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Surface Tension of Aqueous Binary Solutions at Low Temperatures[1]

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The paper is concerned with measurements of the surface tension of aqueous binary solutions at low temperatures. The effects of both temperature and concentration on the surface tension of $CaCl_2$, $NaClO_3$, and propylene glycol have been investigated. A differential capillary-rise method was employed for the measurements. The results showed that the surface tension of $CaCl_2$ and $NaClO_3$ increases monotonically as the concentration of the solution increases, while for the propylene glycol solution the surface tension decreases with increasing concentration. The surface tension of the testing liquids was found to be an almost-linear function of temperature from 20°C to just above the freezing temperature. Equations for the surface tension of the three aqueous binary solutions as a function of temperature and concentration are presented.

KEY WORDS: aqueous solutions; capillary rise; low temperature; surface tension.

1. INTRODUCTION

Aqueous binary solutions, such as $CaCl_2$ in water, are widely utilized in a variety of engineering fields as a secondary coolant in heat exchanger. Recently, great attention has been paid to "liquid ice," which is a kind of frozen layers of aqueous solutions, as a new PCM (phase change material) instead of common ice alone, because the liquid ice can be continuously produced and in practice can be transported by pipe. The authors [1, 2], investigated the freezing characteristics of aqueous binary solution droplets

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on a horizontal/inclined wall under a forced/free convection flow conditions and found that the change in surface tension owing to a change in concentration of the solution exerts a marked effect on the freezing behavior. In an analysis of the freezing problem of solutions with a free surface, such as the freezing of solution droplets, surface-tension data on the liquid as a function of both the concentration and the temperature of solution, in particular at the temperature close to the freezing temperature, are required. However, the dependence of the surface tension on both the concentration and the temperature of solution has not been studied extensively [3], and only a limited amount of data at relatively high temperatures has been reported [4].

The objective of the present paper is to report surface-tension data for three aqueous binary solutions of $CaCl_2$, $NaClO_3$, and propylene glycol. A differential capillary-rise method for the measurement and Sugden's revised method for the data treatment were employed. The effects of both temperature and concentration on the surface tension have been investigated.

2. MEASUREMENTS

2.1. Measurement System

A schematic diagram of the experimental arrangement is shown in Fig. 1. The experimental facility basically consists of a thermostat, a sample-liquid

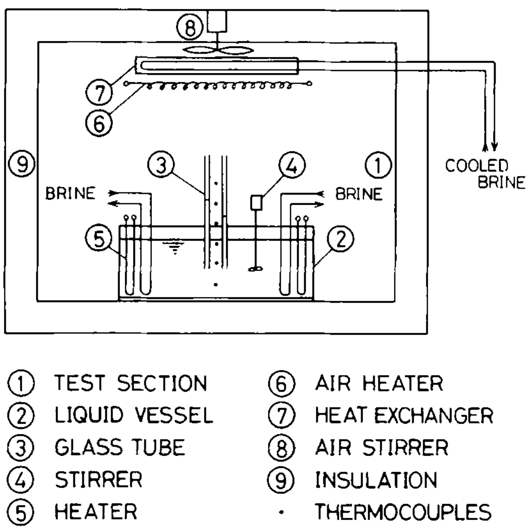

Fig. 1. Schematic diagram of the apparatus.

vessel, a microscopic level meter, and a temperature-regulating system. The thermostat is made up mainly of a transparent lucite box 400 mm in height, 350 mm in width, and 160 mm in depth, which was carefully covered with insulation material during the course of the experiment. Within the thermostat, a heater, a cooler, and a fan for stirring the air were installed to control the temperature from 25 to -25°C.

In the sample-liquid vessel, whose dimensions are $160 \times 200 \times 80$ mm, a heater, a cooling tube, and a stirrer were set to maintain the temperature of the sample. A set of two glass capillaries was installed vertically into the testing liquid. Temperatures of the testing liquid as well as the ambient air were measured with six chromel–alumel thermocouples with a diameter of 0.3 mm.

2.2. Measurement Procedures

A set of two glass tubes 0.29 and 0.68 mm in inner radius was set vertically within the sample vessel as capillaries. After equilibration of the temperatures between the sample and the ambient air was achieved at the prescribed temperature, the levels of the liquid within both the tubes and the sample vessel were measured with a cathetometer with a resolution of 10^{-2} mm.

With the differential capillary-rise method, the surface tension of the liquid, σ, can be determined by the following equations:

$$\sigma = a^2 g(\rho_L - \rho_a)/2 \tag{1}$$

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

where a is the capillary constant, b is the radius of curvature at the bottom part of the meniscus, h is the capillary-rise height of the liquid, ρ_L and ρ_a are the densities of solution and air, respectively, and subscripts 1 and 2 correspond to capillary 1 and capillary 2, respectively. The measurements were corrected by Sugden's revised method [5], where the symbols a and b can be assessed by use of the correction table of Sugden [5]. The measurement precision for the density was estimated to be 0.1%, and that for the capillary-rise height was about 0.05%. Consequently, the precision of the measurement of surface tension can be estimated to be about 0.15% in the present study.

In the measurement, the concentrations of the solution were varied from 5 to 30% for $CaCl_2$ solutions, 5 to 20% for $NaClO_3$ solutions and

3 to 20% for propylene glycol solutions, respectively. The temperatures of the solutions were varied between 25°C and just above equilibrium freezing temperature. The measurement precisions of both the temperature and the concentration of solutions were estimated to be about 0.4 and 0.05%, respectively.

3. RESULTS AND DISCUSSION

3.1. Surface Tension of $CaCl_2$ Solutions

Figure 2 shows the relation between the surface tension and temperature for $CaCl_2$ solutions of various concentrations. The recommended values of water [6] are also indicated. An inspection of Fig. 2 reveals that the measured surface tension of water shows quite good agreement with the values recommended in Ref. 6 and that the surface tension increases as the

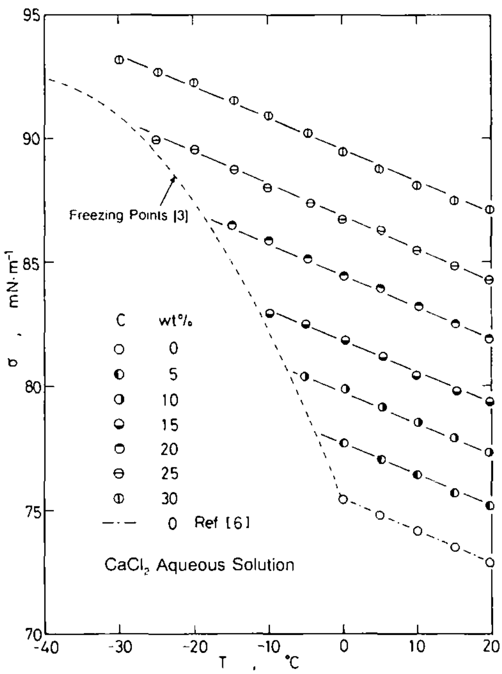

Fig. 2. Surface tension of $CaCl_2$ aqueous solutions versus temperature.

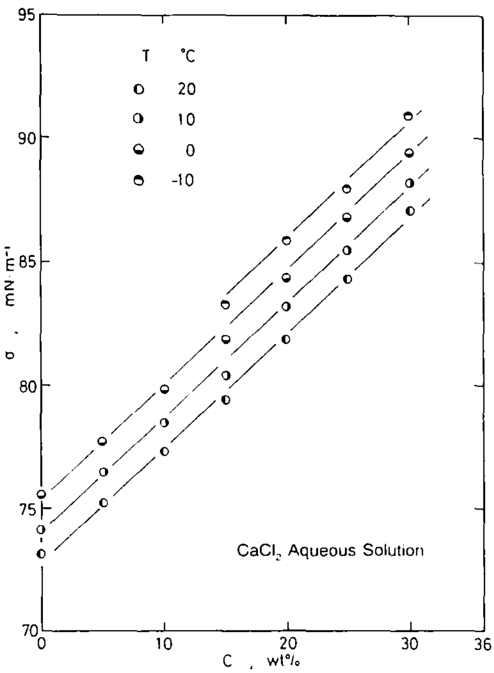

Fig. 3. Surface tension of $CaCl_2$ aqueous solutions versus concentration.

temperature decreases, and also, $\partial\sigma/\partial T$ of the solution is almost the same as for pure water.

The dependence of the surface tension on the concentration is represented in Fig. 3. This figure confirms the fact that increasing concentration causes increasing surface tension of $CaCl_2$ solutions in water.

3.2. Surface Tension of $NaClO_3$ Solution

The relations between the surface tension and temperature of $NaClO_3$ solutions in water are shown in Fig. 4. The measurement results indicate that the surface tension decreases with an increase in temperature, which is quite similar to the behavior of $CaCl_2$ solutions.

Figure 5 represents the effect of concentration on the surface tension of $NaClO_3$ solutions. The figure shows that the surface tension of $NaClO_3$ solutions in water increases with increasing concentrations of the solutions.

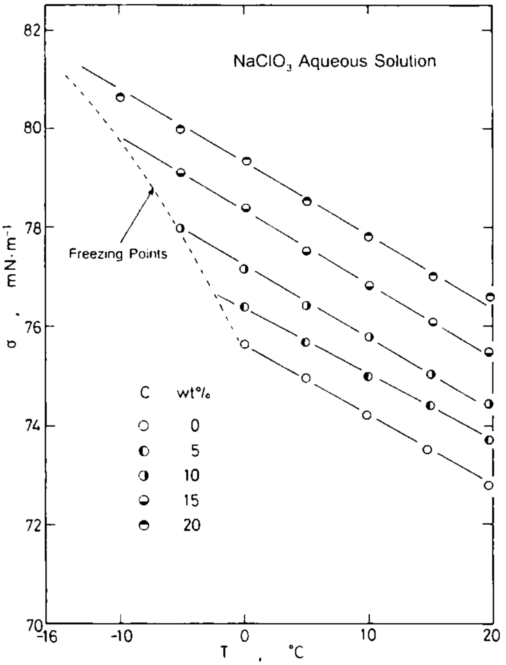

Fig. 4. Surface tension of $NaClO_3$ aqueous solutions versus temperature.

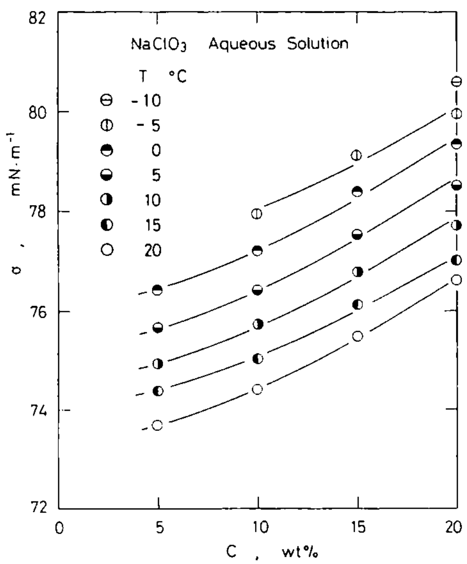

Fig. 5. Surface tension of $NaClO_3$ aqueous solutions versus concentration.

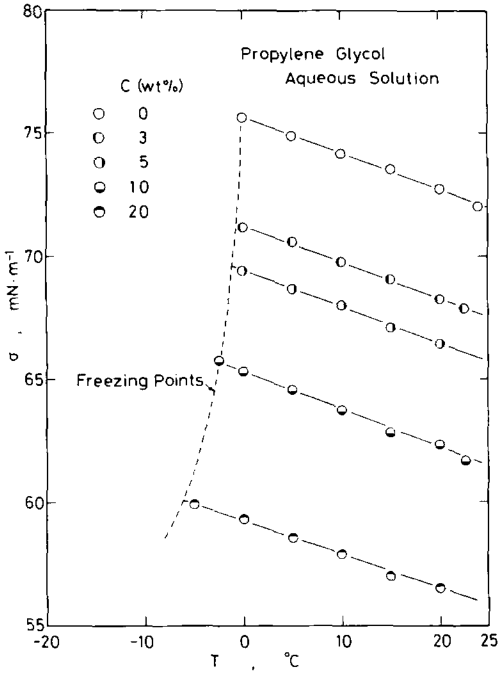

Fig. 6. Surface tension of propylene glycol aqueous solutions versus temperature.

3.3. Surface Tension of Propylene Glycol Solutions

Figure 6 shows the relations between the surface tension and temperature of propylene glycol solutions. The figure reveals that $\partial\sigma/\partial T$ decreases with a decrease in the concentration of the solution. On the other hand, the dependence of the surface tension on the concentration of the solution is represented in Fig. 7. The surface tension of the propylene glycol solution in water increases as the concentration of the solute decreases. In addition, it appears from Figs. 6 and 7 that $\partial\sigma/\partial T$ may depend upon both temperature and concentration.

3.4. Correlation of Experimental Data

Figures 8 to 10 demonstrate the correlated results of the surface tension of $CaCl_2$, $NaClO_3$, and propylene glycol solutions in water, respectively, as a function of both concentration and temperature within the parameter range covered in the present study. The correlating equations and parameter ranges are as follows.

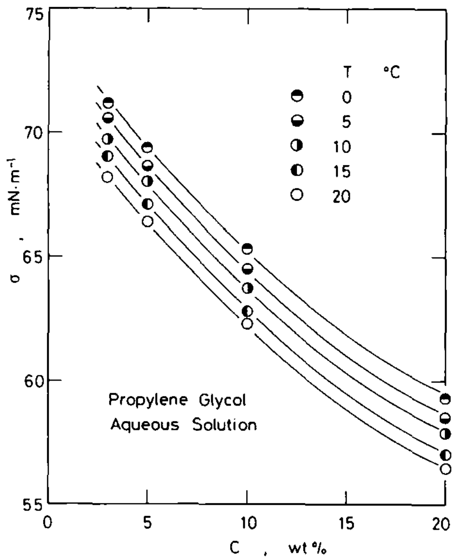

Fig. 7. Surface tension of propylene glycol aqueous solutions versus concentration.

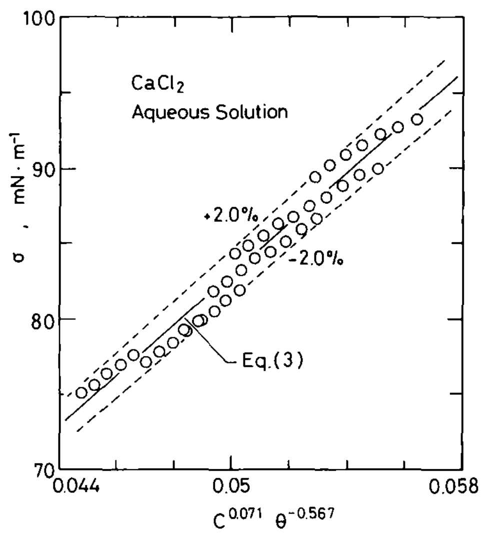

Fig. 8. Correlation of surface tension ($CaCl_2$).

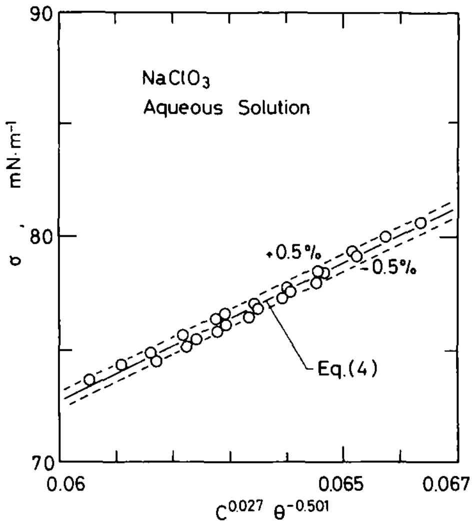

Fig. 9. Correlation of surface tension ($NaClO_3$).

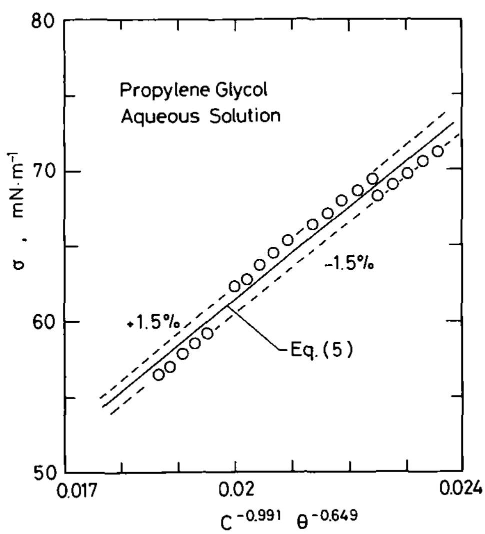

Fig. 10. Correlation of surface tension (propylene glycol).

$CaCl_2$ solution: $\sigma = 1.661 \times 10^3 C^{0.071} \theta^{-0.567}$

$$(5.0 \leqslant C \leqslant 30.0 \text{ wt\%}, 253.0 \leqslant \theta \leqslant 293.0 \text{ K}) \quad (3)$$

$NaClO_3$ solution: $\sigma = 1.216 \times 10^3 C^{0.027} \theta^{-0.501}$

$$(5.0 \leqslant C \leqslant 20.0 \text{ wt\%}, 268.0 \leqslant \theta \leqslant 293.0 \text{ K}) \quad (4)$$

Propylene glycol solution: $\sigma = 3.024 \times 10^3 C^{-0.991} \theta^{0.649}$

$$(3.0 \leqslant C \leqslant 20.0 \text{ wt\%}, 273.0 \leqslant \theta \leqslant 293.0 \text{ K}) \quad (5)$$

Here C is the concentration of solution and θ is the temperature of solution.

4. CONCLUDING REMARKS

Measurements of the surface tension of aqueous binary solutions were performed to determine the effects of both temperature and concentration on the surface tension. $CaCl_2$, $NaClO_3$, and propylene glycol solutions in water were adopted as the testing liquids. A differential capillary-rise method for the measurement was employed. The surface tension of the testing liquids was found to be an almost-linear function of temperature from 25°C to just above the freezing temperature. Correlating equations for the surface tension of the three binary aqueous solutions as a function of temperature and concentration were presented.

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