

## **Determination of Thermal Properties of Dilute LiBr–Water Solutions<sup>1</sup>**

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We are developing an absorption air cooling system which can supply 2°C chilled water for air cooling by the usage of dilute solutions of LiBr in water with an evaporating temperature of  $-6^{\circ}\text{C}$  as a nonfreezing refrigerant. However, there are few published data for the thermal properties of dilute LiBr water solutions (0 to 30%) below  $10^{\circ}\text{C}$ . In this paper, the freezing temperature and the saturated vapor pressure are reported. The results clearly show the possibility of developing a new type of LiBr absorption refrigerating machine to generate evaporating temperatures below  $0^{\circ}\text{C}$ . To obtain accurate data for the design of this new type of absorption refrigerating machine, an apparatus has been developed to measure the thermal properties of dilute LiBr water solutions below  $10^{\circ}\text{C}$ . The experimental arrangement consists of a cooling bath ( $340 \times 240 \times 190$  mm) filled with fluorocarbon, a glass measuring bottle ( $\phi 120 \times 100$  mm), and an absolute pressure gauge (0–1.3 kPa). The accuracy of the temperature, pressure, and density are within  $\pm 0.1^{\circ}\text{C}$ , 0.01 kPa, and  $\pm 0.005\%$ , respectively.

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**KEY WORDS:** absorption; density; LiBr; vapor pressure; water.

### **1. INTRODUCTION**

In recent years, absorption refrigerating machines have attracted attention because they use neither HCFC nor HFC, run on an inexpensive or waste-energy source, and require no large electric motor or engine. For safety reasons, absorption refrigerating machines using LiBr–water as the working fluid are more popular, especially in Japan, although ammonia-based

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machines provide greater overall efficiency. Part of the reason is that in LiBr–water-based machines, the water freezes once the working temperature drops below  $0^{\circ}\text{C}$ . Thus, it is commonly believed that LiBr-type machines cannot achieve a subzero working temperature. Therefore, we are currently developing an absorption air cooling system that would supply  $2^{\circ}\text{C}$  chilled water for air cooling at a  $-6^{\circ}\text{C}$  evaporating temperature. The system will utilize waste heat as its source.

In this new type of absorption system, the most important point is to develop an additional absorber and evaporator unit up to low temperature levels not in the current absorption cooling systems. A nonfreezing refrigerant will be necessary to generate temperatures below  $0^{\circ}\text{C}$  in LiBr–water type of absorption air cooling system. For the nonfreezing refrigerant a dilute LiBr–water solution was selected. This keeps the complexity of the system cycle down to a minimum. However, there are few published data [1–6] for the thermal properties of dilute LiBr–water solutions (0 to 30%) below  $10^{\circ}\text{C}$ .

In this paper, an apparatus to measure the thermal properties of dilute LiBr–water solutions below  $10^{\circ}\text{C}$  to determine its properties for use in designing a new type of absorption refrigerating machine is described.

## 2. EXPERIMENTAL PREPARATION

### 2.1. Determination of the Freezing Point

The freezing point of the LiBr–water solution was determined with a simple apparatus. The apparatus is shown in Fig. 1. The concentrations, weight percentage of LiBr, of the data are 11 points every 5%, from 5 to 55%. Each data plot corresponds to a test piece which is a small bottle

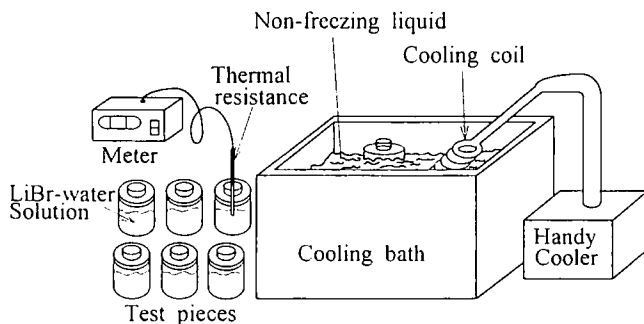


Fig. 1. A simple apparatus for determination of the freezing point.

with 100 g of a concentrated LiBr–water solution inside. Each concentrated solution was made of 55% standard LiBr–water solution. They were cooled in a bath filled with a nonfreezing liquid at  $-50^{\circ}\text{C}$ . Several runs were made for each test piece. When the solution inside had cooled enough and had frozen, each test piece was taken out from the bath. We then inserted a thermal resistance (Pt100) into each piece through its cap and started to measure the solution temperature. This way the temperature of the solution can be obtained within  $\pm 0.2^{\circ}\text{C}$ . The frozen solution melted slowly within 10 min. During this time, we had shaken each piece to achieve a homogeneous state of the solution. The melting temperature was determined at the point of disappearance of ice particles in the solution. The melting temperature can be regarded as the freezing temperature. The result is shown in Fig. 2. The solid line represents the values calculated from the following equation [7] for a dilute solution:

$$\Delta T_f = T_f \left( 1 - \frac{T_f}{(RT_f/\Delta H_f) \ln X_A} \right) \quad (1)$$

The experimental data agree with the calculated values to 5%. However, as the concentration is increased, the experimental data show a decreasing trend compared with the prediction of Eq. (1). This discrepancy between the calculated values and the experimental ones resembles that obtained by Lower [8]. It is supposed that a molar fraction change of water in the crystal causes a bend of the right-hand curve in Fig. 2.

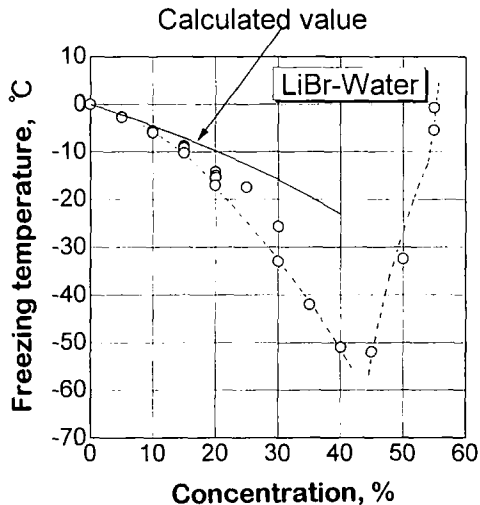


Fig. 2. Freezing temperature of LiBr–water solutions.

## 2.2. Saturated Vapor Pressure of the LiBr–Water Solutions

Additional measurements of the saturated vapor pressure of dilute LiBr–water solutions at low temperatures were made by a remodeled apparatus used primarily for the determination of the absorption heat-transfer coefficient. The apparatus is shown in Fig. 3. The concentrated LiBr–water solution was first installed in the evaporator and then exhausted by the rotary vacuum pump. Its pump capacity is  $150 \text{ L} \cdot \text{min}^{-1}$ , while the solution weight is 10 kg. So the concentration varies less than 0.01% in an hour. The concentration can be regarded as constant. The solution was circulated by a pump. The condenser, which was connected to the evaporator through the glass belljar, has a cooling coil which can cool to below  $-20^\circ\text{C}$ . The condenser pressure became low as vapor condensed within it. As a result, the solution in the evaporator evaporated and the temperature became lower. The solution in the evaporator was cooled, although no cooler was placed in the evaporator. In this way, the saturated vapor pressure can be determined by measuring the pressure and the solution temperature. A diaphragm absolute pressure gauge was used for the determination. The result is shown in Fig. 4. In this figure, experimental data (10, 20%), McNeely's data [3] (60%), and data calculated from Raoult's law [7] are plotted. Raoult's law can be given in the form

$$P_A = \frac{P_A^*}{1 - X_B} \quad (2)$$

The experimental data agreed well with Raoult's law. The small discrepancy found between the data (10, 20%) and Raoult's law may be due

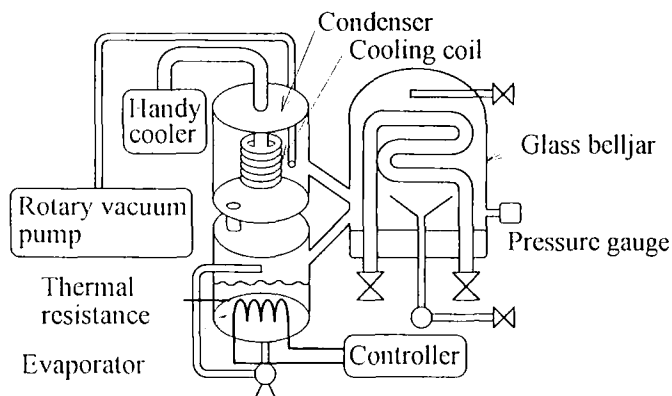


Fig. 3. An apparatus for determination of the saturated vapor pressure of dilute LiBr–water solutions.

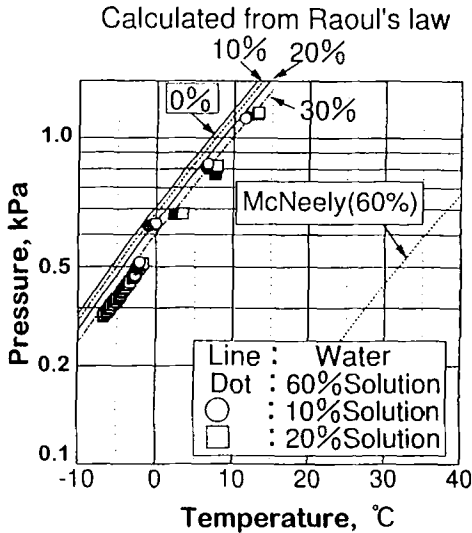


Fig. 4. Saturated vapor pressure of dilute LiBr–water solutions.

to a calibration error of 0.05 kPa of the diaphragm absolute pressure gauge. The data showed vapor saturation characteristics closer to those of water (0% concentration) compared with the 60% concentration (McNeely's data), and it can be seen that the vapor saturation pressure is not linearly dependent upon the concentration.

### 3. APPARATUS FOR DETERMINATION OF BASIC PROPERTIES

From the above experiment, we obtained some useful properties of dilute LiBr–water solutions. However, a higher accuracy is needed to design a working absorption refrigerating machine. For this reason, a more accurate apparatus that can determine basic thermal properties, i.e., freezing temperature, saturated vapor pressure, sonic speed, and density, has been developed. The outline of the apparatus is shown in Fig. 5 and a photograph in Fig. 6. With this apparatus, basic thermal properties between  $-30$  and  $10^{\circ}\text{C}$  can be investigated. The apparatus setup consists of a cooling bath ( $340 \times 240 \times 190$  mm) filled with fluorocarbon, a glass measuring bottle ( $\phi 120 \times 100$  mm), and an absolute capacitance pressure gauge (0–1.3 kPa). There is a cooling coil, a power-controlled heater (1 kW), and two propeller mixers in the cooling bath to achieve high cooling performance and to obtain a uniform temperature of the fluorocarbon.

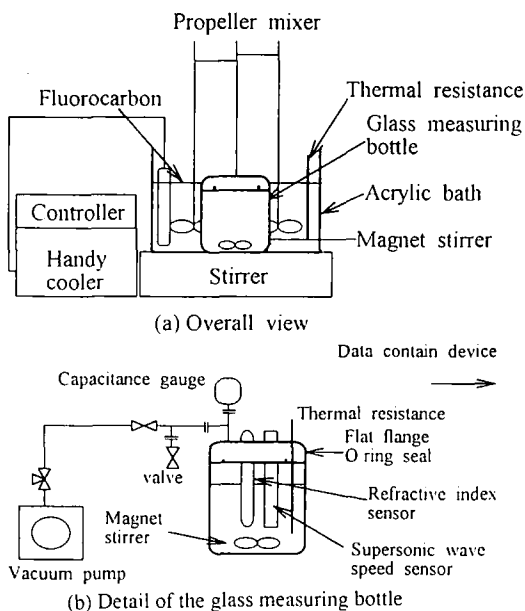


Fig. 5. Schematic representation of an apparatus for determination of the properties of dilute LiBr-water solutions.

The temperature accuracy was kept within  $\pm 0.05^\circ\text{C}$ , and the pressure accuracy within 0.01 kPa. There were a thermal resistance (Pt100) and a magnet stirrer in the glass measuring bottle. The thermal resistance (Pt100) was calibrated at the triple point of water ( $0.01^\circ\text{C}$ ). A flat flange with several connectors was connected to the bottle with an O-ring for sealing. All the valves and connectors were prepared for high-vacuum conditions. This made the saturated vapor pressure detection highly accurate. The outline of the measurement is as follows. First, a concentrated LiBr-water solution was put in the glass bottle. Second, the bottle was exhausted by a rotary vacuum pump for about half an hour while the solution was disturbed by the magnet stirrer. By measuring the pressure of the vessel when the temperature stabilizes, it is possible to measure the saturated vapor pressure. In addition, a calibrator for absolute pressure capacitance gauges was developed. The calibrator with a Pirani pressure gauge, shown in Fig. 7, is connected to a rotary vacuum pump. When the pressure in the calibrator becomes less than 1 Pa, each gauge is independently calibrated according to the reading of the Pirani pressure gauge. Thus, the absolute accuracy of the capacitance pressure gauge is expected to be within 1 Pa. The result of the measurements of the saturated vapor pressure of water is

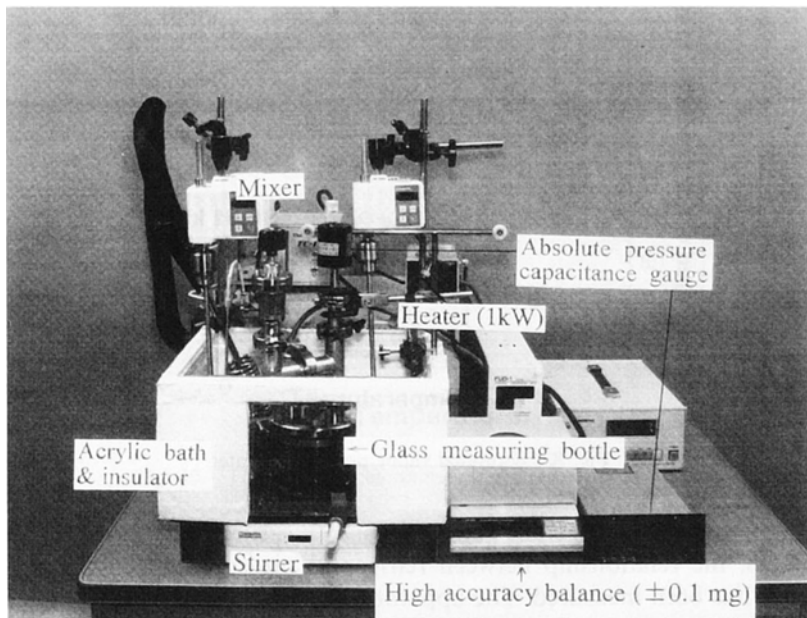


Fig. 6. A photograph of the apparatus for the determination of properties.

shown in Fig. 8. In this figure, a line from the JSME steam table [9] is added. Both data show the same values within 0.01 kPa.

In a conventional type of absorption refrigeration machine, the LiBr concentration is usually determined by closely measuring the temperature and its density. However, the relational data between temperature and density of the dilute solution (under 40%) below 0°C cannot be found. With

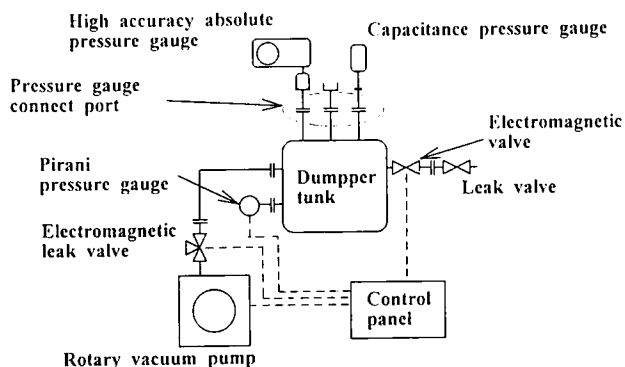


Fig. 7. A calibrator for absolute pressure gauges.

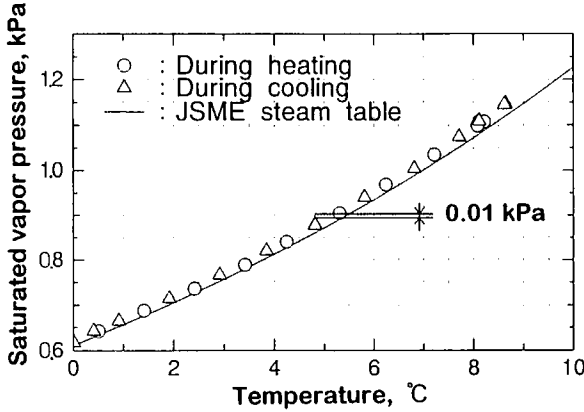


Fig. 8. Saturated vapor pressure of water.

the apparatus for refrigerant vapor pressure measurement, shown in Figs. 5 and 6, the relationship between refrigerant pressure–concentration and density has been measured. The apparatus was slightly modified to include density measurements. An outline of the measurement method is shown in Fig. 9. In this method, the buoyancy of the measuring ball (quartz glass ball; outer diameter,  $\phi$  50 mm) in the solution is measured. Since in the measurement covering a wide range, from  $-30$  to  $10^\circ\text{C}$ , the thermal expansion of the ball greatly affects the accuracy, a quartz glass for the measuring ball was chosen for its minimal thermal expansion coefficient of  $0.5 \times 10^{-6} \text{ K}^{-1}$  (this value is 1/20th that of metal). The mass of the ball  $M$  was predetermined, and the tension of a wire hanging the ball  $L$  was measured with a highly accurate balance. The density  $\rho$  was calculated by Eq. 3. The volume of the ball  $V_0$  had been measured by the method

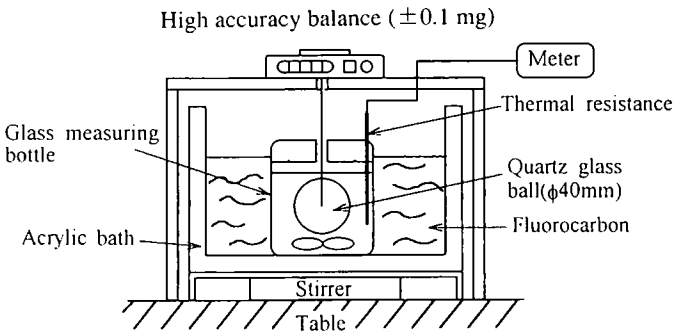


Fig. 9. Determination of the density of dilute LiBr water solutions.



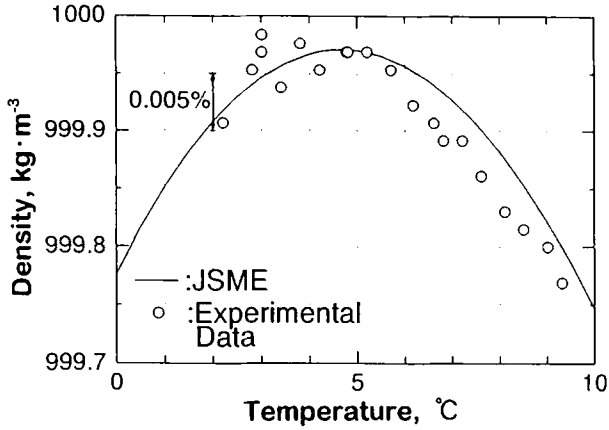


Fig. 10. The result of determination of the density of water.

described above. In Eq. 4 the density of water  $\rho_0$  at 5.2°C was taken from the JSME data book [10].

$$\rho = \frac{Mg - L}{V_0} \quad (3)$$

where

$$V_0 = \frac{Mg - L_0}{\rho_0} \quad (4)$$

The measured density of water is shown in Fig. 10. In this figure a solid line from the JSME data book [10] is also shown. Both data agree within 0.005%.

#### 4. CONCLUSION

Freezing temperatures and saturated vapor pressures were determined. Although the accuracy was not so high, the results obtained clearly showed the possibility of developing a new type of LiBr absorption refrigerating machine achieving cold below 0°C. In addition, we have developed an apparatus to measure the thermal properties of dilute LiBr–water solutions and measured some properties of water. The temperature accuracy was ensured to be within  $\pm 0.1^\circ\text{C}$ , the pressure accuracy within 0.01 kPa, and the density accuracy within  $\pm 0.005\%$ .

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## NOMENCLATURE

$g$	$\text{m} \cdot \text{s}^{-2}$ ; gravitational acceleration
$M$	kg; mass of the measuring ball
$M_{,A}$	$\text{kg} \cdot \text{mol}^{-1}$ ; molecular weight
$m_B$	$\text{mol} \cdot \text{kg}^{-1}$ ; molality
$P_{,A}$	Pa; saturated vapor pressure of water
$R$	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ; gas constant
$L$	N; tension of the wire hanging the measuring ball
$T_f$	K; freezing point of water
$V$	$\text{m}^3$ ; volume of the measuring ball
$X_{,A}$	Molar fraction of water
$X_B$	Molar fraction of LiBr ion
$\Delta h_f$	$\text{J} \cdot \text{mol}^{-1}$ ; heat of fusion
$\Delta T_f$	K; freezing point depression
$\rho$	$\text{kg} \cdot \text{m}^{-3}$ ; density of solution

## SUPERSCRIPT

\* LiBr–water solution

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