Vapor Pressures of Water + Lithium Chloride + Ethylene Glycol and Water + Lithium Chloride + Lithium Bromide + Ethylene Glycol

Jin-Soo 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

Seung-Ho Won

Department of Mechanical Engineering, Keonyang University, San 30, Naedongri, Nonsan, Chungnam 320-800, South Korea

The vapor pressures of water + lithium chloride + ethylene glycol and water + lithium chloride + lithium bromide + ethylene glycol (LiCl/LiBr mass ratio 1:1) ($H_2O/C_2H_6O_2$ mole ratio 10:1) were measured in the temperature ranges from 306.65 to 394.90 K and from 308.10 to 398.20 K and in the absorbent concentration ranges from 11.20 to 45.15 mass % and from 10.01 to 54.17 mass %, respectively. The experimental values were correlated with an Antoine-type equation, and the overall average absolute deviations between the experimental values and the calculated values were found to be 1.65% and 1.03% for the two systems, respectively.

Introduction

Aqueous-based working fluids containing several salts or their mixtures concerning primarily lithium bromide have been of much interest for the application to absorption coolers, absorption heat transformers, and absorption heat pumps. Thermodynamic and transport properties such as heat capacities, enthalpies of mixing, vapor pressures, solubilities, densities, and surface tensions should be closely examined for the improvement of performance characteristics of these machines.

This work was undertaken to determine the vapor pressure of two systems containing ethylene glycol ($H_2O/C_2H_6O_2$ mole ratio 10:1) by using the boiling point method. Iyoki and Uemura (1981) measured the physical and thermal properties of the water + lithium bromide + ethylene glycol system ($H_2O/C_2H_6O_2$ mole ratio 10:1) and Eisa et al. (1988) studied the operational characteristics of experimental absorption cooler using the same system (mole ratio 15:1).

Experimental Section

Materials. The lithium chloride (99+%), lithium bromide (99+%), and ethylene glycol (99+%, Gold Label) were supplied by Aldrich Chemical Co. and were used without further purification. All solutions were prepared with deionized water.

Apparatus and Procedure. The vapor pressure measurement was carried out using the boiling point method similar to that of our previous work (Lee and Hong, 1991) with minor modification. The heating part was replaced with a constant-temperature bath, a heater, a temperature controller, and two stirrers instead of a heating mantle. The equilibrium still was made of Pyrex glass, and all glass pieces were sealed with Dow Corning high-vacuum grease. The constant-temperature bath was maintained to within 0.01 K, and the temperature was measured with a standard thermometer. The vapor pressures were measured with a U-tube mercury manometer capable of reading to 0.05 mm.

Table 1. Vapor Pressures of the H_2O (1) + LiCl (2) + $C_2H_6O_2$ (3) System ($H_2O/C_2H_6O_2$ Mole Ratio 10:1) at Various Mass Fractions w_2

T/K	P/kPa	T/K	P/kPa
$w_2 = 0.1120$		$w_2 = 0.3016$	
306.85	3.933	318.50	2.933
314.00	5.473	330.65	5.053
322.80	8.693	336.20	6.619
324.85	9.633	342.10	8.806
330.00	12.42	350.30	12.91
334.90	15.76	356.25	16.55
340.60	20.41	365.05	23.44
351.75	33.97	376.55	36.65
$w_2 = 0.1562$		$w_2 = 0.3539$	
309.95	3.980	327.65	3.146
318.60	6.299	339.60	5.433
325.80	9.253	347.85	8.119
332.20	12.33	355.85	11.32
337.75	16.05	367.90	18.83
341.50	19.05	379.05	29.14
351.35	29.33	389.95	43.74
$w_2 = 0.2003$		$w_2 = 0.4004$	
306.65	2.826	334.35	2.760
320.85	5.720	339.05	3.560
325.95	7.466	351.50	6.446
336.40	12.35	359.30	9.146
341.90	16.01	367.65	13.27
348.10	21.17	379.20	21.79
355.65	29.52	394.35	38.96
$w_2 = 0.2509$		$w_2 = 0.4515$	
313.40	2.906	340.20	2.706
322.35	4.553	345.20	3.306
331.25	7.266	355.55	5.426
339.35	10.52	363.35	7.719
344.35	13.00	376.00	13.36
352.10	18.41	383.55	18.45
360.10	25.61	394.90	28.86
369.35	37.04		

A sample with approximate volume of 250 cm^3 was placed in the still, and it was then stirred well with a magnetic stirrer to prevent superheating. At thermal equilibrium, the pressure in the apparatus and the temperature of the

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* E-mail hlee@hanbit.kaist.ac.kr.

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Table 2. Vapor Pressures of the H_2O (1) + LiCl (2) + LiBr (3) + $C_2H_6O_2$ (4) System ($H_2O/C_2H_6O_2$ Mole Ratio 10:1 and LiCl/LiBr Mass Ratio 1:1) at Various Total Mass Fractions w_{2+3}

T/K	P/kPa	T/K	P/kPa
$w_{2+3} = 0.1001$		$w_{2+3} = 0.3002$	
308.10	4.246	314.65	3.180
314.90	6.146	323.60	5.240
318.85	7.593	330.05	7.273
324.75	10.27	335.05	9.166
329.90	13.12	347.20	15.45
336.90	18.41	360.30	27.50
350.85	32.99	369.05	38.46
358.35	44.40	376.10	49.96
$w_{2+3} = 0.1513$		$w_{2+3} = 0.3501$	
311.20	4.520	320.25	3.086
317.40	6.373	326.40	4.253
321.35	7.759	332.40	5.820
324.30	9.046	341.20	9.119
335.15	15.47	351.45	14.47
343.65	22.47	360.50	20.86
352.70	32.32	374.35	35.59
362.10	46.93	384.50	51.98
$w_{2+3} = 0.2005$		$w_{2+3} = 0.4510$	
313.65	4.613	337.10	3.246
320.10	6.719	345.45	5.000
328.30	9.939	354.85	8.199
335.40	13.87	364.20	12.36
345.85	22.09	376.55	20.50
353.60	30.34	386.30	29.56
363.05	44.01	393.25	38.51
$w_{2+3} = 0.2500$		$w_{2+3} = 0.5417$	
313.70	3.886	350.15	3.180
318.40	4.993	357.65	4.500
322.45	6.199	365.70	6.866
329.10	8.873	374.20	9.746
336.75	12.70	387.85	17.11
344.80	18.27	398.20	25.47
356.45	29.14		
366.35	42.74		

sample solution were measured. The condenser was worked with sufficiently cooled water (<4 °C) to minimize the amount of condensed vapor because this water-rich vapor can vary the initial concentration and the ratio of $H_2O/C_2H_6O_2$ of the sample solution.

To examine the accuracy of the experimental apparatus and procedure the vapor pressure of pure water and solutions of lithium chloride + water at some given concentrations were measured at various temperatures, and the results agreed with the literature (ASME, 1979; Uemura et al., 1965) within 0.5% and 1.2%, respectively.

Results and Discussion

The vapor pressures of water + lithium chloride + ethylene glycol and water + lithium chloride + lithium bromide + ethylene glycol were measured at various concentrations and in the temperature ranges from 306.65 to 394.90 K and from 308.10 to 398.20 K. The mole ratio of H_2O/C_2H_6O was fixed at 10:1 in both systems and the ratio of LiCl/LiBr at 1:1 by mass in the binary salt system including lithium chloride and lithium bromide.

The experimental results for the two systems are listed in Tables 1 and 2 and are plotted in Figures 1 and 2 against the reciprocal of the temperature. As shown in the two figures, the log(P/kPa) against 1000/(T/K − 43.15) relation for the given concentration was linear over the pressure and temperature range. The vapor pressure results were correlated with an Antoine-type equation which expresses vapor pressure as a function of temperature and concentration

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

where P is the vapor pressure, T the temperature, and w the mass fraction of salt(s). The parameters A_i and B_i were determined by the least-squares method, and the results are listed in Table 3. The average absolute deviations (AAD) were found to be 1.65% for the water + lithium chloride + ethylene glycol system and 1.03% for the water + lithium chloride + lithium bromide + ethylene glycol system.

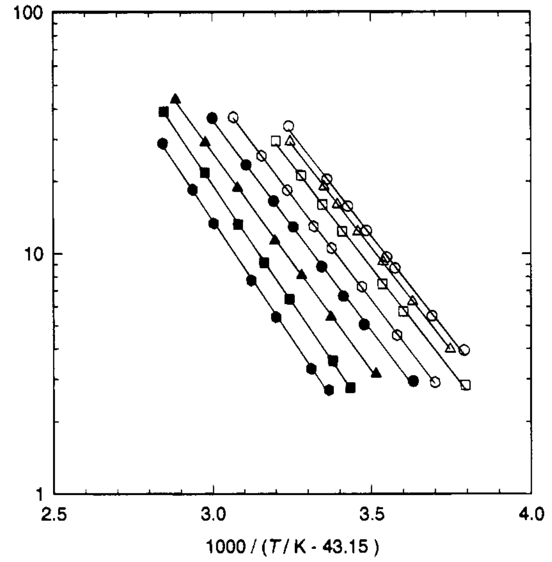

Figure 1. Vapor pressures of the H_2O (1) + LiCl (2) + $C_2H_6O_2$ (3) system at various mass fractions w_2 ($H_2O/C_2H_6O_2$ mole ratio 10:1): ○, $w_2 = 0.1120$; △, $w_2 = 0.1562$; □, $w_2 = 0.2003$; ⬡, $w_2 = 0.2509$; ●, $w_2 = 0.3016$; ▲, $w_2 = 0.3539$; ■, $w_2 = 0.4004$; ⬢, $w_2 = 0.4515$.

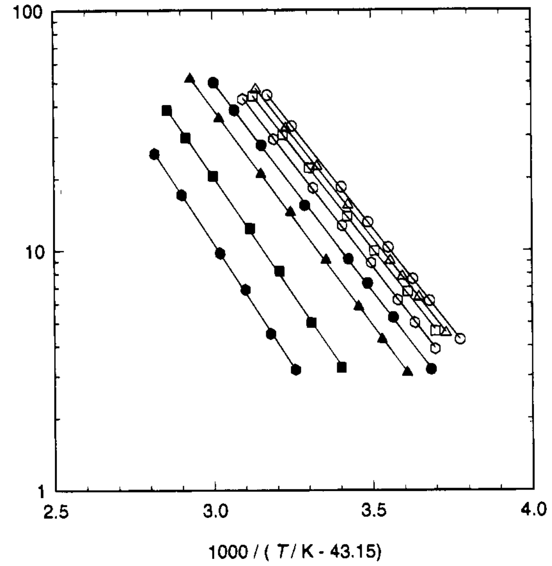

Figure 2. Vapor pressures of the H_2O (1) + LiCl (2) + LiBr (3) + $C_2H_6O_2$ (4) system at various mass fractions w_{2+3} ($H_2O/C_2H_6O_2$ mole ratio 10:1, LiCl/LiBr mass ratio 1:1): ○, $w_{2+3} = 0.1001$; △, $w_{2+3} = 0.1513$; □, $w_{2+3} = 0.2005$; ⬡, $w_{2+3} = 0.2500$; ●, $w_{2+3} = 0.3002$; ▲, $w_2 = 0.3501$; ■, $w_{2+3} = 0.4510$; ⬢, $w_{2+3} = 0.5417$.

Conclusions

The vapor pressures for the two systems water + lithium chloride + ethylene glycol and water + lithium chloride + lithium bromide + ethylene glycol were measured at

Table 3. Values of A_i, B_i, and AAD for Least-Squares Representation by the Antoine-type Equation

	$H_2O + LiCl + C_2H_6O_2$	$H_2O + LiCl + LiBr + C_2H_6O_2$
A_0	6.99074	6.52858
A_1	4.08696×10^{-2}	1.01801×10^{-1}
A_2	-4.20967×10^{-3}	-6.79255×10^{-3}
A_3	1.23300×10^{-4}	1.72195×10^{-4}
A_4	-1.07666×10^{-6}	-1.42752×10^{-6}
B_0	−1.69705	−1.50773
B_1	-7.46671×10^{-3}	-3.67810×10^{-2}
B_2	8.46880×10^{-4}	2.40500×10^{-3}
B_3	-3.15979×10^{-5}	-6.45585×10^{-5}
B_4	2.93524×10^{-7}	5.40224×10^{-7}
AAD[a]	1.65	1.03

[a] AAD $= 100/N\sum_{i=1}^{N}|(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}|$; N = number of points, P_{exptl} = experimental value, P_{calcd} = calculated value.

various temperatures and absorbent concentrations. The experimental results were correlated with an Antoine-type equation, and the calculated value from this model gave good agreement with the experimental data. The vapor pressure data are available for the design of absorption heat pumps.

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