Surface Tensions and Differential Enthalpies of Dilution of the Lithium Bromide + Lithium Iodide + 1,3-Propanediol + Water System

Ki-Sub Kim and Huen Lee*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusung-dong, Yusung-gu, Taejon 305-701, South Korea

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The lithium bromide + lithium iodide + 1,3-propanediol + water (LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ mass ratio = 4) solution was chosen as one of the potential candidates for an air-cooled absorption chiller. For this system, the surface tensions and differential enthalpies of dilution were measured at various temperatures and absorbent (LiBr + LiI + $HO(CH_2)_3OH$) concentration ranges by using the capillary rise method and an Isoperibol solution calorimeter, respectively. The measured data were well correlated with the simple polynomial equations. The deviations between the experimental and calculated values in the surface tension and differential enthalpy of dilution measurements were 0.10 and 2.8%.

Introduction

Various working fluids used for absorption heat pumps have been suggested to improve the performance and overcome the problems such as corrosion and crystallization of the conventional lithium bromide + water absorbent.[1−3,6] One of the most important components of an absorption heat pump is the absorber where the refrigerant vapor is absorbed into the absorbent. The performance of the absorption heat pump is greatly affected by the characteristics of heat and mass transfer in an absorber. The efficiency of the absorber is lowest compared with those of other units such as the generator, condenser, and evaporator in the absorption heat pump. The heat and mass transfer characteristics in the absorber have been understood to cause the difficulties in the optimal design and advanced process development. While the absorber of a falling film type is commonly used in the real machine, there exists limited information on the fundamental data and correlations for the design propose. Also, the enhancement of the heat and mass transfer in the absorber is one of the most important issues in the performance improvement of the absorption heat pump. The surface tension of the working fluid is one of the important properties to investigate the enhancement of the heat and mass transfer in the absorber. In the absorption chiller, both the enthalpy of absorption in the absorber and the enthalpy of condensation in the condenser should be measured by the proper cooling device. In particular, the accurate and direct measurements of the differential enthalpies of dilution become very important because the values of the enthalpies of absorption at the absorber and condenser can be calculated from the differential enthalpy of dilution data.

In our previous study,[1] the lithium bromide + lithium iodide + 1,3-propanediol + water system (LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ mass ratio = 4) was specially chosen to overcome the solubility limit of the lithium bromide + water solution as a possible working fluid for an absorption heat pump, and several experiments such as solubility, vapor pressure, density, and viscosity measurements were carried out. However, in this study, the surface tensions and differential enthalpies of dilution of the proposed working fluid without additives were measured by the capillary rise method and an Isoperibol solution calorimeter, respectively.

Experimental Section

Materials. The lithium bromide (99%), lithium iodide (99%), and 1,3-propanediol (98%) were supplied by Sigma−Aldrich Chemical Co. All materials were used without further purification. All solutions were prepared with triple distilled water.

Apparatus and Procedure. 1. Surface Tension. The surface tensions of the lithium bromide + lithium iodide + 1,3-propanediol + water system were measured by the capillary rise method. The equipment and procedure used for the surface tension measurement were the same as those for our previous investigation.[2] The whole apparatus consists of a water bath, a bath circulator, a capillary tube, a thermometer (mercury-filled glass thermometer), and a cathetometer. The temperature of the capillary tube was controlled within ±0.1 K by the bath circulator. The solution temperature in the capillary tube was measured with the thermometer with an accuracy of ±0.1 K. The height of the liquid rise in the capillary tube was read with the cathetometer with an accuracy of 10^{-5} m. The surface tension was directly calculated from the following simple equation:

$$\sigma = \frac{1}{2}hrdg \tag{1}$$

where σ 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,[1] and g is the gravitational acceleration. The reproducibility of surface tension measurements was within ±1%. The experimental apparatus and procedure were verified in the previous work.[2] A

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* Corresponding author. E-mail: hlee@mail.kaist.ac.kr. Fax: 82-42-869-3910. Telephone: 82-42-869-3917.

10.1021/je0101956 CCC: $22.00

Table 1. Surface Tensions of the LiBr + H_2O (LiBr/(LiBr + H_2O) Mass Ratio = 0.6) System

	σ/mN·m^{-1}		
T/K	Uemura et al.	this work	relative error (%)
298.15	91.22	92.45	1.35
303.15	90.18	91.23	1.16
308.15	89.03	90.34	1.47
313.15	88.02	88.91	1.01
318.15	86.88	87.03	0.17
323.15	85.80	85.50	0.35

similar test experiment was done with a pure water and lithium bromide solution in 60 mass %. Table 1 shows the comparison between the experimental and literature data,[5] and the resulting average absolute deviation was 0.92%.

2. Differential Enthalpy of Dilution. An isoperibol solution calorimeter (CSC4300) was used to measure the differential enthalpy of dilution of absorbent solutions.[7,8] To measure the differential enthalpy of dilution, to begin with, the energy equivalent E in kilojoules per kelvin should be obtained. The following equation defines the energy equivalent E.

$$E = mC_p + \epsilon \tag{2}$$

where m is the mass of the sample solution, C_p is the specific heat capacity of the sample, and ϵ is the heat capacity of the apparatus including the Dewar vessel, stirring rod, heater, and thermistor. For the measurement of the energy equivalent, an accurately weighed sample solution (approximate volume of 25 cm^3) of a desired concentration was placed into the Dewar vessel. The thermistor, calibration heater, and stirring rod were immersed when the vessel was clamped on the isoperibol solution calorimeter. The stirrer and heater were then turned on to heat up the sample solution to a slightly lower temperature than the desired one. After 300 s passed from that point, an actual measuring process including 200 s of holding time without heating, 400 s of heating, and 200 s of holding time began. All the procedures of the measurements were completely controlled by a computer. Before the experiment was run, a calibration procedure was performed to obtain the energy equivalent E which was required to calculate the differential enthalpy of dilution. The actual measuring procedure of the differential enthalpy of dilution was almost similar to the calibration procedure. Prior to an actual measurement, an absorbent solution (approximately 25 cm^3) with a fixed concentration was charged into the Dewar vessel while accurately weighted water (approximately 0.01 g) was placed into the small cylindrical container including fragile glass covers at the top and bottom sides. The mixing was initiated by breaking the glass covers with a plunger rod. The mass of water used for dilution m_{water}, the temperature increase during the mixing process ΔT, and the energy equivalent E were used to calculate the differential enthalpy of dilution H_d at the experimental concentration and temperature.

$$H_d = \Delta TE/m_{\text{water}} \tag{3}$$

The reproducibility of the differential enthalpy of dilution measurements was within ±2.5%. To verify the experimental apparatus and procedure, the enthalpies of dilution for the LiBr + water solution at 298.15 K were measured in the previous work.[6] Figure 1 shows the comparison between the experimental and literature data,[5] and the resulting average absolute deviation was found to be 3%.

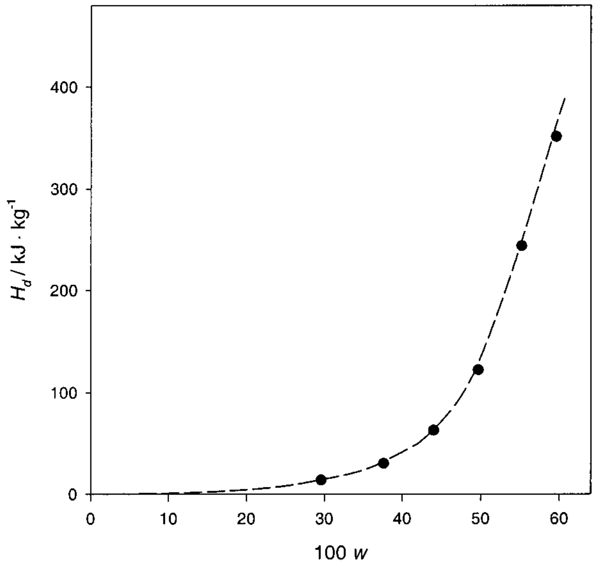

Figure 1. Differential enthalpies of dilution of the LiBr + H_2O system at 298.15 K: ●, this work; - - -, Uemura et al.[5,6]

Table 2. Measured Surface Tensions of the LiBr + LiI + $HO(CH_2)_3OH$ + H_2O (LiBr/LiI Mole Ratio = 4, (LiBr + LiI)/$HO(CH_2)_3OH$ Mass Ratio = 4) System

	σ/mN·m^{-1} at the following values of T/K					
w	298.15	303.15	308.15	313.15	318.15	323.15
0.1614	70.38	69.86	69.10	68.35	67.52	66.93
0.3021	68.41	68.02	67.48	67.05	66.42	65.84
0.4260	66.84	66.32	65.90	65.42	65.03	64.72
0.5358	65.68	65.28	64.92	64.64	64.32	63.92
0.6339	64.78	64.49	64.09	63.91	63.45	63.11
0.7220	64.13	63.69	63.33	63.04	62.70	62.40

Results and Discussion

1. Surface Tension. The surface tensions of the lithium bromide + lithium iodide + 1,3-propanediol + water (LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ mass ratio = 4) system were measured in the temperature range from 298.15 K to 323.15 K and the mass fraction range of the absorbent from (16.14 to 72.20)%. All data are presented in Table 2 and Figure 2, and regressed by the following equation:

$$\sigma = \sum_{i=0}^{2}[(a_i + b_iT)(100w)^i] \tag{4}$$

where σ is the surface tension of the absorbent, T is the absolute temperature, a_i and b_i are the regression parameters, and w is the mass fraction of absorbent (LiBr + LiI + $HO(CH_2)_3OH$). The regression parameters are determined by a least-squares method and listed in Table 4. The average absolute deviation (AAD) was 0.10% between the experimental and calculated values. Figure 3 shows the surface tension values of two systems, which are lithium bromide + water[5] and lithium bromide + lithium iodide + 1,3-propanediol + water at 313.15 K. The surface tensions of the lithium bromide + lithium iodide + 1,3-propanediol + water solution decreased with increasing temperature and absorbent (LiBr + LiI + $HO(CH_2)_3OH$) mass fraction. As shown in Figure 3, the tendency of the surface tension of the LiBr + LiI + $HO(CH_2)_3OH$ + water system was different from that of the LiBr + water system in terms of the effect of absorbent concentration, which naturally resulted from the relatively low surface tension of pure 1,3-propanediol and lithium iodide.

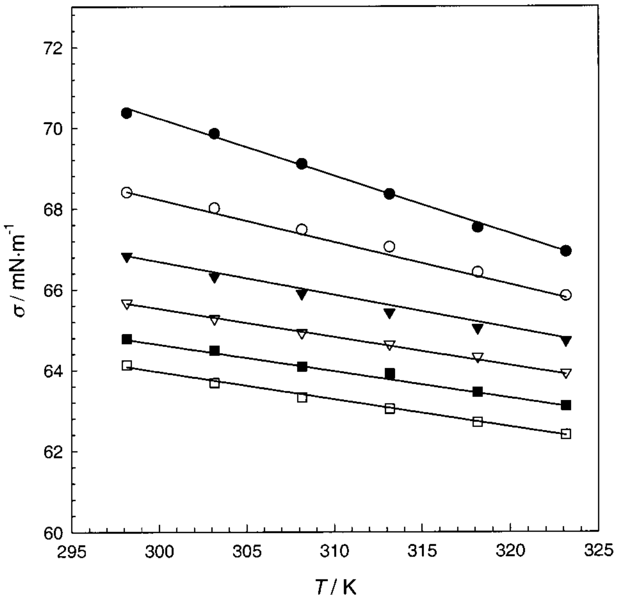

Figure 2. Surface tensions of the LiBr (1) + LiI (2) + $HO(CH_2)_3OH$ (3) + H_2O (4) (LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ mass ratio = 4) solutions: ●, $w_{1+2+3} = 0.1614$; ○, $w_{1+2+3} = 0.3021$; ▼, $w_{1+2+3} = 0.4260$; ▽, $w_{1+2+3} = 0.5358$; ■, $w_{1+2+3} = 0.6339$; □, $w_{1+2+3} = 0.7220$; —, calculated.

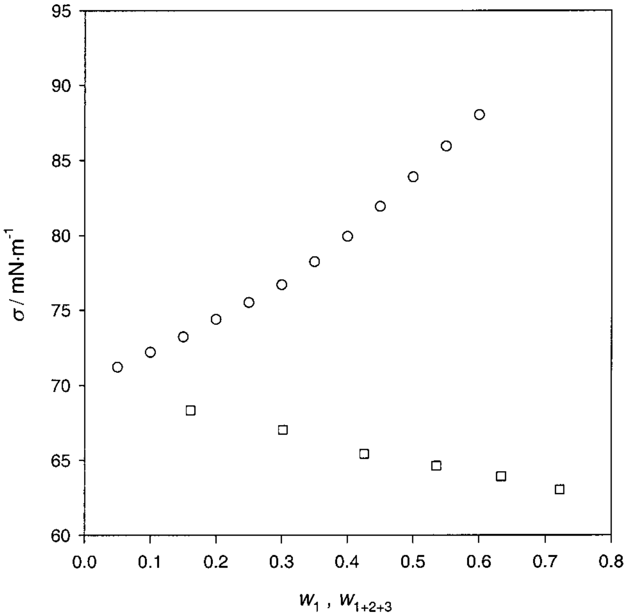

Figure 3. Surface tensions of the LiBr (1) + LiI (2) + $HO(CH_2)_3OH$ (3) + H_2O (4) (LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ mass ratio = 4) and LiBr (1) + water solutions at 313.15 K: ○, LiBr + water solution;[5] □, LiBr + LiI + $HO(CH_2)_3OH$ + water solution (this work).

2. Differential Enthalpy of Dilution. The experimental results of the enthalpy of dilution for the proposed working fluid are presented in Table 3 and Figure 4. The mass fraction and temperature ranges of the absorbent were studied from (48.25 to 67.91)% and from (293.15 to 323.15) K, respectively. With increasing absorbent concentration, the enthalpy of dilution increased exponentially. While the temperature increase resulted in the higher enthalpy of dilution, the effect of temperature was found to be very small.

All data were regressed by using the following equation, and the resulting parameters were listed in Table 4.

Table 3. Measured Enthalpies of Dilution of the LiBr + LiI + 1,3-Propanediol + Water (LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ Mass Ratio = 4) System

w	T/K	H_d/kJ·kg^{-1}	w	T/K	H_d/kJ·kg^{-1}
0.6791	293.15	257.9	0.5358	293.15	52.83
	303.15	270.6		303.15	60.77
	313.15	282.7		313.15	64.12
	323.15	297.0		323.15	69.42
0.6339	293.15	145.3	0.4825	293.15	39.56
	303.15	154.2		303.15	42.79
	313.15	161.9		313.15	45.52
	323.15	173.0		323.15	49.66
0.5862	293.15	93.54			
	303.15	98.53			
	313.15	103.6			
	323.15	111.4			

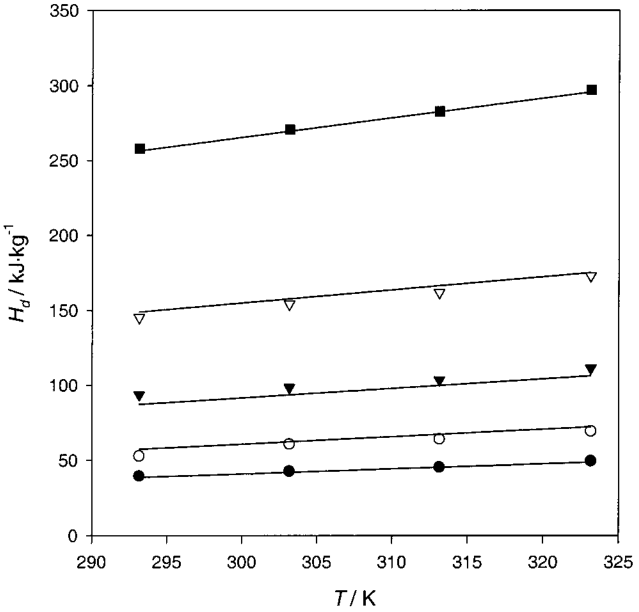

Figure 4. Enthalpies of dilution of the LiBr (1) + LiI (2) + $HO(CH_2)_3OH$ (3) + H_2O (4) (LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ mass ratio = 4) solution: ●, $w_{1+2+3} = 0.4825$; ○, $w_{1+2+3} = 0.5358$; ▼, $w_{1+2+3} = 0.5862$; ▽, $w_{1+2+3} = 0.6339$; ■, $w_{1+2+3} = 0.6791$; —, calculated.

Table 4. Regressed Parameter Values for Eqs 4 and 5

	a_i	b_i
	Eq 4	
$i = 0$	1.333×10^2	-2.014×10^{-1}
$i = 1$	-1.427	4.166×10^{-3}
$i = 2$	1.036×10^{-2}	-3.207×10^{-5}
AAD (%)	0.10	
	Eq 5	
$i = 0$	4.276×10^3	-2.926×10
$i = 1$	-2.199×10^2	1.601
$i = 2$	3.706	-2.910×10^{-2}
$i = 3$	-2.092×10^{-2}	1.790×10^{-4}
AAD (%)	2.8	

$$H_d = \sum_{i=0}^{3} [(a_i + b_i T)(100w)^i] \qquad (5)$$

where H_d is the differential enthalpy of dilution, T is the absolute temperature, a_i and b_i are the regression parameters, and w is the mass fraction of absorbent (LiBr + LiI + $HO(CH_2)_3OH$). The overall average absolute deviation (AAD) was found to be 2.8%.

Conclusions

The lithium bromide + lithium iodide + 1,3-propanediol + water system was chosen as a new working fluid. The surface tensions and enthalpies of dilution of this system were measured at various absorbent concentrations and temperatures. The surface tension values decrease as the temperature and absorbent concentration increase, and enthalpies of dilution increased dramatically with absorbent concentration and slightly with temperature. The experimental data were satisfactorily correlated with the simple polynomial functions of temperature and concentration. These surface tension and enthalpy of dilution data are essential for optimal design of an absorption heat pump along with other important basic physical properties.

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Received for review July 10, 2001. Accepted November 6, 2001. This research was performed for Greenhouse Gas Research Center, one of the critical Technology-21 programs, funded by the Ministry of Science and Technology of Korea, and also was supported partially by the Brain Korea 21 Project.

JE0101956