which is very unstable and easy to freeze with a small disturbance.

## 2. SAMPLE SALT (SODIUM ACETATE HYDRATE)

A phase diagram of sodium acetate hydrate is shown in Fig. 1 [1, 2]. The trihydrate is well-known, corresponds to a composition of mass concentration of 60.3 %, and has a melting point of 331 K. When we use this hydrate as a storage medium, water is added to prevent extraction of the anhydride. In this research, the range of mass concentration of the anhydrite of sodium acetate in water is from 45 to 60.3 %.

## 3. THERMAL CONDUCTIVITY

### 3.1. Measurement Method

As supercooled liquid is very unstable and easy to freeze with a distribance, the sensor is desirable to be small and simple. We have used the small NTC thermistor as a measuring sensor, which is coated with epoxy resin and polyimide tube to insulate it electrically from the sample. The

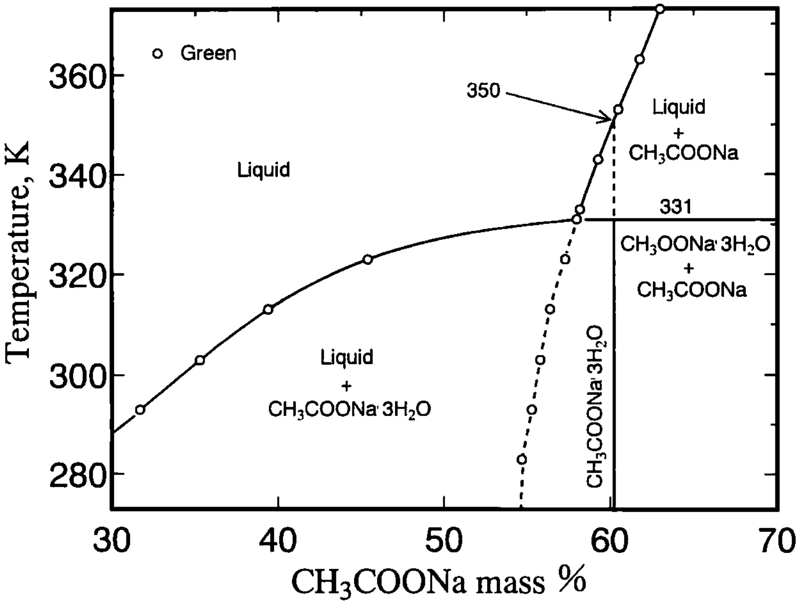

Fig. 1. Phase diagram of sodium acetate hydrate [1, 2].

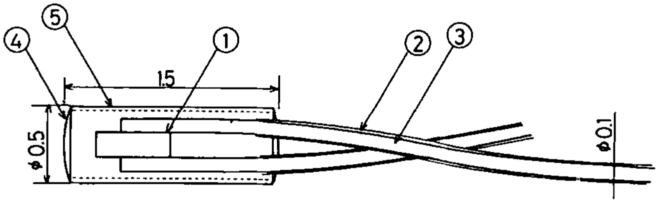

**Fig. 2.** Sensor element of the thermistor: (1) thermistor chip, (2) polyurethane coat, (3) lead wire (Cu), (4) epoxy resin, and (5) polyimide tube. Dimensions are millimeters.

sensor element is very small, with a diameter of 0.5 mm and a length of 1.5 mm, as shown in Fig. 2. This thermistor works as both a temperature sensor and a thermal conductivity sensor.

In the principle of measuring thermal conductivity, it can be assumed that the thermistor has a spherical shape and is heated uniformly in an infinite sample media. When the temperature of thermistor is instantaneously increased by $\Delta T$ from the thermal equilibrium condition by electrical heating, and after this initial time the temperature rise is held at a constant value of $\Delta T$ by adjusting the electric power, the power supplied to the thermistor can be expressed as follows,

$$Q(t) = P + \beta f(t) \tag{1}$$

where $P$ and $\beta$ are constants, and $f(t)$ is a function of time $t$ and approaches zero at infinite time. Then the thermal conductivity, $\lambda$, of the sample can be determined with the following equation [3]:

$$\lambda = \frac{1}{a(\Delta T/P) + b} \tag{2}$$

where $a$ and $b$ are constants that depend on the thermal conductivity and the radius of the thermistor. For the ideal case these constants are expressed as follows:

$$a = 4\pi r_1, \qquad b = -\frac{1}{5\lambda_1} \tag{3}$$

where $r_1$ is the radius of the thermistor and $\lambda_1$ is the thermal conductivity of the thermistor.

An actual thermistor is not uniform, and its shape is not spherical because of the lead wires and the coating materials. The constants $a$ and $b$ cannot be expressed theoretically. Accordingly, $a$ and $b$ are determined

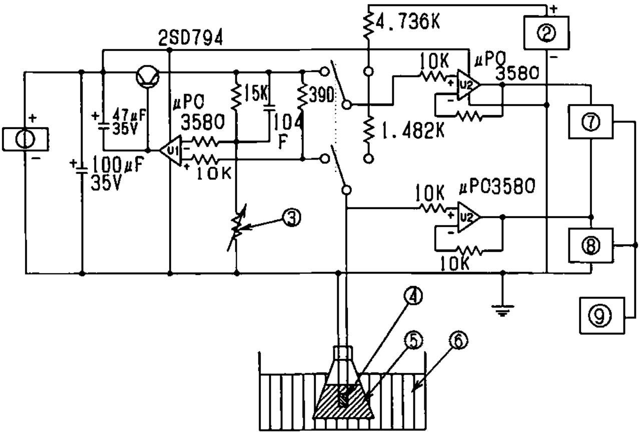

Fig. 3. Schematic diagram of the measuring apparatus with the electric circuit for the thermistor: (1) 15-V DC power supply, (2) 1.5-V DC power supply, (3) variable resistor for changing the temperature rise, (4) sensor element of the thermistor, (5) sample, (6) hot water bath with temperature controller, (7 and 8) voltmeters, and (9) personal computer.

empirically with at least two reference materials, the thermophysical properties of which are known.

A schematic diagram of the measuring apparatus with the electric circuit for the thermistor is shown in Fig. 3. The temperature of the sample (5) in a flask is held constant and its value is measured with the thermistor element (4). By switching on the electric circuit and supplying electric power $P(t)$ to the thermistor, the temperature of the thermistor is instantaneously increased by the amount $\Delta T$ from the equilibrium temperature. The temperature rise $\Delta T$ is held constant and the electric power $P(t)$ supplied to the thermistor is recorded as a function of elapsed time. The value of the temperature rise $\Delta T$ is adjusted at a proper value by the adjustable resistor (3). Thermal conductivity is calculated with Eq. (2). For determining the apparatus constants $a$ and $b$, water, glycerol, and ethylene glycol were used as the reference materials.

### 3.2. Measurement Results

Thermal conductivity was measured for the following mass concentrations of the anhydride in water: 60.3, 58.0, 56.0, 54.3, 52.0, 50.0, 47.5, and 45.3%. Measured values are shown in Figs. 4, 5, and 6 for concentrations of 60.3, 56.0, and 45.3%. Considerable scatter exists in the solid-phase

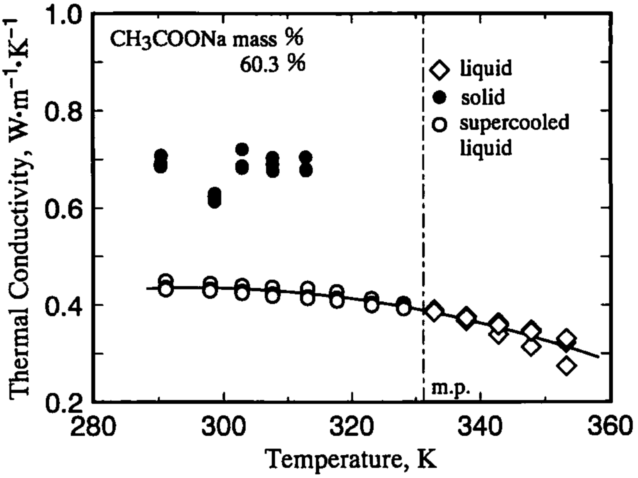

Fig. 4. Thermal conductivity of sodium acetate hydrate ($Y = 60.3\,\%$).

measurements presumably because of poor contact between the thermistor and the solid phase. The scatter in the data is especially wide in the temperature range near the melting point. The thermal conductivity values for the solid phase are about 30% larger than those for the liquid phase.

In the liquid phase, the measured values decrease as temperature increases. Data for both the ordinary liquid and the supercooled liquid can

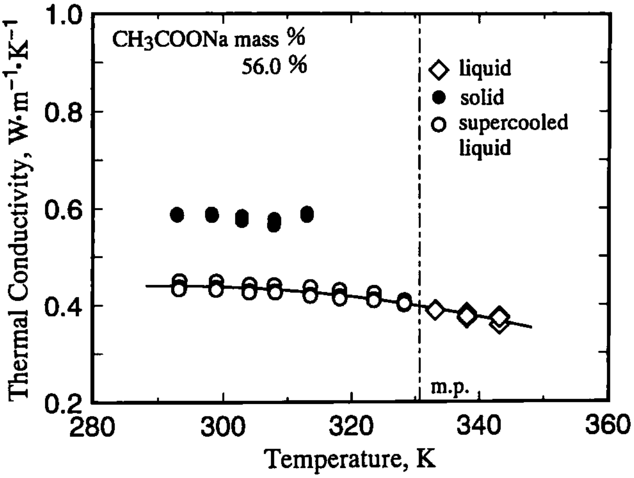

Fig. 5. Thermal conductivity of sodium acetate hydrate ($Y = 56.0\,\%$).

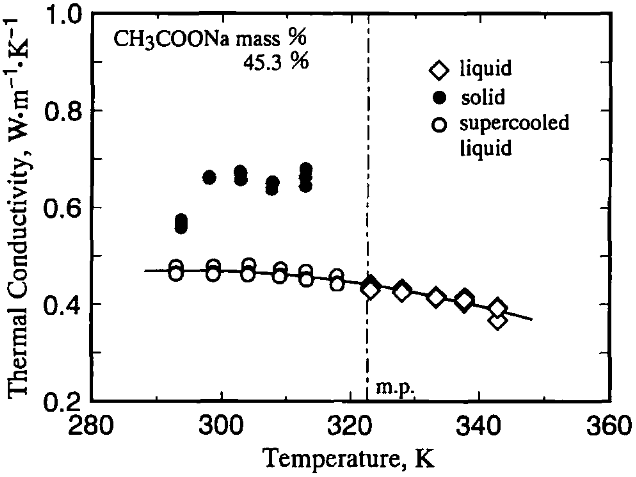

Fig. 6. Thermal conductivity of sodium acetate hydrate ( $Y = 45.3\,\%$ ).

be smoothly connected to each other. The temperature dependence in the supercooled condition is smaller than that in the ordinary liquid phase. Measured data in the liquid phase including the supercooled condition for other concentrations shown in Figs. 5 and 6 are shown in Fig. 7. Solid lines in the figure are the empirical equations, which were obtained with a

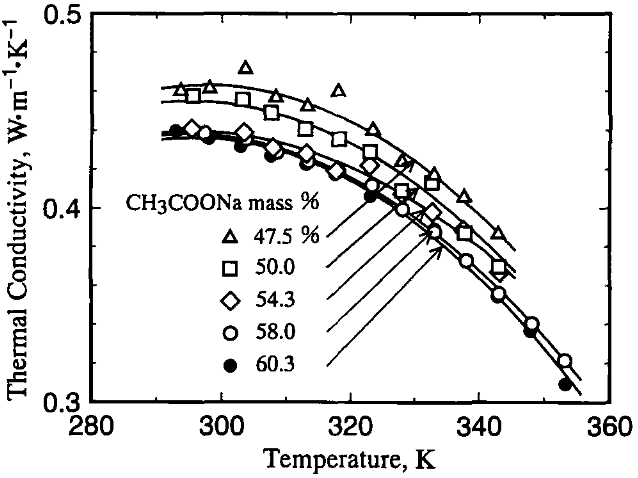

Fig. 7. Thermal conductivity of sodium acetate hydrate for various concentrations in the liquid phase including the supercooled condition.

least-squares processing technique, and two of them are expressed representatively as follows. For $Y = 60.3\,\%$ and in the range $290 \leqslant T \leqslant 353$ K,

$$\lambda = -2.76 + 2.16 \times 10^{-2} T - 3.66 \times 10^{-5} T^2 \tag{4}$$

For $Y = 45.3\,\%$ and in the range $293 \leqslant T \leqslant 343$ K,

$$\lambda = -2.48 + 2.01 \times 10^{-2} T - 3.43 \times 10^{-5} T^2 \tag{5}$$

where $\lambda$ is the thermal conductivity in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, $T$ is the temperature of the sample in $K$, and $Y$ is the mass concentration of the anhydride in water. The thermal conductivity decreases with increasing mass concentration of the anhydride. The dependence of thermal conductivity on mass concentration is shown in Fig. 8 for different supercooling levels. The thermal conductivity becomes less dependent on concentration at the higher levels of anhydride. This tendency may be correlated with the extraction of the anhydride. Slight differences in thermal conductivity, depending on the degree of supercooling, appear in the range of high concentration. This seems to be due to the temperature dependence of thermal conductivity.

Uncertainty of thermal conductivity measurements is ±5% for the liquid phase and ±20% for the solid phase. We suspect that the main reasons for the error are caused by the convection of the liquid sample that occurred around the thermistor element and the imperfect thermal contact between the solid sample and the thermistor element.

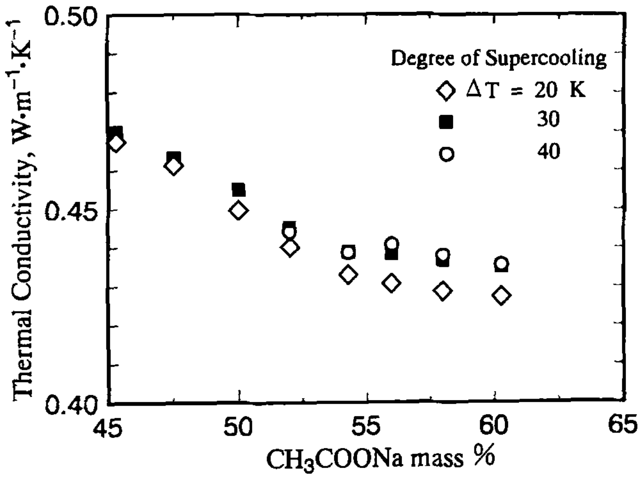

**Fig. 8.** Concentration dependence of the thermal conductivity of sodium acetate hydrate.

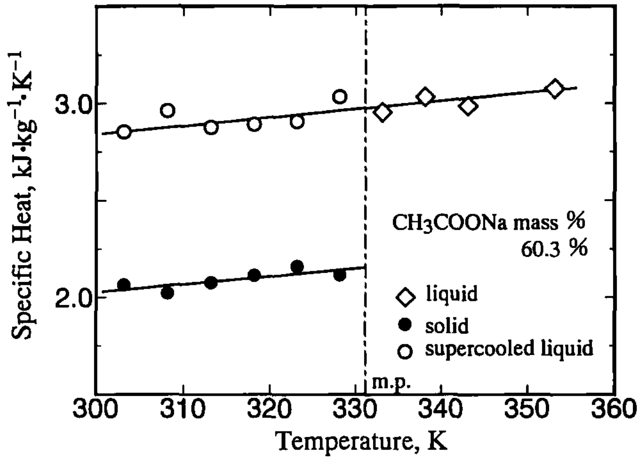

Fig. 9. Specific heat capacity of sodium acetate hydrate ( $Y = 60.3\,\%$ ).

## 4. SPECIFIC HEAT CAPACITY

Specific heat capacity was measured using a twin calorimeter (heat transfer type). This method has two vessels for samples, which are isolated from each other and have comparatively large capacities (about 20 cm$^3$).

Figures 9 and 10 show the measured results of the specific heat capacity for 60.3 and 54.3%. The measured values increase with increasing

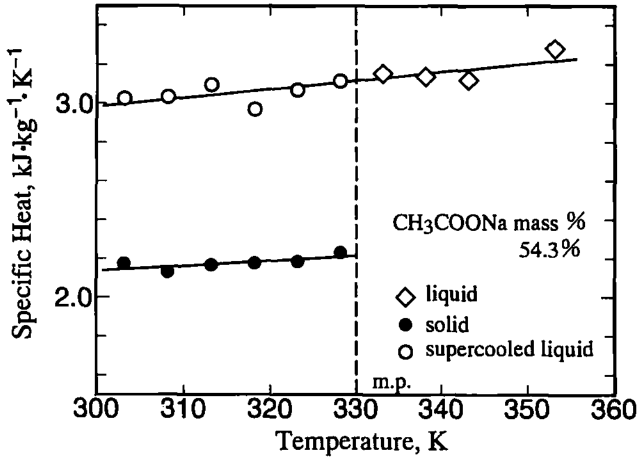

Fig. 10. Specific heat capacity of sodium acetate hydrate ( $Y = 54.3\,\%$ ).

temperature for both liquid and solid phases. In the liquid phase, the measured values are about 50% larger than that in the solid phase, and the data for the supercooled state can be smoothly connected to those for the ordinary liquid. The empirical equations, which are represented by solid lines in the figures, are expressed as follows. For the liquid phase $Y = 60.3\%$, and in the range $303 \leqslant T \leqslant 353$ K,

$$C = 1.56 + 4.27 \times 10^{-3} T \tag{6}$$

For the liquid phase $Y = 54.3\%$, and in the range $303 \leqslant T \leqslant 353$ K,

$$C = 1.65 + 4.44 \times 10^{-3} T \tag{7}$$

For the solid phase $Y = 60.3\%$, and in the range $303 \leqslant T \leqslant 328$ K,

$$C = 0.811 + 4.06 \times 10^{-3} T \tag{8}$$

For the solid phase $Y = 54.3\%$, and in the range $303 \leqslant T \leqslant 328$ K,

$$C = 1.36 + 2.58 \times 10^{-3} T \tag{9}$$

where $C$ is in $\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$ and $T$ is in K. Figures 11 and 12 show the dependence of the mass concentration for the specific heat capacity for the liquid phase and the solid phase, respectively. The lines in the figures express the harmonic mean between the specific capacity of the trihydrate and water.

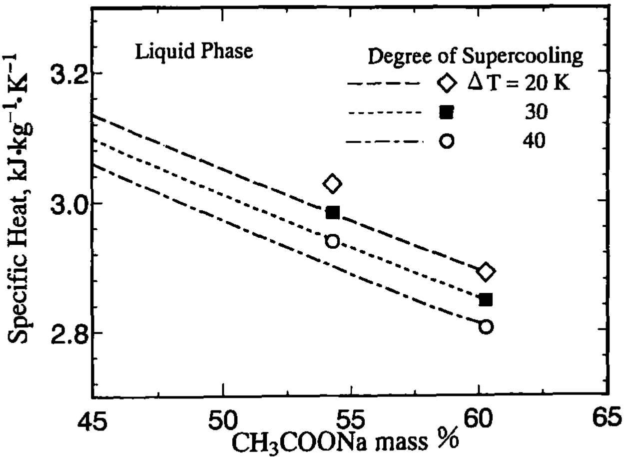

Fig. 11. Concentration dependence of the specific heat capacity for the liquid phase of sodium acetate hydrate.

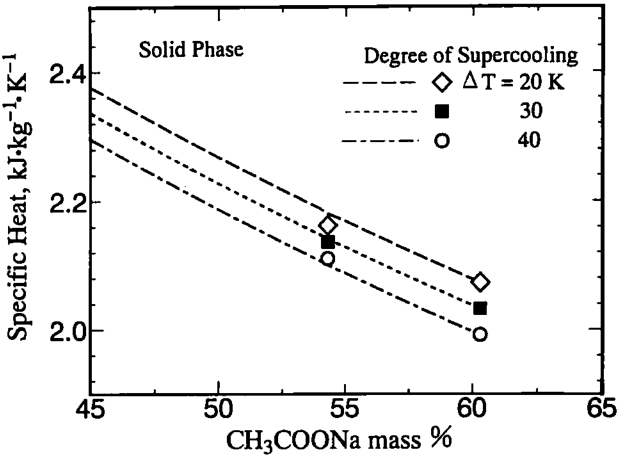

Fig. 12. Concentration dependence of the specific heat capacity for the solid phase of sodium acetate hydrate.

Uncertainty of the specific heat capacity measurement is estimated to be ±5%, which depends mainly on the temperature control of the measuring system.

## 5. LATENT HEAT OF FUSION

The latent heat of solidification was measured using the same twin calorimeter as that for measuring the specific heat capacity. However, one of the sample vessels was exchanged by a container with a trigger system for beginning solidification with seed crystals as shown in Fig. 13. The container is attached to a cylinder (3) containing a small crystal of the trihydrate. The crystal is dropped into a supercooled liquid by breaking a rubber film (2) with a needle (5). Upon solidification, the temperatures of the sample and its container rise above the initial temperature, and then the temperatures return to the initial temperature. Heat released during this process is measured; that is the latent heat of fusion.

The measured values of the latent heat of fusion increase linearly with increasing mass concentration of the anhydride to water as shown in Fig. 14. The data in the literature [4, 5] for the trihydrate are almost the same as the present values. Any difference is not recognized by the initial temperatures, which are related to the degree of supercooling. The empirical equation for the latent heat of fusion, in $\mathrm{kJ \cdot kg^{-1}}$, is expressed as a function of the mass concentration as follows. For $47.5 \leqslant Y \leqslant 60.3\%$,

$$L = -4.62 \times 10^2 + 1.18 \times 10Y \tag{10}$$

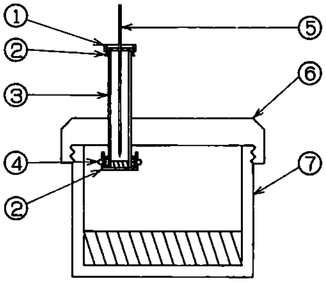

**Fig. 13.** Sample container for measuring the latent heat of fusion: (1) cylinder cap (needle support), (2) rubber film, (3) cylinder, (4) rubber band, (5) needle, (6) adiabatic cover, and (7) sample container.

Uncertainty in measuring the latent heat of fusion is estimated to be ±5%.

## 6. CONCLUDING REMARK

Methods for measuring thermal conductivity, specific heat capacity, and latent heat of fusion have been developed which are applicable to the supercooling condition of sodium acetate hydrate. These thermophysical properties have been measured for mass concentrations in the range 45 to 60.3% and for various degrees of supercooling in the range of 0 to 40 K.

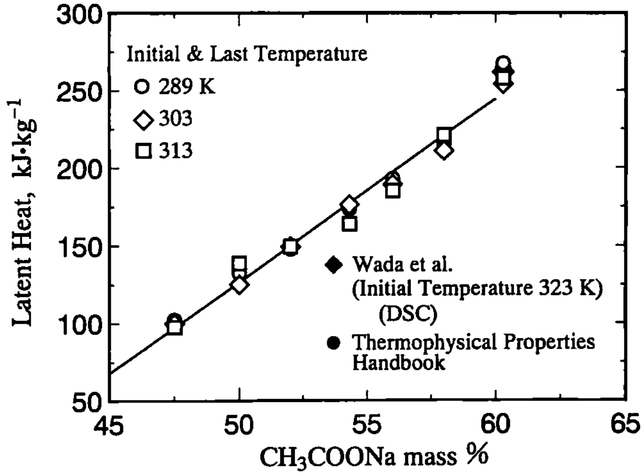

**Fig. 14.** Latent heat of fusion of sodium acetate hydrate.

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