J. Chem. Eng. Data **1996,** *41,* 279−281

Solubilities and Vapor Pressures of the Water + Lithium Bromide + Ethanolamine System

Jin-Soo Kim, Young Park, 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

Solubilities of lithium bromide in the water (1) + lithium bromide (2) + ethanolamine (3) system at three different ratios (w_2/w_3 = 4.5, 4, and 3.5) were measured by using the visual polythermal method in temperature ranges of (281.35 to 333.55) K, (281.65 to 333.55) K, and (275.45 to 345.95) K, respectively. Each set of experimental measurements was correlated with two least-squares regression equations as a function of temperature. The average absolute deviations between the experimental and the calculated solubilities were less than 0.04%. Vapor pressures of the water + lithium bromide + ethanolamine system (LiBr/$H_2N(CH_2)_2OH$ mass ratio 3.5/1) were also measured by a boiling point method in the temperature range of (319.75 to 418.35) K and in the absorbent concentration range of (50.0 to 79.3) mass %. The experimental values were well correlated with an Antoine-type equation, and the overall average absolute deviation was found to be 0.85 %. These experimental results indicate that the mixture studied can be used as a new working fluid in an absorption chiller.

Introduction

A heat-powered absorption chiller is attractive in view of its low energy consumption. Recently, much effort (Iizuka et al., 1989, 1990; Inoue, 1993; Okano et al., 1994) has been made to develop an air-cooled absorption chiller, because the existing water-cooled absorption unit needs an additional cooling tower to lower the temperature of the absorber in the absorption cycle, which increases the equipment size and cost of the machine. However, many additional problems occur in the construction of the air-cooled absorption cycle. The most serious problem becomes the crystallization of the working fluid because the high absorber temperature caused by air-cooling needs a high absorbent concentration of the working fluid in order to maintain a low vapor pressure in the absorber. Anticrystallization additives with a high boiling point and hygroscopic property are used in order to overcome the crystallization problem and ensure a safe cycle operation. Iizuka et al. (1989) and Inoue (1993) suggested water + lithium bromide + ethylene glycol as a new working fluid for the air-cooled absorption chiller and Iizuka et al. (1990) the water + lithium bromide + lithium iodide + ethylene glycol, where ethylene glycol was added as an anticrystallization agent. Rockenfeller and Langeliers (1988) carried out extensive research concentrating on the water + lithium bromide system with addition of several high-boiling anticrystallization organics for the air-cooled absorption chiller. In this work the water + lithium bromide + ethanolamine system was selected using high-boiling ethanolamine as an anticrystallization additive. Firstly, the solubility experiments were carried out at three different LiBr/$H_2N(CH_2)_2OH$ mass ratios. Secondly, the vapor pressures at a fixed condition (LiBr/$H_2N(CH_2)_2OH$ mass ratio 3.5/1) were measured at various concentrations and temperatures. Each set of results was correlated with a proper equation.

Experimental Section

Materials. Lithium bromide (99+%) and ethanolamine (99+%) were supplied by Aldrich Chemical Co., and were used without further purification. All solutions were prepared with deionized water.

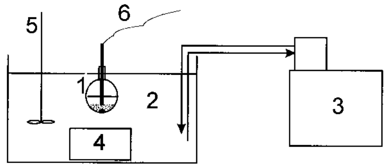

Figure 1. Experimental apparatus for the measurement of solubility: (1) equilibrium still; (2) constant temperature bath; (3) bath circulator; (4, 5) stirrers; (6) thermistor thermometer.

Apparatus and Procedure. The visual polythermal method (Chou and Lee, 1983; Iyoki et al., 1993) was used to measure the solubility of each sample. The apparatus which is similar to that of Chou and Lee (1983) is shown in Figure 1. It consists of a Pyrex glass vessel (50 cm^3) sealed by a Teflon adapter, a thermistor thermometer (Cole Parmer, 08502-16), the accuracy of which is ±0.2 K, a constant temperature bath, a circulator for both cooling and heating, and two stirrers. Each sample solution of a desired absorbent concentration at a given mixing ratio was accurately prepared by weighing each component with a precision balance (Mettler, PM2000). The prepared sample solution (approximately 30 cm^3) was placed in the vessel and stirred well. The solution was first incrementally heated above the crystallization temperature to dissolve all the salts. Then the solution temperature was lowered slowly to nucleate a small amount of crystals. The temperature of the solution was lowered and raised at a very slow rate (less than 0.1 K/min) using the constant temperature bath and the circulator. Through a series of dissolving and nucleation procedures, the temperature at which the last crystal disappeared was taken as the dissolution temperature for a given solution in this polythermal run. The accuracy of the apparatus and the procedure was checked with the water + lithium bromide system, and the relative errors between the measured and the literature values (Boryta, 1970) were less than 1%. Vapor pressures were measured using the boiling point method. The schematic diagram of the experimental apparatus is shown in Figure 2. The apparatus consists primarily of an

---

* To whom correspondence should be addressed. E-mail: hlee@hanbit.kaist.ac.kr.

0021-9568/96/1741-0279$12.00/0

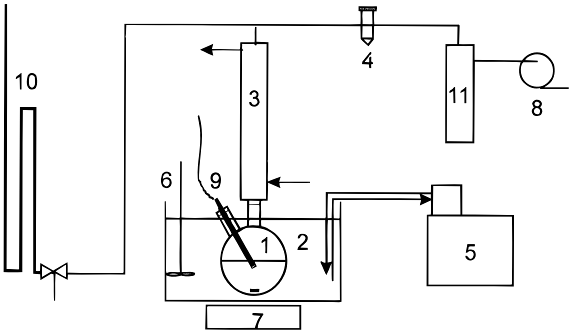

Figure 2. Experimental apparatus for the measurement of vapor pressure: (1) equilibrium still; (2) constant temperature bath; (3) condenser; (4) needle valve; (5) bath circulator; (6, 7) stirrers; (8) vacuum pump; (9) thermocouple; (10) mercury manometer; (11) cold trap.

equilibrium vessel (500 cm^3), a constant temperature bath, a condenser, a U-tube mercury manometer capable of being read to 0.05 mm, a K type thermocouple (Cole Parmer, 93750-20), the accuracy of which is ±0.4% of the reading (°F), and two stirrers. A sample solution (approximately 250 cm^3) of a desired absorbent concentration was used in each run. The amount of water-rich vapor and condensed liquid was minimized (<0.5 g); thus, the initial concentration that was calculated in preparing each sample solution was scarcely varied (increase of less than 0.1 mass % absorbent). More details about the experimental apparatus and the procedure were described in our previous work (Kim et al., 1995).

Results and Discussion

The solubilities of lithium bromide in water + lithium bromide + ethanolamine were measured at three different mass ratios, LiBr/$H_2N(CH_2)_2OH$ = 4.5/1, 4/1, and 3.5/1. The temperature ranges used for each set were (281.35 to 333.55) K, (281.65 to 333.55) K, and (275.45 to 345.95) K, respectively. The measured solubility values for each system were regressed by a least-squares method represented by the following equation:

$$100S = \sum_{i=0}^{2} a_i (T/\mathrm{K})^i \qquad (1)$$

where S is the solubility represented by the mass fraction of absorbent (LiBr + $H_2N(CH_2)_2OH$), T is the absolute temperature, and a_i are the regression coefficients. The experimental and calculated results are listed in Tables 1 and 2 and are plotted in Figure 3. The average absolute deviations between experimental and calculated values are less than 0.04% for all data sets. In Figure 3, the solubility curves show a shift to the right, indicating a solubility enhancement when the relative amount of ethanolamine increases. For the specified temperature and concentration ranges of this study the maximum solubility was found to be about 80.9 mass % absorbent at 345.95 K with a mass ratio 3.5/1. These results can assist in extending the operation range of the absorption chiller. However, further tests of other thermodynamic and transport properties are required before this mixture can be utilized as a working fluid.

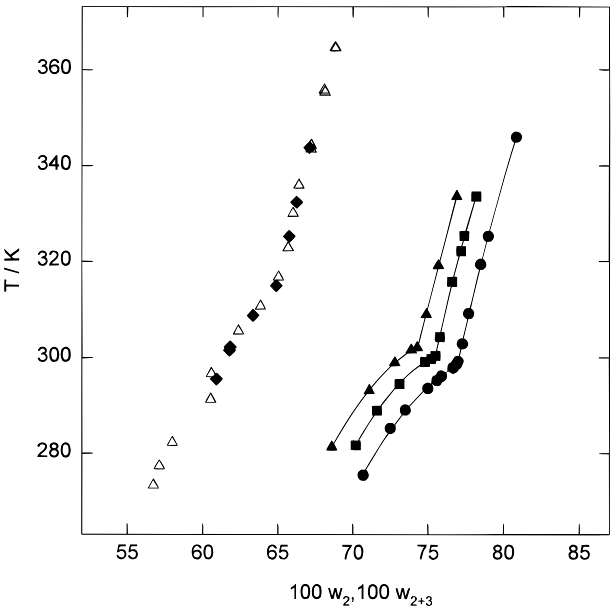

Figure 3. Mass fraction solubilities w_2 and w_{2+3} of the H_2O (1) + LiBr (2) and H_2O(1) + LiBr (2) + $H_2N(CH_2)_2$ OH (3) systems at various temperatures: △, H_2O + LiBr (Boryta, 1970); ◆, H_2O + LiBr (this work); ▲, w_2/w_3 = 4.5; ■, w_2/w_3 = 4.0; ●, w_2/w_3 = 3.5; —, calculated.

Table 1. Solubilities Represented by the Mass Fraction of Absorbent w_{2+3} for the H_2O (1) + LiBr (2) + $H_2N(CH_2)_2OH$ (3) System (w_2/w_3 = 4.5, 4, and 3.5) at Various Temperatures

T/K	w_{2+3}	T/K	w_{2+3}
w_2/w_3 = 4.5		w_2/w_3 = 3.5	
281.35	0.686	275.45	0.707
293.15	0.711	285.25	0.725
298.95	0.728	289.05	0.735
301.65	0.739	293.55	0.750
302.15	0.743	295.25	0.756
308.95	0.749	296.15	0.759
319.15	0.757	297.85	0.767
333.55	0.769	298.75	0.769
		299.25	0.770
w_2/w_3 = 4.0		302.85	0.773
281.65	0.702	309.15	0.777
288.95	0.716	319.35	0.785
294.45	0.731	325.25	0.790
299.15	0.748	345.95	0.809
299.75	0.752		
300.35	0.755		
304.35	0.758		
315.75	0.766		
322.15	0.772		
325.35	0.774		
333.55	0.782		

The vapor pressures of water + lithium bromide + ethanolamine were measured at various concentrations in the range of temperature from (319.75 to 418.35) K. The mass ratio of LiBr/$H_2N(CH_2)_2OH$ was fixed at 3.5/1 to ensure a broad cycle operation. The experimental values are listed in Table 3, and correlated with the following Antoine-type equation which expresses vapor pressure as a function of temperature and concentration:

$$\log(P/\mathrm{kPa}) = \sum_{i=0}^{4} [A_i + \{1000B_i/(T/\mathrm{K} - 43.15)\}](100w)^i \qquad (2)$$

where P is the vapor pressure, T the absolute temperature, and w the mass fraction of absorbent. The parameters A_i and B_i were determined by a least-squares method, and the results are listed in Table 4. The average absolute deviation (AAD) was found to be 0.85%. The experimental and calculated results are plotted in Figure 4. This figure shows that the log(P/kPa) against 1000/(T/K − 43.15) relation for the given concentration is linear over the pressure and temperature range.

Table 2. Values of a_i for Least-Squares Representation by Eq 1

	a_0	a_1	a_2
	$w_2/w_3 = 4.5$		
$281.35 \le T/\mathrm{K} \le 302.15$	5.83530×10^2	-3.78328	6.94189×10^{-3}
$302.15 \le T/\mathrm{K} \le 333.55$	4.70004×10	9.77056×10^{-2}	-2.42131×10^{-5}
	$w_2/w_3 = 4.0$		
$281.65 \le T/\mathrm{K} \le 300.35$	7.12680×10^2	-4.68126	8.52188×10^{-3}
$300.35 \le T/\mathrm{K} \le 333.55$	9.94836×10	-2.24452×10^{-1}	4.81575×10^{-4}
	$w_2/w_3 = 3.5$		
$275.45 \le T/\mathrm{K} \le 298.75$	5.18757×10^2	-3.37482	6.34661×10^{-3}
$298.75 \le T/\mathrm{K} \le 345.95$	8.27938×10	-1.08610×10^{-1}	2.98909×10^{-4}

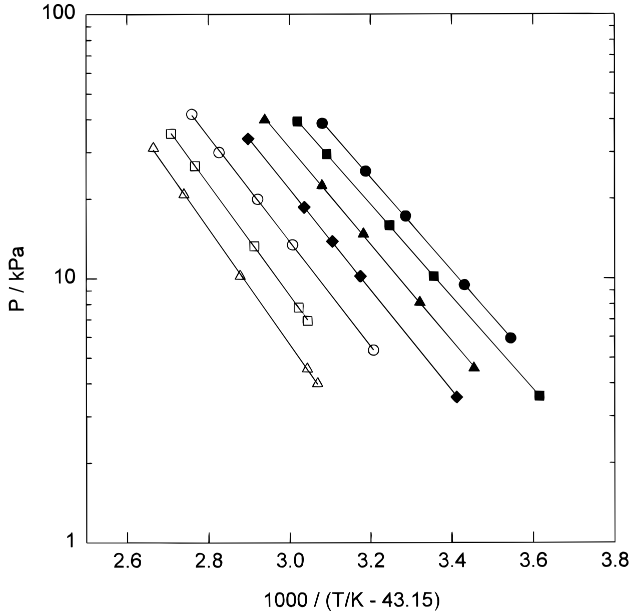

Figure 4. Vapor pressures of the H_2O (1) + LiBr (2) + $H_2N(CH_2)_2OH$ (3) system ($w_2/w_3 = 3.5$) at various mass fractions: ●, $w_{2+3} = 0.500$; ■, $w_{2+3} = 0.550$; ▲, $w_{2+3} = 0.600$; ◆, $w_{2+3} = 0.648$; ○, $w_{2+3} = 0.699$; □, $w_{2+3} = 0.747$; △, $w_{2+3} = 0.793$; —, calculated.

Table 3. Vapor Pressures for H_2O (1) + LiBr (2) + $H_2N(CH_2)_2OH$ (3) ($w_2/w_3 = 3.5$) at Various Mass Fractions of Absorbent w_{2+3}

T/K	P/kPa	T/K	P/kPa
$w_{2+3} = 0.500$		$w_{2+3} = 0.550$	
325.15	5.920	319.75	3.573
334.55	9.439	341.15	10.19
347.35	17.18	351.15	15.89
356.75	25.38	366.55	29.53
367.75	38.58	374.35	39.28
$w_{2+3} = 0.600$		$w_{2+3} = 0.648$	
332.55	4.566	336.15	3.540
344.15	8.099	358.05	10.19
357.35	14.71	365.15	13.81
367.85	22.42	372.55	18.56
383.45	39.88	388.25	33.73
$w_{2+3} = 0.699$		$w_{2+3} = 0.747$	
354.95	5.340	371.65	6.913
375.65	13.41	374.05	7.766
385.45	19.90	386.45	13.27
396.95	29.93	404.55	26.62
405.55	41.83	412.45	35.34
$w_{2+3} = 0.793$			
368.95	3.993		
371.75	4.540		
390.55	10.23		
408.15	20.76		
418.35	31.08		

Table 4. Values of A_i, B_i, and AAD for Least-Squares Representation by Eq 2

A_0	1.22730×10^2	B_0	-3.83335×10^1
A_1	-7.18812	B_1	2.25982
A_2	1.65853×10^{-1}	B_2	-5.16583×10^{-2}
A_3	-1.68830×10^{-3}	B_3	5.19714×10^{-4}
A_4	6.41261×10^{-6}	B_4	-1.95693×10^{-6}
AAD[a]	0.85%		

[a] AAD = $(1/N)\sum_{i=1}^{N}|(P_{\mathrm{exp}} - P_{\mathrm{cat}})/P_{\mathrm{exp}}|$; N = number of points, P_{exp} = experimental value, P_{cal} = calculated value.

Conclusions

Solubilities of lithium bromide in water (1) + lithium bromide (2) + ethanolamine (3) at three different ratios (w_2/w_3 = 4.5, 4, and 3.5) were measured at various temperatures. The solubility represented by the concentration of absorbent increases with decreasing mass ratios of LiBr/$H_2N(CH_2)_2OH$. The remarkable enhancement of solubility by the addition of ethanolamine indicates that this mixture can possibly be used as a new working fluid. However, other thermodynamic and transport properties should be determined. All experimental results were correlated, and the results show good agreement between the experimental and calculated values.

Literature Cited

Boryta, D. A. Solubility of Lithium Bromide in Water between −50° and +100 °C. (45 to 70% Lithium Bromide). *J. Chem. Eng. Data* **1970**, *15*, 142−144.

Chou, I-M.; Lee, R. D. Solubility Relation in the Ternary System NaCl-CsCl-H_2O at 1 atm. 1. Solubilities of Halite from 20 to 100 °C. *J. Chem. Eng. Data* **1983**, *28*, 390−393.

Iizuka, H.; Nagamatsuya, K.; Takahashi, K.; Kuroda, J.; Takigawa, T. Some Properties of Absorption Fluid containing Ethylene Glycol for Air-cooled Chiller. *Proceedings of the International Gas Research Conference*, Tokyo, 1989.

Iizuka, H.; Nagamatsuya, K.; Takahashi, K.; Kuroda, J.; Takigawa, T. New Working Fluid Containing Ethylene Glycol for Air Cooled Chiller - 2. *Proceedings of the 3rd International Energy Agency Heat Pump Conference*, Tokyo, 1990.

Inoue, N. H_2O/LiBr + $C_2H_2(OH)_2$ System and H_2O/LiBr + $ZnCl_2$ System. *Retio* **1993**, *68*, 719−723.

Iyoki, S.; Iwasaki, S.; Kuriyama, Y.; Uemura, T. Solubilities for the Two Ternary Systems Water + Lithium Bromide + Lithium Iodide and Water + Lithium Chloride + Lithium Nitrate at Various Temperatures. *J. Chem. Eng. Data* **1993**, *38*, 396−398.

Kim, J.-S.; Lee, H.; Won, S.-H. Vapor Pressures of Water + Lithium Chloride + Ethylene Glycol and Water + Lithium Chloride + Lithium Bromide + Ethylene Glycol. *J. Chem. Eng. Data* **1995**, *40*, 496−498.

Okano, T.; Asawa, Y.; Fujimoto, M. Development of an Air-cooled Absorption Refrigerating Machine Using a New Working Fluid. *Proceedings of the International Absorption Heat Pump Conference*, New Orleans, 1994.

Rockenfeller U.; Langeliers, J. Aqueous Absorption Fluids. Annual Report; Gas Research Institute: Chicago, 1988.

Received for review October 2, 1995. Accepted November 28, 1995.

JE950249+

⊗ Abstract published in *Advance ACS Abstracts*, February 1, 1996.