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Surface Tensions and Thermal Conductivities of Aqueous LiBr-Based Solutions Containing *n*-Octanol and 2-Ethyl-1-Hexanol: Application to an Absorption Heat Pump[1]

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Surface tensions and thermal conductivities were measured for LiBr + 1,3-propanediol + water and LiBr + LiI + 1,3-propanediol + water. These two mixtures were chosen as one of the potential candidates for working fluids for absorption heat pumps. Surface tensions and thermal conductivities were measured by the capillary rise method equipped with a cathetometer and the transient hot wire method with a coated tantalum wire, respectively. The measured surface tension and thermal conductivity data were well correlated with a simple polynomial function of temperature and absorbent concentration. In addition, the surface tensions of LiBr + 1,3-propanediol + water containing a small amount of alcohol-based surfactants, *n*-octanol and 2-ethyl-1-hexanol, were also measured at 298.15 K by the ring method. An increase in the surfactant concentration up to about 500 ppm leads to a gradual decrease in the mixture surface tensions.

KEY WORDS: absorption heat pump; capillary rise method; LiBr aqueous solutions; surface tension; thermal conductivity; transient hot wire method.

1. INTRODUCTION

Aqueous electrolyte solutions with organics are frequently used in industrial processes. Many research areas such as interfacial phenomena, colloidal systems, gas absorption, and absorption heat pumps require reliable data of surface tension and thermal conductivity of aqueous electrolyte solutions.

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Highly concentrated aqueous LiBr-based solutions have commonly been used as working fluids for absorption heat pumps. In this connection, many studies on surface tension related to absorption heat pumps have been restricted mainly to aqueous LiBr solutions [1, 2]. In our previous studies [3, 4], LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5, by mass) and LiBr + LiI + 1,3-propanediol + water [LiBr/LiI = 4, by mole, and (LiBr + LiI)/1,3-propanediol = 4, by mass] mixtures were proposed as possible candidates for air-cooled absorption chillers. In this study, the surface tensions of these two mixtures were measured by the capillary rise method to provide basic information for new working fluids. In particular, the decrease in surface tension by alcoholic additives greatly influences the heat/mass transfer enhancement of absorption heat pumps. To examine this additive effect, the surface tensions of LiBr + 1,3-propanediol + water with *n*-octanol and with 2-ethyl-1-hexanol at 298.15 K were measured by the ring method.

Besides surface tension, the optimum design of the individual units of absorption heat pumps, including heat transfer analysis, requires reliable thermal conductivity data at the operating conditions. Recently, the transient hot wire method [5–7] has been widely used to measure the thermal conductivity for gas and liquid mixtures. This method comprises many advantages such as exclusion of the convection error, fast measurement, high accuracy, and better reproducibility compared with the steady-state method. To apply the transient hot wire method to electrolyte solutions, proper insulation of the metal wire is needed. In this study, a tantalum wire coated by anodization was used to overcome problems caused by the bare wire. The measured surface tension and thermal conductivity data were well correlated with a simple polynomial function expressed in terms of temperature and concentration.

2. EXPERIMENTAL

2.1. Materials

Lithium bromide (+99.5 %), lithium iodide (+99.5 %), and 1,3-propanediol (+98 %) manufactured by Sigma–Aldrich Chemical Company were used without further purification. The water used for all solutions was triply distilled.

2.2. Surface Tension

The apparatus for the capillary rise method consists of a water bath, bath circulator, capillary tube, thermometer, and cathetometer. The temperature of the capillary tube was controlled by the bath circulator (JEIO Tech. RBC-20) within ±0.1 K. The temperature of the fluid in the capillary tube was measured by a thermometer with an uncertainty of ±0.1 K. The height of the liquid rise in the capillary tube was measured by a cathetometer (N.O.W. NCM 30) with an uncertainty of 10^{-5} m. Determination of the capillary radius was carried out using benzene as a reference fluid. During the experiment, the height difference between the capillary and the outer tube meniscus was measured using the cathetometer. The height difference was measured at least five times for each data point, with a reproducibility of $\pm 2 \times 10^{-4}$ m. The surface tension could then be calculated from a simple equation that includes the radius of the capillary, the height difference between two menisci, and the density of a sample.

The surface tensions of electrolyte solutions containing additives were measured by a commercially available dynamic contact angle analyzer (DCA314; Cahn Corp.) using the ring method. Since the experimental apparatus and procedure for the ring method are available elsewhere [1], a detailed description is omitted here. The temperature of the solution was maintained at 298.15 K with an uncertainty of ±0.1 K. The experiments were carried out under automatic operation. The measurements were performed at least three times, and the reproducibility was within ±0.5%.

2.3. Thermal Conductivity

The measurement was performed in an absolute manner with a coated tantalum wire. Since a detailed description of the experimental procedure and the reduction of the raw data is available in the literature [5–7], only the revised parts of our apparatus are introduced in this paper. A schematic diagram of the experimental apparatus is presented in Fig. 1. The whole apparatus is divided into two major parts of a Wheatstone bridge and measurement system. The Wheatstone bridge includes two standard resistors of 10 kΩ (R_1 and R_2), a variable resistor (R_V), and a coated tantalum wire (R_S) used as both a heat source and a detector of the temperature rise. A tantalum (99.9%) wire with a nominal diameter of 25 μm from ESPI was mounted to the cell by spot welding. The length of the wire was measured by a cathetometer with an uncertainty of 10^{-5} m. The wire was anodized to form tantalum pentoxide by a method described in the literature [5]. The fluid temperature was measured by a K-type thermocouple, inserted into the cell, with an uncertainty of ±0.1 K. The entire cell was placed in the water bath, whose temperature was controlled by an external circulator to within ±0.2 K. The measurement system consists of two digital multimeters (DMM), a function generator, a power supply, and a personal computer. The DMM (HP3410) equipped with an HP-IB interface was purchased

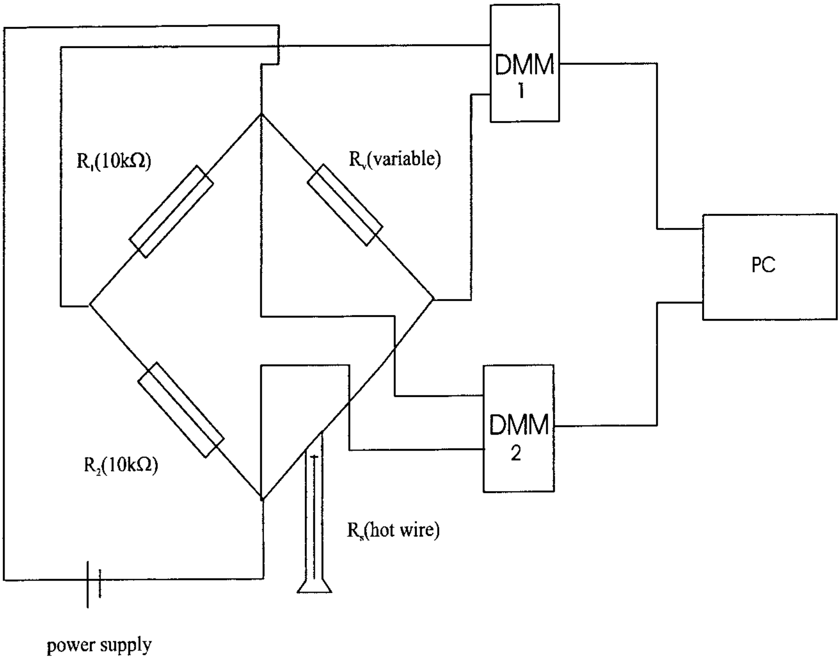

Fig. 1. Schematic diagram of the experimental apparatus for thermal conductivity measurement.

from Hewlett Packard and connected to the computer to receive the offset voltage from the Wheatstone bridge and the applied power from the power supply. A power supply for the step voltage input and a function generator for the external triggering were manufactured by LG Electronics. The offset voltage and the applied power were simultaneously recorded to the computer, controlled by a Visual Basic program.

3. RESULTS

3.1. Surface Tension

The surface tensions measured by the capillary rise method were calculated from the following simple equation:

$$y = \tfrac{1}{2} hrdg \tag{1}$$

where y is the surface tension, h is the height difference between the capillary and the outer tube meniscus, r is the capillary radius, d is the density of sample, and g is the gravitational acceleration. To determine the radius of the capillary tube, the calibration was carried out using the known surface tension and density of benzene. The resulting radius of the capillary tube was found to be 2.71×10^{-4} m. To check the reliability of the experimental apparatus and procedures used in this study, the surface tensions of the LiBr + water solution were measured at various temperatures and found to be in good agreement with literature values [8] as shown in Fig. 2. The maximum deviation was less than 2.0%, which is acceptable in the measurement of surface tension. The surface tensions of the LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5, by mass) system were measured in the temperature range of 298.15 to 323.15 K and an absorbent concentration range up to 65 mass%. The experimental results are presented in Table I and depicted in Fig. 3. As shown in Fig. 3, the surface tension of the ternary system decreased as the temperature increased over the entire absorbent concentration range. The temperature

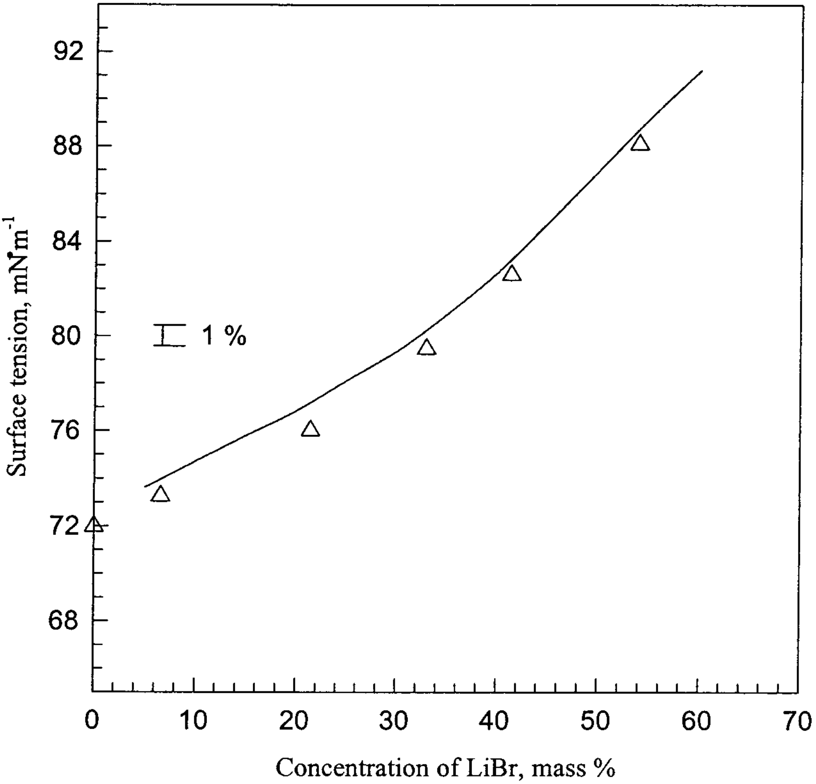

Fig. 2. Surface tensions of LiBr + water at 298.15 K versus concentration (mass%) of LiBr: △, this work; ——, Ref. 8.

Table I. Surface Tensions for LiBr + 1,3-Propanediol + Water (LiBr/1,3-Propanediol = 3.5, by Mass) with Absorbent Concentration X (Mass%)

	Surface tension, σ (mN · m^{-1})					
X	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0.00	71.98	71.20	70.40	69.60	68.77	67.94
12.5	70.97	70.42	69.73	68.98	68.33	67.86
35.5	69.19	68.77	68.29	67.95	67.74	67.30
46.2	68.04	67.83	67.67	67.37	66.97	66.56
56.3	66.52	66.55	66.40	66.26	66.11	65.88
61.1	65.83	65.79	65.73	65.53	65.38	65.27
65.9	65.27	64.94	64.79	64.68	64.55	64.41

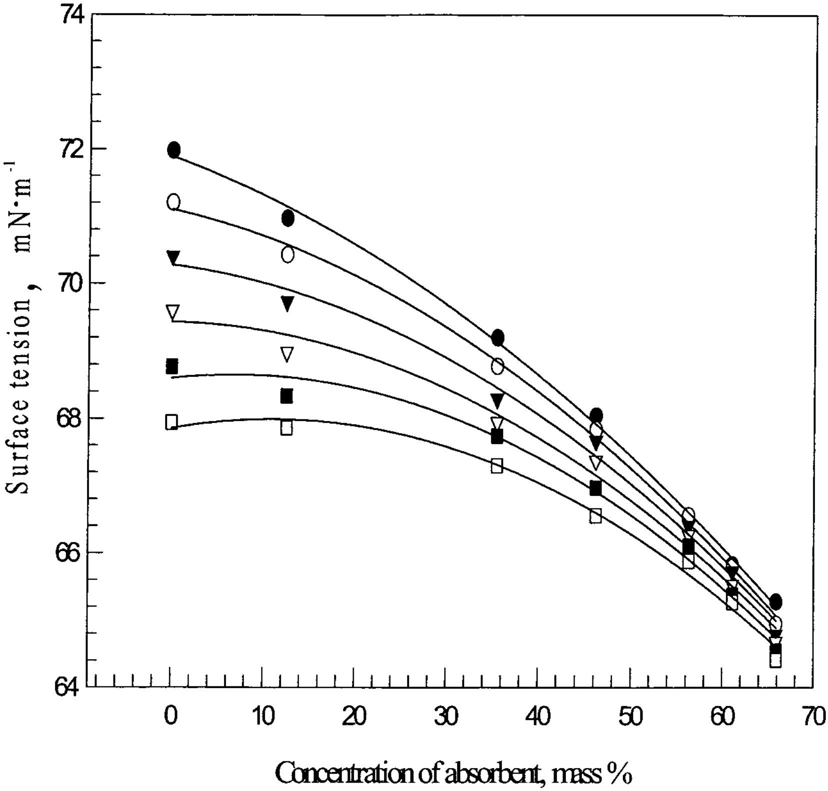

Fig. 3. Surface tensions of LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5, by mass) at various temperatures: ●, T = 298.15 K; ○, T = 303.15 K; ▼, T = 308.15 K; ▽, T = 313.15 K; ■, T = 318.15 K; □, T = 323.15 K; ——, calculated values.

effect on surface tension decreases with an increase in the absorbent concentration. The surface tensions of the solutions, highly concentrated with absorbents of LiBr + 1,3-propanediol, became lower than those of the diluted solutions, which is the opposite trend, and quite different from the surface tensions of the LiBr + water solution shown in Fig. 2. This might be due to the low surface tension of 1,3-propanediol in the solution. The increase in LiBr as well as 1,3-propanediol concentrations made the overall surface tensions of the mixed solutions lower. The experimental surface tension data were correlated with the following polynomial equation:

$$\sigma = \sum_{i=0}^{2} [(A_i + B_i T + C_i T^2)\, X^i] \tag{2}$$

σ is the surface tension in $\mathrm{mN \cdot m^{-1}}$, T is the temperature in K, and X is the concentration of the absorbent in mass%. The resulting coefficients for Eq. (2) are listed in Table II. The overall average absolute deviation (AAD) was found to be 0.188%.

The surface tensions of LiBr + LiI + 1,3-propanediol + water [LiBr/LiI = 4, by mole, and (LiBr + LiI)/1,3-propanediol = 4, by mass] were measured up to 53 mass% absorbent concentration over a temperature range from 298.15 to 323.15 K as shown in Table III and Fig. 4. The effect of absorbent concentration and temperature of this mixture appears to be similar to that of LiBr + 1,3-propanediol + water. The experimental surface tensions of LiBr + LiI + 1,3-propanediol + water were fitted by the following equation:

$$\sigma = \sum_{i=0}^{2} [(A_i + B_i T)\, X^i] \tag{3}$$

The resulting regressed coefficients are listed in Table IV. The overall deviation between the experimental results and the calculated values was found to be 0.286% in AAD.

Table II. Coefficients Regressed in Eq. (2) for the Surface Tension of LiBr + 1,3-Propanediol + Water (LiBr/1,3-Propanediol = 3.5, by Mass)

	A_i	B_i	C_i
$i = 0$	1.337×10^{2}	-2.485×10^{-1}	1.379×10^{-4}
$i = 1$	-3.078	1.676×10^{-2}	-2.214×10^{-5}
$i = 2$	2.853×10^{-2}	-1.767×10^{-4}	2.628×10^{-7}

Table III. Surface Tensions for LiBr + LiI + 1,3-Propanediol + Water [LiBr/LiI = 4, by Mole, and (LiBr + LiI)/1,3-Propanediol = 4, by Mass] with Absorbent Concentration X (Mass%)

	Surface tension, σ (mN · m^{-1})					
X	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
16.1	70.38	69.86	69.10	68.35	67.52	66.93
30.2	68.41	68.02	67.48	67.05	66.42	65.84
42.6	66.84	66.32	65.90	65.43	65.03	64.72
53.6	65.68	65.28	64.92	64.64	64.32	63.92

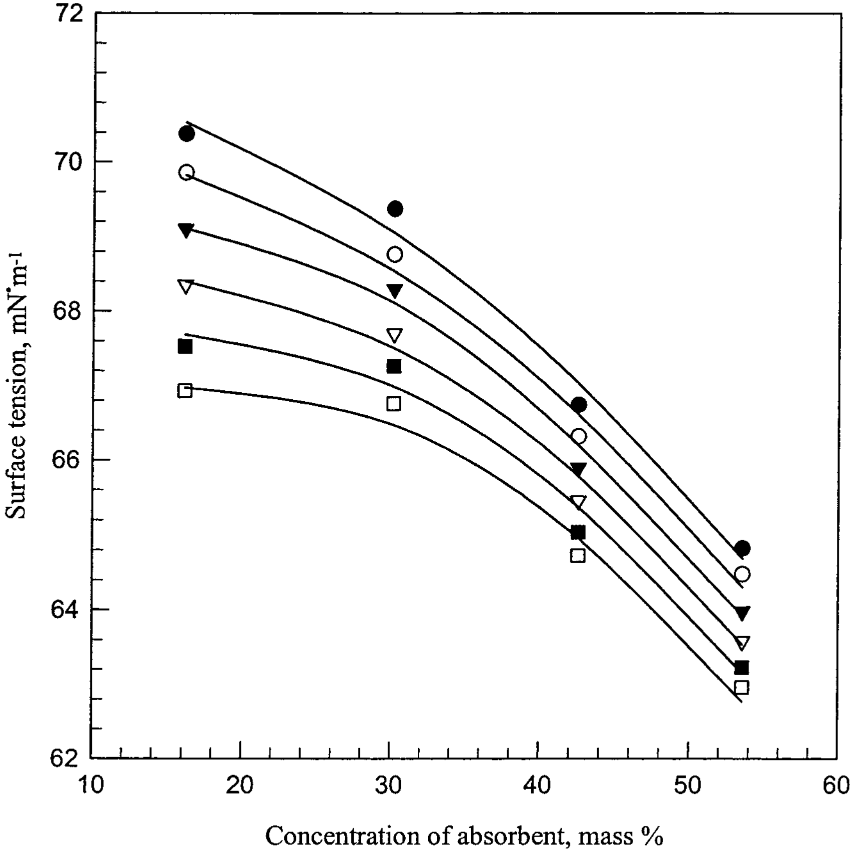

Fig. 4. Surface tensions of LiBr + LiI + 1,3-propanediol + water [LiBr/LiI = 4, by mole, and (LiBr + LiI)/1,3-propanediol = 4, by mass] at various temperatures: ●, $T = 298.15$ K; ○, $T = 303.15$ K; ▼, $T = 308.15$ K; ▽, $T = 313.15$ K; ■, $T = 318.15$ K; □, $T = 323.15$ K; ——, calculated values.

Table IV. Coefficients Regressed in Eq. (3) for the Surface Tension of $LiBr + LiI + 1,3$-Propanediol + Water [LiBr/LiI = 4, by Mole, and (LiBr + LiI)/1,3-Propanediol = 4, by Mass]

	$i = 0$	$i = 1$	$i = 2$
A_i	1.336×10^{2}	-1.459×10^{2}	1.117×10^{2}
B_i	-2.095×10^{-1}	4.878×10^{-1}	-4.475×10^{-1}

The surface tensions of LiBr + 1,3-propanediol + water with *n*-octanol and 2-ethyl-1-hexanol were measured at 298.15 K by the Dunoy ring method. The absorbent concentrations of LiBr + 1,3-propanediol were 54.5 and 67.9 mass %. The experimental surface tensions with the two surfactants are presented in Table V. As shown in Figs. 5 and 6, the addition of *n*-octanol and 2-ethyl-1-hexanol up to approximately 25 ppm has little influence on the surface tensions of the solution, but above 25 ppm the surface tensions abruptly decrease. The decreasing rate of surface tension for the 67.9 mass % absorbent concentration solution is steeper than that for the 54.5 mass % absorbent concentration solution. The critical concentrations of the two additives appeared near a few hundreds of parts per million, and above this concentration, the surface tension did not decrease further. The critical concentration of *n*-octanol was higher than that of 2-ethyl-1-hexanol because of the higher solubility of *n*-octanol in the solution [9].

3.2. Thermal Conductivity

To verify the experimental apparatus and procedure, thermal conductivities of the aqueous 15.3 mass % NaCl solution were measured and

Table V. Surface Tension ($mN \cdot m^{-1}$) of LiBr + 1,3-Propanediol + Water (LiBr/1,3-Propanediol = 3.5, by Mass) with Surfactants at 298.15 K

Additive concentration (ppm)	Absorbent concentration (mass %)			
	54.5	67.9	54.5	67.9
	With *n*-octanol		With 2-ethyl-1-hexanol	
25	64.15	61.00	63.50	63.08
50	62.98	55.98	61.42	58.00
100	54.73	48.05	57.75	51.20
200	50.83	37.50	50.65	42.23
500	37.00	27.20	42.08	40.05
1000		27.05	36.90	38.40

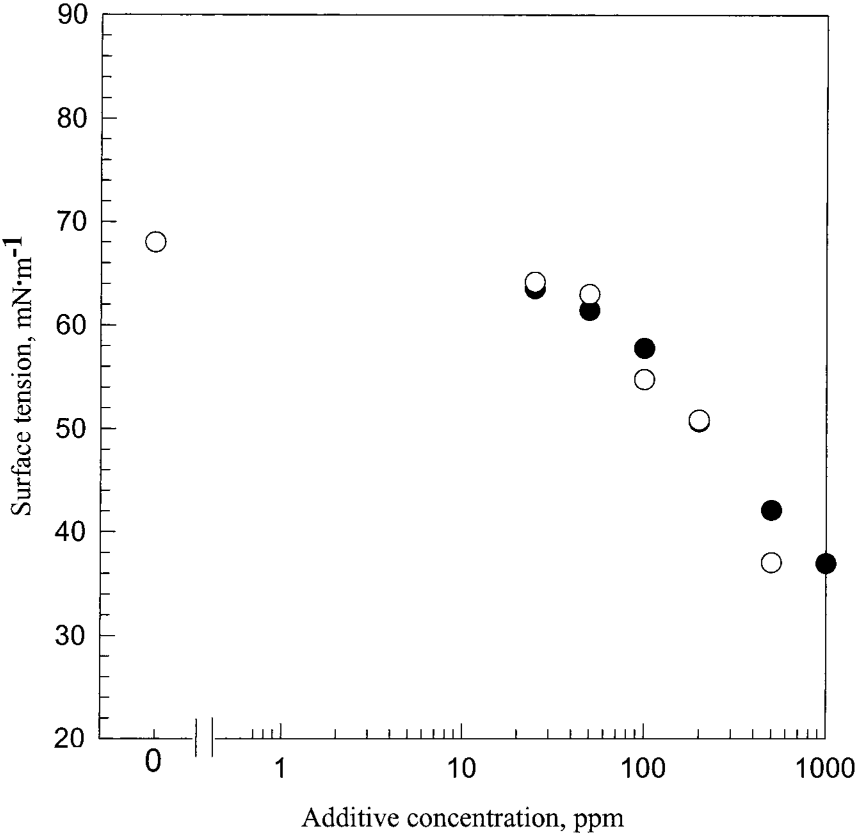

Fig. 5. Surface tensions of a 54.5 mass% LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5, by mass) solution with *n*-octanol and 2-ethyl-1-hexanol at 298.15 K: ●, 2-ethyl-1-hexanol; ○, *n*-octanol.

compared with the literature data of Nagasaka and Nagashima [10]. The reduction of thermal conductivity from the offset voltage and correction of temperature to compensate for the deviation from the ideal model were carried out in a manner similar to that given in the literature [5–7, 10]. The experimental results were in agreement within ±1%. In this work, the total correction for the temperature rise was less than ±0.7% and was found to have a negligible effect on thermal conductivity. The measurements of thermal conductivity were performed for the LiBr + 1,3-propanediol + water and LiBr + LiI + 1,3-propanediol + water solutions with the same absorbent ratios in the temperature range from 285 to 305 K. The concentrations of the absorbents treated in this work are 67.9 mass% for LiBr +

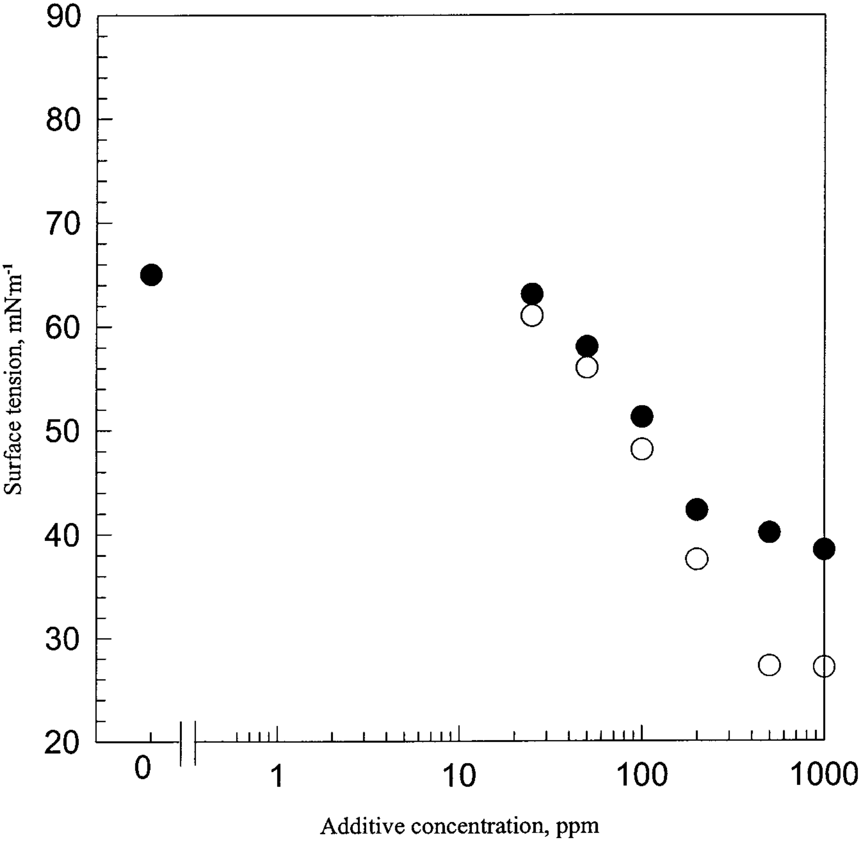

Fig. 6. Surface tensions of a 67.9 mass% LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5, by mass) solution with *n*-octanol and 2-ethyl-1-hexanol at 298.15 K: ●, 2-ethyl-1-hexanol; ○, *n*-octanol.

1,3-propanediol + water and 69.9 mass% for the LiBr + LiI + 1,3-propanediol + water system. The corresponding density and heat capacity data for the temperature correction were obtained from our previous studies [3, 4]. The experimental data are listed in Table VI and presented graphically in Fig. 7. The solution thermal conductivity increased slightly with temperature, which is similar to the trend of the aqueous LiBr solution. Considering the working fluid conditions for an absorber of air-cooled absorption chillers, the present thermal conductivity data are expected to give the basic information for the design of absorption systems. Each data set was satisfactorily regressed to linear equations of $\lambda = 0.222 + 0.000635T$ for LiBr + 1,3-propanediol + water and $\lambda = 0.215 + 0.000596T$ for LiBr +

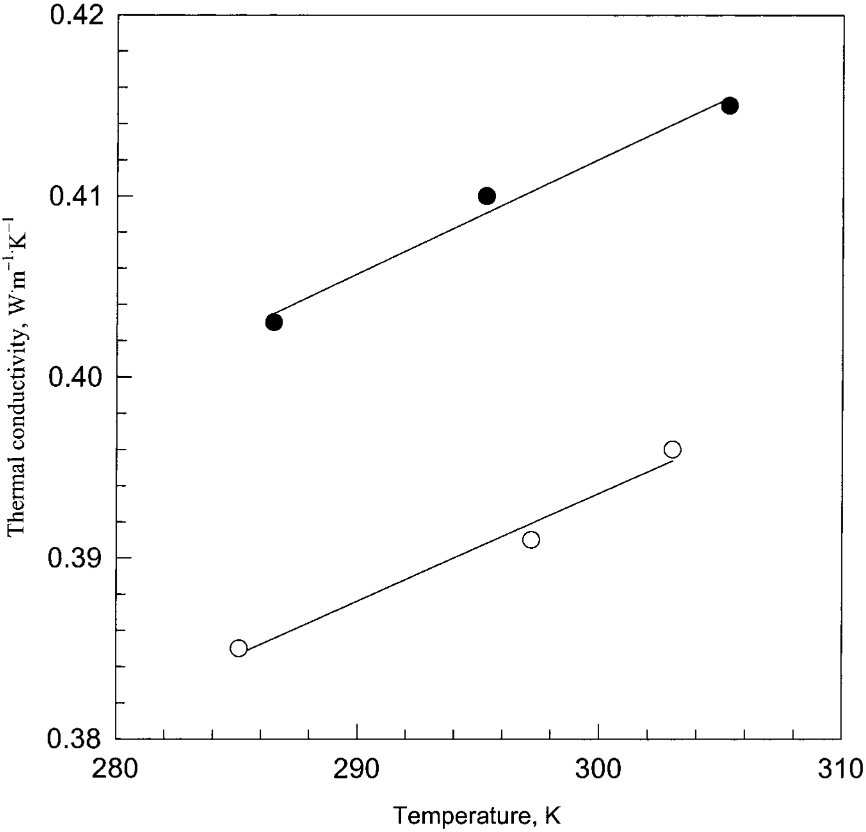

Fig. 7. Thermal conductivities of 67.9 mass% LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5, by mass) and 69.9 mass% LiBr + LiI + 1,3-propanediol + water [LiBr/LiI = 4, by mole and (LiBr + LiI)/1,3-propanediol = 4, by mass] versus temperature: ●, LiBr + 1,3-propanediol + water; ○, LiBr + LiI + 1,3-propanediol + water.

LiI + 1,3-propanediol + water. λ is the thermal conductivity measured in $W \cdot m^{-1} \cdot K^{-1}$, and T is the temperature in K. The AAD between the experimental and the calculated values did not exceed 0.4%.

4. CONCLUSION

Surface tensions of the LiBr + 1,3-propanediol + water (LiBr/1,3-propanediol = 3.5, by mass) and LiBr + LiI + 1,3-propanediol + water [LiBr/LiI = 4, by mole, and (LiBr + LiI)/1,3-propanediol = 4, by mass] systems were measured with the capillary rise method. The mixture surface tensions decreased with increasing temperature and concentration of the absorbents.

Table VI. Thermal Conductivities of LiBr + 1,3-Propanediol + Water (LiBr/1,3-Propanediol = 3.5, by Mass) and LiBr + LiI + 1,3-Propanediol + Water [LiBr/LiI = 4, by Mole, and (LiBr + LiI)/1,3-Propanediol = 4, by Mass]

Absorbent mass %, X	Temperature, T (K)	Thermal conductivity, λ ($W \cdot m^{-1} \cdot K^{-1}$)
	LiBr + 1,3-propanediol + water	
67.9	286.5	0.403
	295.3	0.410
	305.3	0.415
	LiBr + LiI + 1,3-propanediol + water	
69.9	285.1	0.385
	297.2	0.391
	303.0	0.396

The experimental data were successfully regressed by simple polynomial equations. The effect of an alcoholic surfactant on the surface tension was investigated for LiBr + 1,3-propanediol + water at 298.15 K. The addition of the surfactant resulted in an abrupt decrease in the solution surface tension, particularly at a high absorbent concentration. The thermal conductivities of the same system were measured by the transient hot wire method with a coated tantalum wire at the concentration at which the treated solutions exist in an absorber in air-cooled absorption chillers. The experimental thermal conductivities increased with temperature and were regressed by a linear equation of temperature.

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