Surface Tension of Low-Temperature Aqueous Solutions

A. Horibe,¹ S. Fukusako,^{1,2} and M. Yamada¹

Received March 1, 1995

Measurements of the surface tension have been carried out to determine the effects of both temperature and concentration on the surface tension of aqueous solutions of sodium chloride, propylene glycol, and ethylene glycol. A differential capillary-rise method was employed for the measurements. The results show that the surface tension of the ethylene glycol solution and the propylene glycol solution increases as the concentration of the solution decreases, while for the sodium chloride solution the surface tension increases monotonically as the concentration increases. The surface tension of the 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 binary aqueous solutions as a function of temperature and concentration are presented.

KEY WORDS: aqueous solutions; capillary-rise method; surface tension.

1. INTRODUCTION

Aqueous binary solutions, such as ethylene glycol in water, are widely utilized in a variety of engineering fields as a secondary coolant in heat exchangers. Recently, frozen layers of aqueous solutions are increasingly used as thermal storage material, so called liquid ice. The authors [1] have carried out an experimental study of the freezing problem of aqueous solution droplets on a horizontal wall and have found that the change in surface tension due to a change in concentration of the solution exerted a considerable effect on the freezing characteristics. In an analysis of the freezing problem of solutions with a free surface, such as the freezing of solution droplets, surface-tension data of the liquid as a function of both the concentration and the temperature of solution, in particular at the temperature

² To whom correspondence should be addressed.

¹ Department of Mechanical Engineering, Hokkaido University, Sapporo 060, Japan.

close to the freezing temperature, are needed. However, the dependence of the surface tension on both the concentration of solution and the temperature has not been investigated extensively, and only restricted data for normal temperature have been reported [2].

In the present study, the surface tension of aqueous binary solutions has been measured to determine the effects of both temperature and concentration on the surface tension. Specifically, aqueous solutions of sodium chloride, propylene glycol, and ethylene glycol were investigated. A differential capillary-rise method for the measurement and Sugden's revised method for the data treatment were employed.

2. MEASUREMENTS

2.1. Measurement System

Figure 1 shows a schematic diagram of the experimental setup. The experimental facility essentially consists of a thermostat, a sample liquid vessel, a microscope level meter, and a temperature-regulating system. The thermostat consists of a transparent lucite box $(400 \times 350 \times 160 \text{ mm})$ and was carefully covered with insulation material. Within the thermostat, a heater, a cooler, and a fan for stirring the air were installed to control the temperature from 20 to -25° C.



Fig. 1. Schematic diagram of experimental setup.

Surface Tension of Aqueous Solutions

In the sample vessel, whose dimensions are $160 \times 200 \times 80$ mm, a heater, a cooling tube, and a stirrer were set to keep the temperature of the sample constant. Two glass tubes of 0.29 mm and 0.68 mm in inner radius were used for the capillary and were installed horizontally within the testing liquid.

Temperatues of testing liquid and ambient air were measured by six chromel-alumel thermocouples with a diameter of 0.3 mm.

2.2. Measurement Procedures

Two glass tubes with inner diameters of 0.29 and 0.68 mm were cleaned with pure water and acetone in advance. Then they were set vertically into the sample vessel as capillaries. After the equilibration of the temperatues of both the sample and the ambient air were achieved at the prescribed temperature, the levels of the liquid both within the tubes and sample vessel were measured with a cathetometer with a resolution of 0.01 mm.

A differential capillary-rise method was used for measuring the surface tension. The measurement results were corrected by Sugden's revised method [3].

According to the differential capillary-rise method, the surface tension of the liquid σ is determined by the following equations:

$$\sigma = a^2 g(\rho_{\rm L} - \rho_{\rm a})/2 \tag{1}$$

$$a^{2}(h_{1}-h_{2})^{-1} = (1/b_{1}-1/b_{2})^{-1}$$
⁽²⁾

where a^2 is a capillary constant; b, the radius of curvature at the bottom part of the meniscus; g, the gravity acceleration; 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, respectively. Symbols a and b are assessed using the correctrion table by Sugden.

Measurements were obtained at temperature from 25 to -25° C. The concentrations of the solution were 5 to 15 wt% for the ethylene glycol solution, and 3 to 20 wt% for the propylene solution.

3. RESULTS AND DISCUSSION

3.1. Sodium Chloride Solution

Figure 2 and Table I show the relations between the surface tension and the temperature for various concentrations of sodium chloride solution. In the figure, the recommended values of water [4] are also shown.



Fig. 2. Surface tension of sodium chloride aqueous solution.

It can be seen from Fig. 2 that the measured surface tension of water shows quite good agreement with the values recommended by IAPS [4] and that the surface tension increases as the temperature decreases, and also $d\sigma/d\theta$ for the solution is almost the same as for pure water.

The dependence of the surface tension on the concentration of solution is shown in Fig. 3. From this figure, the fact that the surface tension of solutions of sodium chloride in water increases with increasing concentration of the sodium chloride is confirmed. The present data at 20° C agree well with previous data [5, 6].

| | σ (mN·m ⁻¹) at θ (°C) | | | | | | | | |
|----------|---|------|------|------|------|------|-------|------|------|
| C (wt %) | 25 | 20 | 15 | 10 | 5 | 0 | - 2.5 | -5 | -10 |
| 0.0 | 72.0 | 72.7 | 73.6 | 74.2 | 74.9 | 75.7 | | | |
| 5.0 | | 74.4 | 75.1 | 75.8 | 76.4 | 77.5 | 77.7 | _ | |
| 10 | | 76.2 | 76.9 | 77.6 | 78.3 | 79.2 | 79.5 | 79.9 | |
| 15 | _ | 77.9 | 78.6 | 79.3 | 80.0 | 80.6 | 81.0 | 81.4 | 81.9 |

Table I. Surface Tension of Sodium Chloride Aqueous Solution



Fig. 3. Surface tension of sodium chloride aqueous solution.

3.2. Ethylene Glycol Solution

Figure 4 and Table II show the relations between the surface tension and the temperature of the ethylene glycol solution. The measurement results show that $d\sigma/d\theta$ decreases as the concentration of the solution decreases. The measured values for 100 wt% of ethylene glycol at -10 to

| | σ (mN·m ⁻¹) at θ (°C) | | | | | | | | | |
|---------|---|------|------|------|------|------|------|------|------|------|
| C (wt%) | 25 | 20 | 15 | 10 | 5 | 0 | -5 | -10 | -15 | -20 |
| 0.0 | 72.0 | 72.7 | 73.6 | 74.2 | 74.9 | 75.7 | | _ | _ | _ |
| 5.0 | 70.3 | 70.7 | 71.2 | 71.9 | 72.6 | 73.0 | | | | |
| 10 | 68.1 | 68.5 | 69.0 | 69.4 | 70.0 | 70.5 | | _ | _ | _ |
| 20 | 64.6 | 64.9 | 65.3 | 66.0 | 66.6 | 67.0 | 67.7 | _ | _ | |
| 30 | 61.4 | 61.9 | 62.2 | 62.9 | 63.2 | 63.6 | 64.2 | 65.0 | 65.4 | _ |
| 50 | | 57.0 | | 58.0 | _ | 59.0 | _ | 59.6 | | 60.9 |
| 100 | 47.7 | 48.2 | | 48.9 | _ | 50.0 | _ | 50.8 | — | — |

Table II. Surface Tension of Ethylene Glycol Solution



Fig. 4. Surface tension of ethylene glycol aqueous solution.

20°C are well predicted by the following reference equation for the ethylene glycol solution:

$$\sigma = 50.21 - 0.089\theta \tag{3}$$

where θ is the temperature of liquid (°C). The dependence of the surface tension on the concentration of solution is shown in Fig. 5. Being different from that of inorganic salts, the surface tension of the ethylene glycol solution increases as the concentration of the solute decreases. And it appears from the figures that $d\sigma/d\theta$ may depend on both temperature and concentration.

3.3. Propylene Glycol Solution

Figures 6 and 7 and Table III show the dependence of the surface tension of propylene glycol solution on both the temperature and the concentration of the solution, respectively. It can be seen from the figures that



Fig. 5. Surface tension of ethylene glycol aqueous solution.

| | $\sigma (mN \cdot m^{-1})$ at θ (°C) | | | | | | | | |
|----------|---|------|------|------|------|------|------|------|--|
| C (wt %) | 25 | 22 | 20 | 15 | 10 | 5 | 0 | -5 | |
| 0.0 | 72.0 | | 72.7 | 73.6 | 74.2 | 74.9 | 75.7 | | |
| 3.0 | _ | 67.9 | 68.3 | 69.0 | 69.8 | 70.6 | 71.2 | — | |
| 5.0 | | | 66.4 | 67.1 | 68.0 | 68.7 | 69.4 | _ | |
| 10 | _ | 61.7 | 62.4 | 62.8 | 63.7 | 64.6 | 65.3 | | |
| 20 | — | — | 56.5 | 57.0 | 57.9 | 58.6 | 59.3 | 59.9 | |

Table III. Surface Tension of Propylene Glycol Aqueous Solution



Fig. 8. Surface tension of sodium chloride aqueous solution.



Fig. 9. Surface tension of ethylene glycol aqueous solution.



Fig. 10. Surface tension of propylene glycol aqueous solution.

4. CONCLUDING REMARKS

Measurements of the surface tension of aqueous binary solutions have been carried out to determine the effects of both temperature and concentration on the surface tension. The surface tension of the solutions was found to increase as the concentration of solute decreases for both ethylene glycol solutions and propylene glycol solutions, while it increases monotonically as the concentration increases for sodium chloride solutions within the parameter range covered in the present study. Furthermore, correlation equations for the surface tension as a function of temperature and concentration have been determined.

REFERENCES

- A. Horibe, S. Fukusako, M. Yamada, M. Tago, and O. Okagaki, in *Proceedings of the 6th* Int. Symp. Transport Phenom. Therm. Eng., J. S. Lee, S. H. Chang, and K. H. Kim, eds. (Seoul, Korea, 1993), Vol. IV, p. 59.
- 2. J. J. Jasper, J. Phys. Chem. Ref. Data 1:841 (1972).
- 3. S. Sugden, J. Chem. Soc. 119:1483 (1921).
- 4. JSME Steam Tables (Japan Society of Mechanical Engineering, Tokyo, 1980).
- 5. R. Aveyard and S. M. Saleem, J. Chem. Soc. Faraday 72:1609 (1976).
- 6. Thermophysical Properties Handbook (Yokendo, Tokyo, 1990).