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Thermophysical Properties of Aqueous Solutions Near the Equilibrium Freezing Temperature[1]

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Measurements of the surface tension, viscosity, and thermal conductivity of LiBr and LiSCN aqueous binary solutions have been performed to determine the thermophysical properties near the equilibrium freezing temperature. A differential capillary-rise method for surface tension and the transient hot-wire method for thermal conductivity were employed. Furthermore, a rotational viscometer was utilized for the measurement of viscosity. Correlation equations for the data of the aqueous binary test solutions as a function of temperature and concentration are presented.

KEY WORDS: aqueous solutions; capillary-rise method; surface tension; thermal conductivity; transient hot-wire method; viscosity.

1. INTRODUCTION

Water and aqueous solutions play important roles in many fields including, for example, medical science, foods, and various kinds of industries. Blood and numerous kinds of liquids in the human body which govern our life systems are aqueous solutions in which a variety of salts dissolve in subtle balances. Consequently, the consideration of freezing problem of solution is indispensable for research on the freezing problem of fresh foods as well as biomaterial.

Recently, great attention has been paid to active utilization of aqueous binary solutions in a variety of engineering fields using its thermochemical characteristics. For example, slush ice, which is produced by freezing

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aqueous solutions, is increasingly utilized as a cold thermal energy storage material [1]. Therefore, the thermophysical properties and freezing characteristics of aqueous solutions have been investigated [2, 3].

When aqueous solutions freeze under the condition of the existence of a free surface, precise data for surface tension, in particular, at a temperature close to the freezing point, are indispensable in order to achieve the active control of its freezing heat transfer performance.

The authors have previously performed measurements of surface tension of aqueous binary solutions such as sodium chloride solutions at low temperatures and have reported its dependences on both temperature and concentration [4, 5]. Measurement results for other thermophysical properties of aqueous solutions have also been reported. However, the results are restricted to a narrow range of conditions. Therefore, the previous data may be insufficient to satisfy needs in the engineering fields.

The goal of the present measurements is to obtain data for the thermophysical properties near the equilibrium freezing temperature for a variety of solutions, which are widely utilized in the engineering fields, over wide ranges of temperature and concentration. For both aqueous LiBr and LiSCN solutions, which are utilized in absorption refrigerators, surface tension, viscosity, and thermal conductivity were measured from room temperature to their equilibrium freezing temperatures.

The effects of both the concentration and the temperature on the surface tension were extensively investigated. Furthermore, correlation equations for the surface tension of the aqueous solutions as a function of temperature and concentration are presented.

2. MEASUREMENTS

2.1. Apparatus

Schematic diagrams of apparatus for surface tension and thermal conductivity measurements are depicted in Figs. 1 and 2, respectively. In the present measurements, the differential capillary-rise method for surface tension and the transient hot-wire method for thermal conductivity were employed.

The apparatus for surface tension (Fig. 1) consists basically of a thermostat, a sample liquid vessel, a cathetometer, and a cooling brine circulating system. Within the thermostat, the heater, cooler, and fan were installed to control the temperature at any value between -25 and $20\,^{\circ}\mathrm{C}$. Two glass tubes of 0.29- and 0.68-mm inner radius were used for the capillary and were installed vertically within the test liquid. The levels of

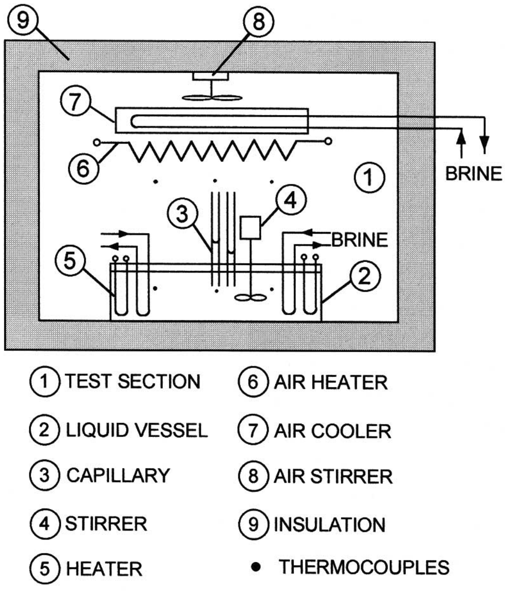

Fig. 1. Schematic diagram of measurement facilities for surface tension.

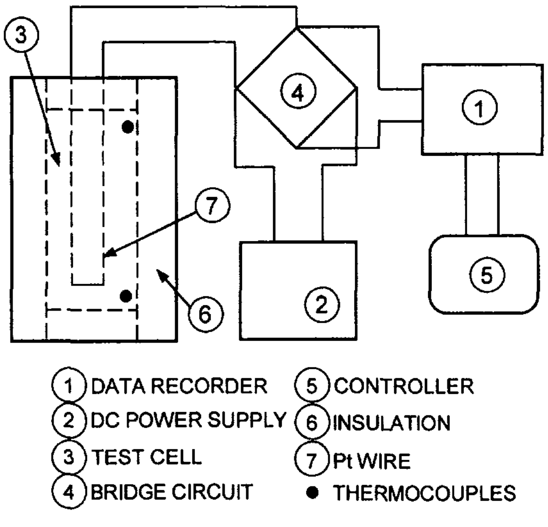

Fig. 2. Schematic diagram of measurement facilities for thermal conductivity.

the liquid within both the tubes and the sample vessel were measured by use of a cathetometer with a resolution of 0.001 mm.

The measurement apparatus for thermal conductivity (Fig. 2) consists essentially of a test cell, a bridge circuit containing the thin platinum wire, and the measurement instrumentation. The test cell is a coaxial vertical tube with a 30-mm inner radius. Through the annular section of test cell, temperature-regulated brine was circulated to maintain the temperature of test liquid. Within the test cell, a thin hot wire (platinum wire which is coated with a polyester film of 7 μm for electrical insulation, 40 μm in diameter) was installed vertically.

In the present measurement, the temperature of the test solution was set below the freezing point, i.e., at supercooled condition. To make the temperature control easier and to avoid damage to the measurement facility being subjected to sudden freezing, a rotational viscometer (TOKIMEC Co. Ltd., Type B-80) was used for the measurement of viscosity.

2.2. Procedure

In the measurement of surface tension, two glass tubes, with inner radii of 0.29 and 0.68 mm, were cleaned with pure water and acetone prior to each run. Then they were set vertically into the sample vessel as capillaries.

After the equilibria of the temperatures of both the sample and the ambient air were achieved at a prescribed point, the levels of the liquid within both the tubes and the sample vessel were measured with a cathetometer. The measurement results were corrected by Sugden's revised method [6]. According to the differential capillary-rise method, the surface tension of the liquid is determined by the following equations:

$$\sigma = a^2 g(\rho_L - \rho_a)/2 \qquad (1)$$

$$a^2(h_1 - h_2)^{-1} = [(1/b_1) - (1/b_2)]^{-1} \qquad (2)$$

where a is a capillary constant; b, the radius of curvature at the bottom part of the meniscus; g, the acceleration of gravity; h, the liquid level in the capillary; ρ_L, the density of the testing liquid; and ρ_a, the density of ambient air. Subscripts 1 and 2 correspond to capillary 1 and capillary 2. Symbols a and b are evaluated using the correction table of Sugden [6]. The precision of the surface tension measurement, which is determined from the precision of the temperature, density, and capillary height, is estimated to be 0.4%.

In the measurement of thermal conductivity, after balance of the bridge circuit was attained completely using a galvanometer, the variation of nonbalanced voltage, which was caused by the change of the electric resistance of the hot wire, was measured.

The thermal conductivity was obtained from the following basic equation for the transient hot-wire method:

$$\lambda = (q/4\pi)/(d\theta/d \ln t) \tag{3}$$

where q and t denote the heat generation in the hot wire per unit length and time, respectively, and the temperature variation of the hot wire d is determined based on the change of the nonbalanced voltage of the bridge circuit caused by the change of the electric resistance of the platinum wire. The precision of the thermal conductivity measurement in the present study is estimated to be about 1.6%. Furthermore, the precision of the rotational viscometer which was employed in the present measurement is 3.5%.

LiBr and LiSCN aqueous binary solutions were adopted as the test solutions. The concentration of test solution was varied from 0 to 20%, by mass. The temperature of the test solutions ranged from 25°C to a temperature below their equilibrium freezing points, i.e., supercooled conditions. In the present study, pure water ($R = 18.0\ \mathrm{M}\Omega$), which was purified from well water through the reverse osmosis, ultrafiltration, and ion-exchange process, was employed.

3. RESULTS AND DISCUSSION

3.1. Surface Tension

Figures 3 and 4 show the results of surface tension measurements of aqueous binary solutions of LiBr and LiSCN, respectively. In the figures, reference data for pure water [8, 9] are also indicated for comparison. An inspection of the figures reveals that the surface tension of the solution tends to decrease with increasing temperature. Its slope decreases slightly as the temperature increases.

In general, the surface tension of the liquid decreases with an increase in temperature. According to Eötbös' equation, the decreasing rate of surface tension is in proportion to $V^{-2/3}$, where V is the liquid volume per mole. Namely, it is in proportion to $(M/\rho)^{-2/3}$, where M is the mean molar mass. Consequently, the decrease in the slope with an increase in temperature in Figs. 3 and 4 can be interpreted in terms of the decreasing density of the solution with increasing temperature.

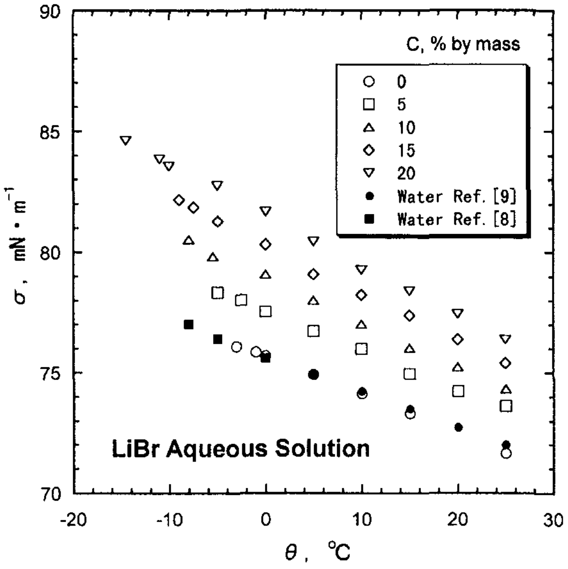

Fig. 3. Surface tension of aqueous LiBr solutions.

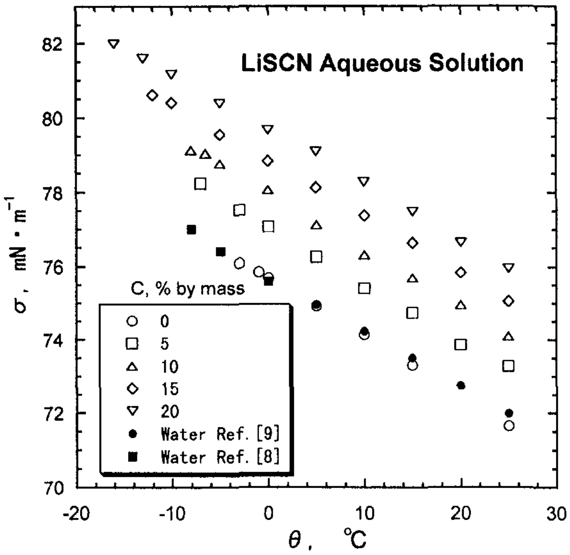

Fig. 4. Surface tension of aqueous LiSCN solutions.

Both LiBr and LiSCN are electrolytes, and they were respectively ionized in the state of the aqueous solution. In the solution, ions tend to be repelled from the surface by the hydration effect, which increases with an increase in the ratio of ion charge and surface area. Therefore, as the ion concentration of the solution increases, the traction effect on the water molecules at the interface also increases, which results in an increasing surface tension of the electrolyte solution.

Both aqueous solutions in the present study possess the same cation (Li^{2+}). The electric charge of Br^{2-} and that of SCN^{2-} are also the same. On the other hand, the degree of hydration effect for Br^{2-} is greater than that for SCN^{2-} because the ion radius of Br^{2-} is smaller than that of SCN^{2-}. This is the reason why the surface tension of aqueous LiBr solutions is greater than that of aqueous LiSCN solutions, and the difference between them increases as the concentration of the solution increases. Furthermore, in the supercooled region, no anomaly in the behavior of surface tension was observed in the figure.

3.2. Viscosity

Figures 5 and 6 show the viscosity of aqueous binary LiBr and LiSCN solutions. For both solutions, the viscosity increases at higher concentrations and at lower temperatures.

For the LiBr solutions in Fig. 5, the viscosity of the LiBr solution with a 5% (by mass) concentration is lower than that for pure water. This tendency may be interpreted by the fact that the bromine ion (Br^{2+}) shows a negative-hydration effect which is accentuated at low temperatures and low concentrations.

On the other hand, for the LiSCN solutions in Fig. 6, the increment of viscosity to that of pure water with concentration of the salt is comparatively small. This may be due to the fact that the B coefficient in the Jones–Dole equation is small for the LiSCN solution. Consequently, within the parameter range of the present study, the temperature of the solution is the most dominant parameter independent of the material and concentration.

3.3. Thermal Conductivity

Figures 7 and 8 present the results of thermal conductivity measurements of the aqueous LiBr and LiSCN solutions, respectively. From Fig. 7, the present results agree well with the reference data [10, 11], although they are slightly smaller than the latter. Comparing Figs. 7 and 8, the thermal conductivity of aqueous LiBr solutions is higher than that of aqueous LiSCN

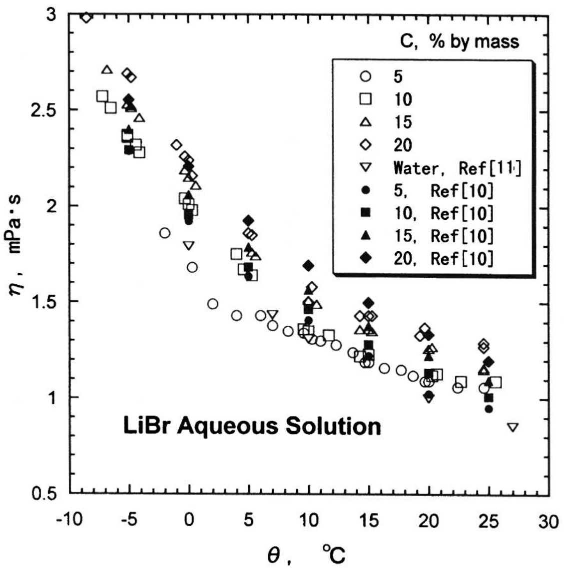

Fig. 5. Viscosity of aqueous LiBr solutions.

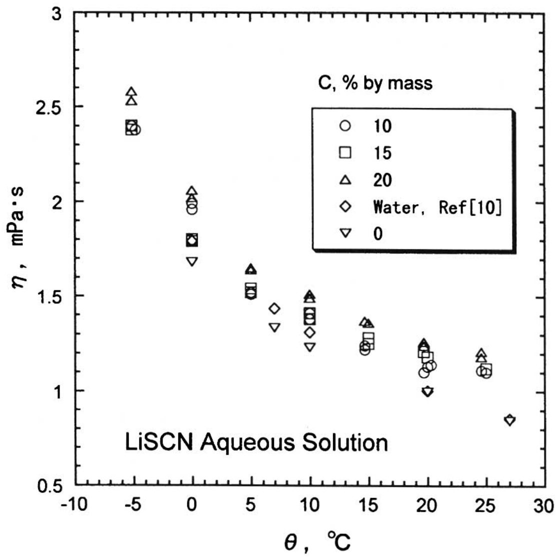

Fig. 6. Viscosity of aqueous LiSCN solutions.

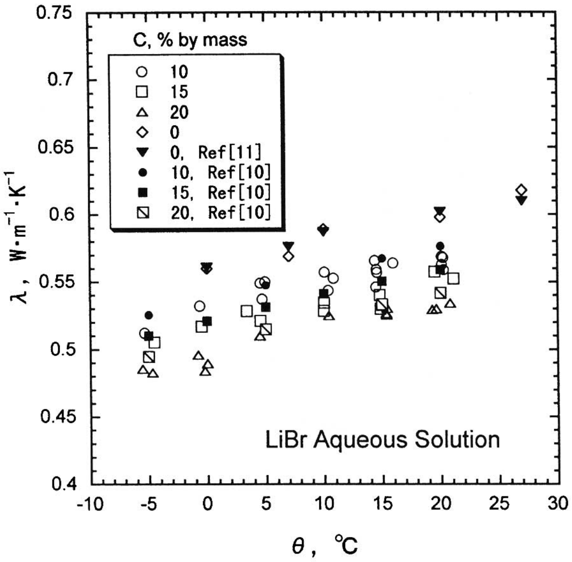

Fig. 7. Thermal conductivity of aqueous LiBr solutions.

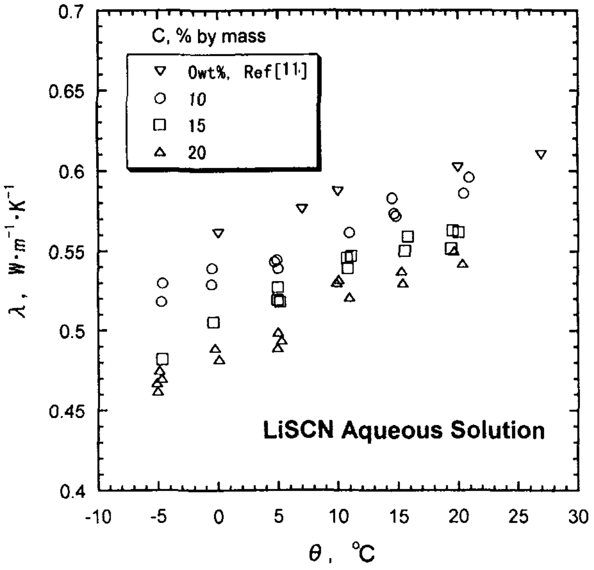

Fig. 8. Thermal conductivity of aqueous LiSCN solutions.

solutions, while the difference between them decreases as the temperature increases.

Furthermore, the difference in thermal conductivity between these aqueous solutions due to the concentration of solution increases as the temperature decreases. It is considered that this tendency of the thermal conductivity of the solution has a close correlation with the viscosity of the solution.

3.4. Correlation of the Experimental Data

For the experimental condition in the present study, the results for the thermophysical properties might be expressed by the following equations within the deviation range indicated along with each equation.

Surface tension of aqueous LiBr solution:

$$\sigma = 2.978 \times 10^{3} \theta^{-0.662} C^{0.0366}$$
$$[255 \leqslant \theta \leqslant 298 \text{ K}, 5 \leqslant C \leqslant 20\%, \text{by mass}, \pm 0.2\%] \tag{4}$$

Surface tension of aqueous LiSCN solution:

$$\sigma = 1.339 \times 10^{3} \theta^{-0.518} C^{0.0276}$$
$$[255 \leqslant \theta \leqslant 298 \text{ K}, 5 \leqslant C \leqslant 20\%, \text{by mass}, \pm 0.2\%] \tag{5}$$

Viscosity of aqueous LiBr solution

$$\eta = 3.136 \times 10^{19} \theta^{-7.954} C^{0.2517}$$
$$[263 \leqslant \theta \leqslant 298 \text{ K}, 5 \leqslant C \leqslant 20\%, \text{by mass}, \pm 10\%] \tag{6}$$

Viscosity of aqueous LiSCN solution:

$$\eta = 2.477 \times 10^{17} \theta^{-7.085} C^{0.1341}$$
$$[268 \leqslant \theta \leqslant 298 \text{ K}, 10 \leqslant C \leqslant 20\%, \text{by mass}, \pm 10\%] \tag{7}$$

Thermal conductivity of aqueous LiBr solution:

$$\lambda = 2.673 \times 10^{-3} \theta^{0.9823} C^{-0.0951}$$
$$[268 \leqslant \theta \leqslant 298 \text{ K}, 10 \leqslant C \leqslant 20\%, \text{by mass}, \pm 5.0\%] \tag{8}$$

Thermal conductivity of aqueous LiSCN solution:

$$\lambda = 3.908 \times 10^{-5} \theta^{1.730} C^{-0.1397}$$
$$[268 \leqslant \theta \leqslant 298 \text{ K}, 10 \leqslant C \leqslant 20\%, \text{by mass}, \pm 5.0\%] \tag{9}$$

where θ denotes the absolute temperature of solution.

4. CONCLUSIONS

Measurements of the surface tension, viscosity, and thermal conductivity of aqueous binary LiBr and LiSCN solutions have been carried out at low temperatures to determine the effects of both temperature and concentration. The results of the present study do not show any anomaly under supercooled conditions, i.e., below the equilibrium freezing temperature. The effect of hydration of ions in aqueous binary solutions on both the viscosity and the thermal conductivity was identified. Furthermore, correlating equations for the thermophysical properties as a function of temperature and salt concentration were presented.

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