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Differential Enthalpies of Dilution of the Lithium Bromide + 1,3-Propanediol + Water and Lithium Bromide + Lithium Iodide + Lithium Chloride + Lithium Nitrate + Water Systems

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

The differential enthalpies of dilution of the LiBr + 1,3-propanediol + water [LiBr/$HO(CH_2)_3OH$ mass ratio = 3.5:1] and LiBr + LiI + LiCl + $LiNO_3$ + water (mole ratio = 5:1:1:0.5) systems were determined at the four temperatures of 293.15, 303.15, 313.15, and 323.15 K and in the absorbent concentration ranges of 24.3−65.6 and 44.4−64.5%, respectively. These two aqueous mixtures were selected as potential working fluids for an absorption heat pump to overcome crystallization and corrosion problems caused by the LiBr + water system. The measured data were correlated with a simple polynomial equation, and the deviations between the experimental and calculated values were found to be 3.8 and 2.8%, respectively.

Introduction

An absorption heat pump consists of four working components: condenser, evaporator, absorber, and generator.[1] Both the enthalpy of absorption in the absorber and the enthalpy of condensation in the condenser should be removed from these two components by a cooling device. For an absorption heat pump using aqueous LiBr-based absorbents, the enthalpy of absorption is defined as the enthalpy released during the phase change when the water vapor is absorbed into the absorbent solution. A lower enthalpy of absorption reduces the absorber duty to give a higher efficiency of the overall performance. Although actual measurements of the enthalpy of absorption are crucial for the better design of an absorber operated with various types of working fluids, few data are available in the literature because of the difficulties inherent in measuring this thermal property. The enthalpy of absorption is expressed as the change in enthalpy of water as it undergoes a phase change from vapor to liquid plus the differential enthalpy of dilution of the absorbent

$$H_a = H_f - H_g + H_d \quad (1)$$

where H_a is the specific enthalpy of absorption, H_g is the specific enthalpy of water vapor at the absorber gas temperature, H_f is the specific enthalpy of liquid water at the solution temperature, and H_d is the specific differential enthalpy of dilution of the absorbent. As in our previous studies,[3,6] the LiBr + 1,3-propanediol + water [LiBr/$HO(CH_2)_3OH$ mass ratio = 3.5:1] and LiBr + LiI + LiCl + $LiNO_3$ + water (mole ratio = 5:1:1:0.5) systems were chosen as possible working fluids for an absorption heat pump to overcome the solubility limit and corrosion problems of conventional aqueous lithium bromide solutions.[2,3] As continuing research into the basic physical properties of aqueous LiBr systems, the enthalpies of dilution of the suggested working fluids have been measured using an isoperibol solution calorimeter.

Experimental Section

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

Apparatus and Procedure. An isoperibol solution calorimeter (CSC4300) was used to measure the differential enthalpy of dilution of the absorbent solutions.[3,5] To measure the differential enthalpy of dilution, the energy equivalent E in kJ K^{-1} should first be obtained. The following equation defines the energy equivalent E

$$E = mC_p + \epsilon \quad (2)$$

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. To measure 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 onto the isoperibol solution calorimeter. The stirrer and heater were then turned on to heat the sample solution to a temperature slightly lower than desired. After 300 s at that temperature, the actual measuring process including 200 s of holding time without heating, 400 s of heating, and 200 s of holding time began. All of the measurement procedures were completely controlled by a computer. Preceding the experiment was the calibration procedure to obtain the energy equivalent E required to calculate the differential enthalpy of dilution. The actual measurement of the differential enthalpy of dilution was quite similar to the calibration procedure. Prior to an actual measurement, an absorbent solution sample (approximately 25 cm^3) with a fixed concentration was charged into the Dewar vessel while an accurately weighed quantity of water (approximately 0.01 g) was placed into a small cylindrical container with fragile glass covers at the top and bottom sides. The mixing was initiated by breaking

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

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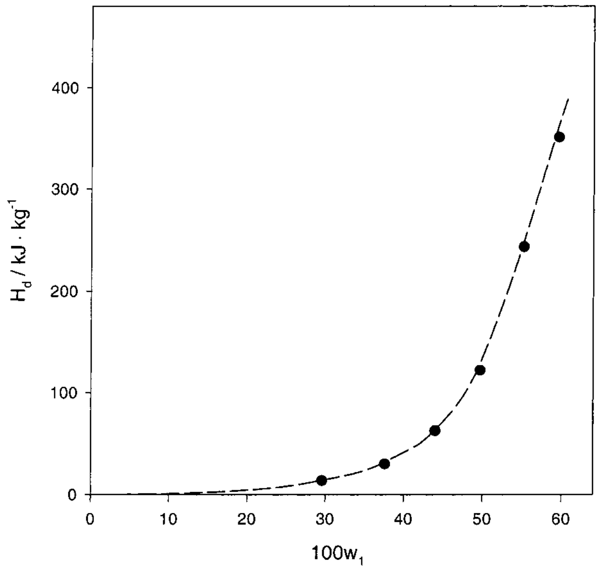

Figure 1. Differential enthalpies of dilution of the LiBr (1) + H_2O (2) system at 298.15 K: ●, this work; - - -, Uemura et al.[4]

Table 1. Measured Enthalpies of Dilution for the LiBr (1) + 1,3-Propanediol (2) + Water (3) Solution[a]

T (K)	$100w_{1+2}$	H_d (kJ kg^{-1})	$100w_{1+2}$	H_d (kJ kg^{-1})
293.15	65.61	224.6	35.53	15.17
303.15		233.3		25.52
313.15		244.5		26.30
323.15		251.9		30.46
293.15	56.25	91.57	24.32	10.09
303.15		102.8		12.56
313.15		110.3		14.71
323.15		112.9		16.26
293.15	46.15	33.91		
303.15		44.47		
313.15		47.51		
323.15		50.56		

[a] LiBr/$HO(CH_2)_3OH$ mass ratio = 3.5:1

Table 2. Measured Enthalpies of Dilution for the LiBr (1) + LiI (2) + LiCl (3) + $LiNO_3$ (4) + Water (5) Solution[a]

T (K)	$100w_{1+2+3+4}$	H_d (kJ kg^{-1})	$100w_{1+2+3+4}$	H_d (kJ kg^{-1})
293.15	64.48	–	49.75	107.7
303.15		343.4		120.6
313.15		357.8		127.6
323.15		374.3		135.1
293.15	59.76	234.6	44.43	53.46
303.15		254.6		70.13
313.15		268.4		76.18
323.15		280.8		81.03
293.15	54.86	168.0		
303.15		173.7		
313.15		183.7		
323.15		192.4		

[a] Mole ratio = 5:1:1:0.5.

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

$$H_d = E\ \Delta T / m_{water} \tag{3}$$

The temperature resolution was 4 × 10^{-5} K. 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 a previous work.[5] Figure 1 shows the comparison of between the experimental and literature data.[4] The resulting average absolute deviation was found to be 3%.

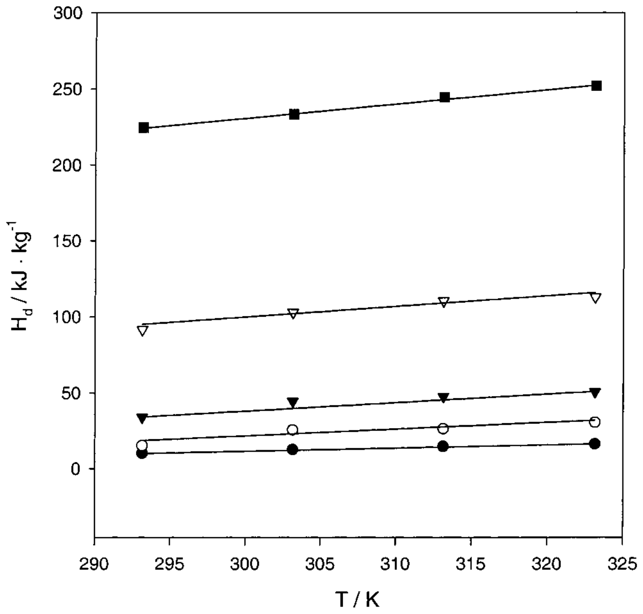

Figure 2. Differential enthalpies of dilution of the LiBr (1) + $HO(CH_2)_3OH$ (2) + water (3) solution: ●, w_{1+2} = 24.32%; ○, w_{1+2} = 35.53%; ▼, w_{1+2} = 46.15%; ▽, w_{1+2} = 56.25%; ■, w_{1+2} = 65.61%; —, eq 4.

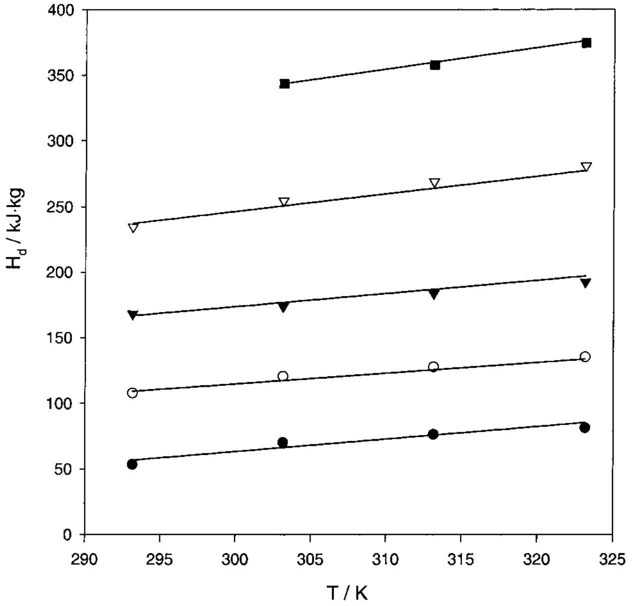

Figure 3. Differential enthalpies of dilution of the LiBr (1) + LiI (2) + LiCl (3) + $LiNO_3$ (4) +water (5) solution: ●, $w_{1+2+3+4}$ = 44.43%; ○, $w_{1+2+3+4}$ = 49.75%; ▼, $w_{1+2+3+4}$ = 54.86%; ▽, $w_{1+2+3+4}$ = 59.76%; ■, $w_{1+2+3+4}$ = 64.48%; —, eq 4.

Results and Discussion

The enthalpies of dilution of the lithium bromide + 1,3-propanediol + water [LiBr/$HO(CH_2)_3OH$ mass ratio = 3.5:1] and lithium bromide + lithium iodide + lithium chloride + lithium nitrate + water [mole ratio = 5:1:1:0.5] were measured, and the results are presented in Tables 1 and 2 and Figures 2 and 3. Absorbent concentrations of 24.3−65.6 mass % for LiBr + $HO(CH_2)_3OH$ + water and 44.43−64.48 mass % for LiBr + LiI + LiCl + $LiNO_3$ +

Table 3. Regressed Values of the Coefficients in Eq 4

	a_i	b_i
	$LiBr + HO(CH_2)_3OH$ + water	
$i = 0$	2.127×10^{2}	-1.463
$i = 1$	-1.423×10^{1}	$1.176\ 10^{-1}$
$i = 2$	1.273×10^{-1}	-2.460×10^{-3}
$i = 3$	4.339×10^{-4}	1.866×10^{-5}
AAD	3.8%	
	$LiBr + LiI + LiCl + LiNO_3$ + water	
$i = 0$	-1.319×10^{4}	3.999×10^{1}
$i = 1$	6.941×10^{2}	-2.090
$i = 2$	-1.221×10^{1}	3.629×10^{-2}
$i = 3$	7.101×10^{-2}	-2.032×10^{-4}
AAD	2.8%	

water were investigated in the temperature range from 293.15 to 323.15 K. To verify the experimental apparatus and procedure, the enthalpies of dilution for the LiBr + water solution at 298.15 K were measured in a previous work.[5] With increasing absorbent concentration, the enthalpy of dilution increased exponentially. The enthalpy of dilution of the two systems of interest increased with increasing temperature.

All data were regressed by eq 4, and the resulting parameters are listed in Table 3

$$H_{\mathrm{d}}/(\mathrm{kJ\ kg^{-1}}) = \sum_{i=0}^{3}[(a_i + b_i T/\mathrm{K})(100w)^i] \qquad (4)$$

where H_{d} is the differential enthalpy of dilution; T is the absolute temperature; a_i, b_i, and c_i are the regression parameters; and w the absorbent concentration in mass percent. The average absolute deviations (AADs) were 3.8 and 2.8% for the LiBr + 1,3-propanediol + water and $LiBr + LiI + LiCl + LiNO_3$ + water systems, respectively.

Conclusions

The lithium bromide + 1,3-propanediol + water and lithium bromide + lithium iodide + lithium chloride + lithium nitrate + water systems were chosen to overcome the crystallization and corrosion problems of aqueous lithium bromide solution. The enthalpies of dilution for both systems were measured using an isoperibol solution calorimeter. The temperature and absorbent concentration ranges were from 293.15 to 323.15 K and up to 66 mass %, respectively. The enthalpies of dilution increased dramatically with absorbent concentration and slightly with temperature. These data are important for calculating the enthalpy of absorption and enthalpy of condensation in the absorber and condenser, respectively.

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