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Surface Tension of Aqueous Binary Solutions

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Measurements of surface tension have been performed to determine the effects of both temperature and concentration on the surface tension of aqueous solutions of D-Sorbitol, potassium chloride, and ammonium chloride. A differential capillary-rise method was employed for the measurements. The results showed that the surface tension of test solutions increased as the temperature decreased and that the surface tension of chloride solutions increased with an increase in its concentration, while for D-Sorbitol solution the surface tension decreased with increasing concentration. Correlation equations for the surface tension of three aqueous binary solutions as a function of temperature and concentration were determined.

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

1. INTRODUCTION

Water is the most prevalent liquid. Water has some extraordinary characteristics and it is an excellent solvent. Water and aqueous solutions play important roles in many fields including, for example, medical-science, foods, and industries. Consequently, consideration of freezing of aqueous solution is indispensable for research on the preservation of fresh foods and biomaterials.

Recently, a variety of engineering fields has began using aqueous binary solutions. For example, slush ice, which is produced by freezing aqueous solutions, is increasingly used as a cold thermal-energy storage material [1]. This use has stimulated investigation of the thermophysical properties and freezing characteristics of aqueous solutions [2, 3].

When aqueous solutions freeze under the existence of a free surface, surface-tension data, in particular, at temperatures close to the freezing

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point, are indispensable for achieving active control of its freezing heat transfer performance. We have performed measurements of the surface tension of aqueous binary solutions such as sodium chloride solution at low temperatures and reported its dependence on both temperature and concentration [4, 5].

In the present study, measurements of the surface tension of three typical aqueous binary solutions at various concentrations such as NH_4Cl, KCl, and D-Sorbitol, are presented. The first two solutions are closely related to biomaterials, such as human blood, and technologies in absorption refrigerators. D-Sorbitol is widely used as a basic material for both plastics and ascorbic acid and also as a food additive.

As for the properties of the solutions, a lot of measurements have been made. Measurements of surface tensions of aqueous solutions have also been reported. Though almost all these measurements were made with a high precision, the results are restricted to a narrow range. Therefore, previous data may be insufficient for actual use in engineering.

The present measurements aim to obtain surface-tension data for a variety of solutions which are widely used in engineering over a wide range of temperature and concentration. The effects of both the concentration and the temperature on the surface tension have been determined. 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

Figure 1 shows a schematic diagram of the apparatus. The apparatus consists basically of a thermostat, a sample liquid vessel, a cathetometer, and a cooling brine circulating system.

The thermostat, which has a height of 400 mm, a width of 350 mm, and a depth of 160 mm, was made of transparent lucite. Inside the thermostat, a heater, cooler, and fan were installed to regulate the temperature at any value between 30 and −25°C.

In the sample vessel, whose dimensions are 160 × 200 × 80 mm, a heater, a cooling tube, and a stirrer were set to keep the temperature of the sample constant. The temperatures of the liquid under test and the ambient air were measured with six chromel–alumel thermocouples (diameter, 0.3 mm). The apparatus was totally insulated by foamed polystyrene 100 mm thick. Two glass tubes 0.29 and 0.68 mm in inner radius were used for the capillary and were installed vertically within the testing liquid. The

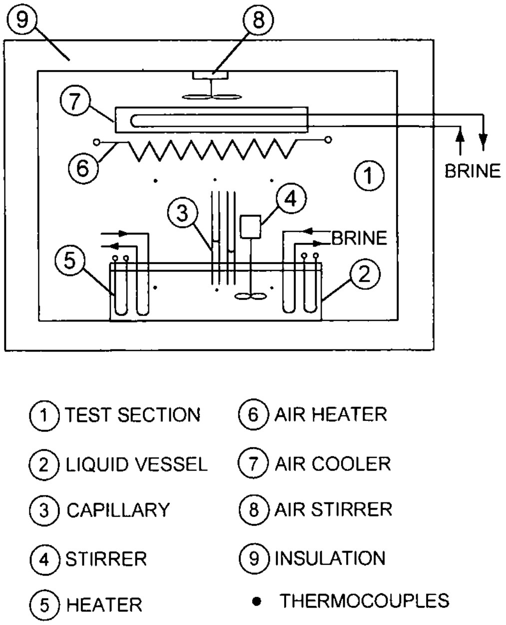

Fig. 1. Schematic diagram of measurement facilities.

levels of the liquid within both the tubes and the sample vessel were measured with a cathetometer whose resolution was 0.001 mm.

2.2. Measurement Procedure

Two glass tubes with inner radii of 0.29 and 0.68 mm were cleaned with pure water and acetone prior to each run. They were then set vertically into the sample vessel as capillaries. After equilibrium between the temperatures of the sample and the ambient air was reached at the prescribed temperature, the levels of the liquid in both the tubes and the sample vessel were measured with a cathetometer.

The differential capillary-rise method was used for measuring the surface tension. The measurement results were corrected by Sugden's revised method. According to the differential capillary-rise method, the surface tension of the liquid σ is determined by the following equations:

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

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

where a is the capillary constant; b, the radius of curvature at the bottom part of the meniscus; g, the gravitational acceleration constant; h, the liquid level in the capillary; ρ_L, the density of the liquid under test; ρ_a, the density of ambient air. Subscripts 1 and 2 correspond to capillary 1 and capillary 2, respectively. The quantities a and b are evaluated with the correction table of Sugden [6].

The measurements were obtained at temperatures ranging from +30°C to the temperature close to its equilibrium freezing temperature. The concentration of the solution was varied from 5 to 30 wt% for the D-Sorbitol solution and from 5 to 20 wt% for the other solutions.

In the present study, pure water ($R = 18.0$ MΩ), which was made by purifying water through a reverse-osmosis membrane, an ultrafiltration membrane, and the ion exchange process, was employed.

3. RESULTS AND DISCUSSION

3.1. Surface Tension of Water

Figure 2 shows the measurement results for the surface tension of pure water, as well as the reference data from different authors. From the figure, it can be noted that the present results are about 0.8% lower than the other data.

Considering the fact that the theoretical resistance of ideal pure water is 18.3 MΩ, the purity of the water in the present study is considered to be

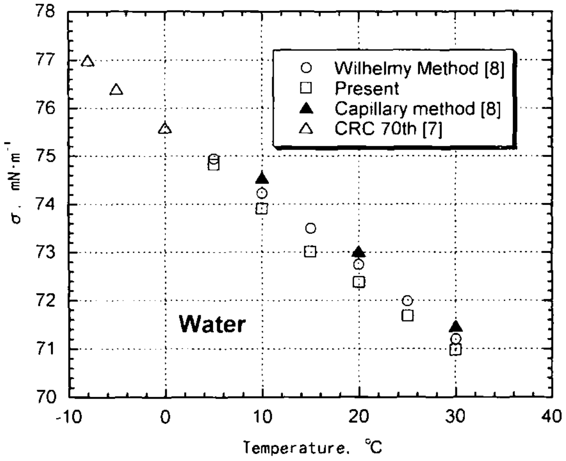

Fig. 2. Surface tension of water.

Tabel I. Surface Tension of D-Sorbitol Solution

	σ (mN · m^{-1}) at T (°C)						
C (wt%)	25	20	15	10	5	0	−3
5.0	69.96	70.78	71.72	72.69	73.56	74.25	
10.0	69.03	70.10	71.03	71.94	72.60	73.60	
15.0	68.52	69.33	70.30	71.04	71.93	72.98	
20.0	67.35	68.51	69.06	70.18	71.02	72.02	
25.0	66.94	67.73	68.28	69.40	70.02	71.12	
30.0	66.32	66.90	67.50	68.34	69.25	70.31	70.71

adequate. Therefore, the difference between the present results and the reference data is due to the inner-surface condition of the capillary.

3.2. Surface Tension of D-Sorbitol Aqueous Solution

Table I gives the measurement results for the surface tension of the D-Sorbitol solution, while Fig. 3 shows the surface tension versus the temperature of the solution. An inspection of Fig. 3 reveals that the surface tension of the solution decreases with an increase in temperature. And its slope decreases slightly as the temperature increases.

In general, the surface tension of the liquid decreases with an increase in temperature. According to the Eötbös equation, the decrease in surface

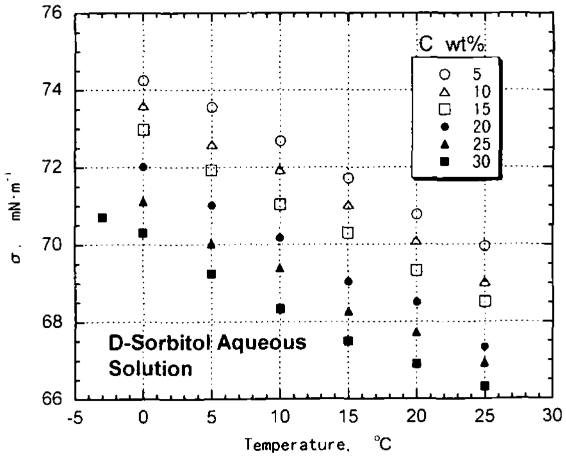

Fig. 3. Surface tension of D-Sorbitol aqueous solution.

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 molecular weight. Consequently, the decrease in slope with an increase in temperature in Fig. 3 can be interpreted in terms of the decrease in density of the solution with increasing temperature.

It can be observed that the surface tension of D-Sorbitol solution decreases with an increase in concentration, indicating surface-active characteristics. This tendency is due to absorption of the molecules of D-Sorbitol to the interface of the liquid and, also, to the fact that the absorbed molecules of D-Sorbitol increase as the concentration increases.

The increment in the surface tension $\Delta\sigma$ relative to that of pure water is presented in Fig. 4. It can be observed from the figure that the increment in surface tension is almost independent of the temperature. This is explained by the fact that the absorption of D-Sorbitol molecules decreases with an increase in temperature, with the effect of the temperature being canceled.

3.3. Surface Tension of Potassium Chloride Solution

Table II gives the measurement results for the surface tension of potassium chloride solutions, while Fig. 5 shows the surface tension versus the concentration of the solution. From the figure, it is observed that the surface tension decreases with an increase in temperature and that it increases with an increase in the concentration of solution.

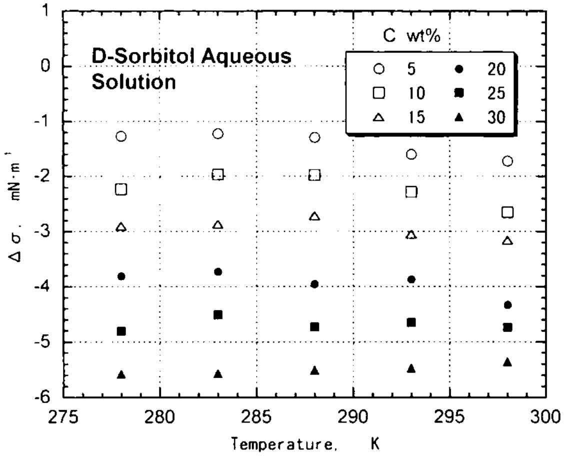

Fig. 4. Surface tension of D-Sorbitol aqueous solution.

Tabel II. Surface Tension of Potassium Chloride Solution

	$\sigma(\mathrm{mN \cdot m^{-1}})$ at $T(^{\circ}\mathrm{C})$							
C(wt%)	25	20	15	10	5	0	−5	−8
5.0	72.71	73.46	74.08	74.88	75.47	76.02		
10.0	73.40	74.29	75.27	75.96	76.53	77.25	77.73	
15.0	74.73	75.47	76.03	76.78	77.58	78.25	78.96	
20.0	76.05	76.78	77.20	78.04	78.71	79.30	79.98	80.33

In Fig. 5, reference data at 20°C are also included. The present results are slightly lower than the reference data. Considering the measurement results for the surface tension of water in Fig. 2, the present data appear to agree well with the reference data.

3.4. Surface Tension of Ammonium Chloride Solution

The measurement results for the surface tension of ammonium chloride solutions are shown in Table III and Fig. 6. The dependence of the surface tension on the temperature and concentration is similar to that of the potassium chloride solution mentioned in the previous section.

The increment in surface tension $\Delta\sigma$ relative to that of pure water is indicated in Fig. 7. It is said in general that $\Delta\sigma$ is in proportion to the

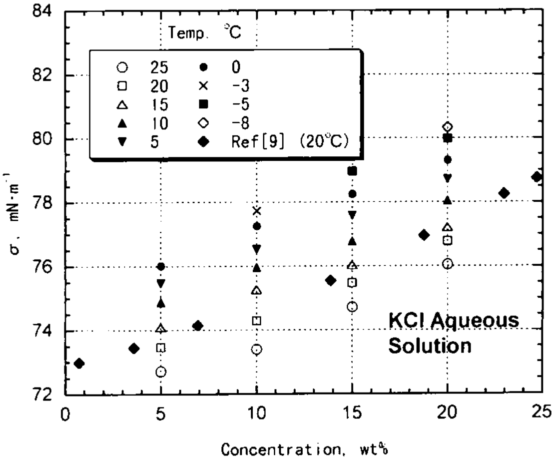

Fig. 5. Surface tension of KCl aqueous solution.

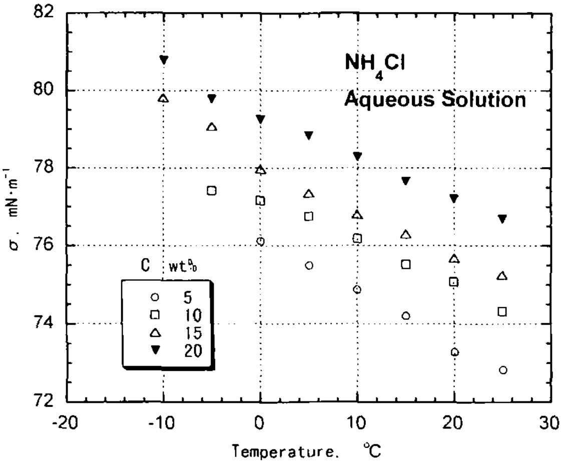

Fig. 6. Surface tension of NH_4Cl aqueous solution.

Tabel III. Surface Tension of Ammonium Chloride Solution

	σ (mN · m^{-1}) at T (°C)							
C (wt%)	25	20	15	10	5	0	−5	−10
5.0	72.83	73.28	74.21	74.88	75.50	76.12		
10.0	74.32	75.07	75.52	76.18	76.76	77.16	77.42	
15.0	75.25	75.68	76.30	76.81	77.35	77.97	79.08	79.81
20.0	76.69	77.20	77.66	78.29	78.84	79.26	79.78	80.79

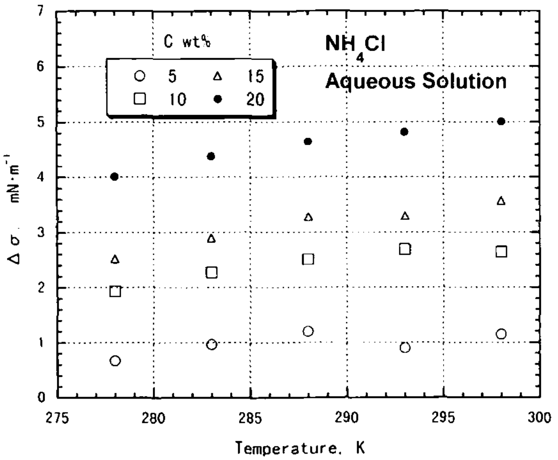

Fig. 7. Surface tension of NH_4Cl aqueous solution.

absolute temperature. An inspection of Fig. 7 reveals that $\Delta\sigma$ increases with an increase in temperature, while the rate of increase decreases as the temperature increases.

Both ammonium chloride and potassium chloride are electrolytes, and they are ionized in aqueous solutions. In a solution ions tend to be repelled from the surface by the hydration effect, and the effect increases with an increase in the ratio of the charge of the ion to its surface area, so that the surface tension increases as that ratio increases. Therefore, as the concentration of the solution, namely, the concentration of ions, increases, the traction effect to the molecules of water at the interface tends to increase, which results in an increase in the surface tension of the electrolyte solution.

As for the electrolyte solutions in the present study, both of them possess the same anion (Cl^-). The electric charge of the ammonium ion (NH_4^+) and that of the potassium ion (K^+) are exactly the same. Accordingly, though the ion radius of NH_4^+ is slightly greater than that of K^+, the degree of hydration effect is almost the same. This is the reason that only small differences between their surface tensions are observed.

3.5. Correlation of the Experimental Data

Figures 8–10 present the correlated results for the surface tension of D-Sorbitol solution, potassium chloride solution, and ammonium chloride

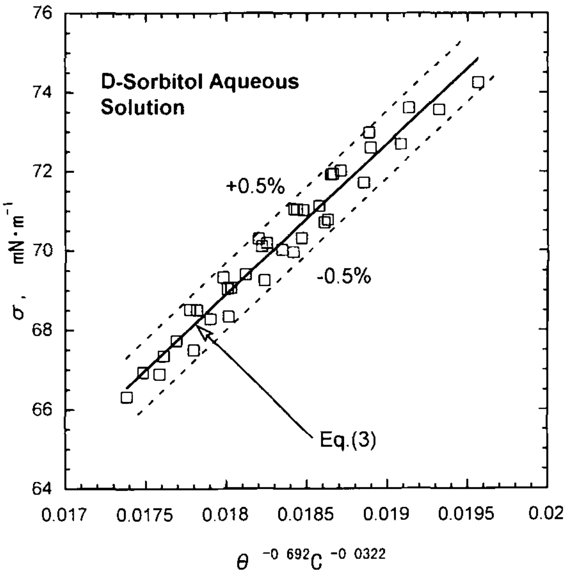

Fig. 8. Surface tension of D-Sorbitol aqueous solution.

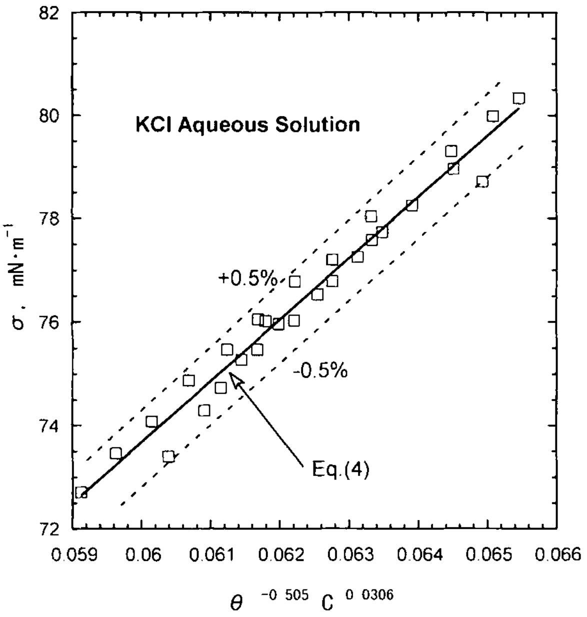

Fig. 9. Surface tension of KCl aqueous solution.

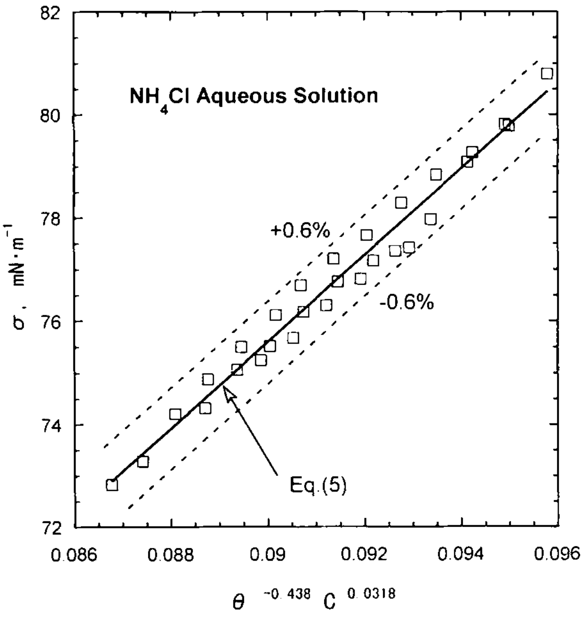

Fig. 10. Surface tension of NH_4Cl aqueous solution.

solution, respectively, as a function of both concentration and temperature within the deviation range shown in each figure. The correlation equations and parameter ranges are as follows.

D-Sorbitol solution:

$$\sigma = 3.828 \times 10^{3} \theta^{-0.692} C^{0.0322} \qquad [270 \leqslant \theta \leqslant 298\ \mathrm{K},\ 5 \leqslant C \leqslant 30\ \mathrm{wt\%}] \qquad (3)$$

Potassium chloride solution:

$$\sigma = 1.228 \times 10^{3} \theta^{0.505} C^{0.0306} \qquad [265 \leqslant \theta \leqslant 298\ \mathrm{K},\ 5 \leqslant C \leqslant 20\ \mathrm{wt\%}] \qquad (4)$$

Ammonium chloride solution:

$$\sigma = 8.398 \times 10^{2} \theta^{0.483} C^{0.0318} \qquad [263 \leqslant \theta \leqslant 298\ \mathrm{K},\ 5 \leqslant C \leqslant 20\ \mathrm{wt\%}] \qquad (5)$$

where θ denotes the absolute temperature of the solution.

4. CONCLUSIONS

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 solution was found to decrease as the concentration of the solution increases for D-Sorbitol, while it increases as the concentration of the solution increases for the other materials within the parameter range covered in the present study. Furthermore, correlation equations for surface tension as a function of temperature and concentration have been determined.

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