J. Chem. Eng. Data **1997,** *42,* 145−148

Density, Vapor Pressure, Solubility, and Viscosity for Water + Lithium Bromide + Lithium Nitrate + 1,3-Propanediol

Young Park, 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

Sun Il Yu

R & D Laboratory, Rinnai Korea, 217-2 Sinsung-dong, Yusung-gu, Taejon, 305-345, South Korea

Four physical properties (solubility, vapor pressure, density, and viscosity) of water + lithium bromide + lithium nitrate + 1,3-propanediol ($LiBr/LiNO_3$ mole ratio = 4, ($LiBr + LiNO_3$)/$HO(CH_2)_3OH$ mass ratio = 3.5) were measured. The system, a possible working fluid for an absorption heat pump, mainly consists of absorbent ($LiBr + LiNO_3 + HO(CH_2)_3OH$) and refrigerant ($H_2O$). Solubilities were measured by the visual polythermal method in the temperature range (285.55 to 346.65) K and in the absorbent concentration range (68.0 to 75.0) mass %. Vapor pressures were measured by the boiling point method in the temperature range (325.35 to 395.15) K and in the absorbent concentration range (46.0 to 69.6) mass %. Densities and viscosities were measured by a set of hydrometers and viscometers, respectively, in the temperature range (283.15 to 343.15) K and in the absorbent concentration range (24.3 to 70.3) mass %. The measured values were correlated.

Introduction

Absorption heat pump systems (chiller and heat transformer) are of interest in the areas of refrigeration and air conditioning with respect to energy saving and environment protection. Recently, various types of working fluid pairs (refrigerant/absorbent) (Hihara, 1993) for absorption units were developed to improve the performance characteristic of the cycle or to satisfy specific conditions required for such systems as air-cooled absorption chiller (Iizuka et al., 1989; Inoue, 1993; Okano et al., 1994), low-temperature heat driven heat pump (Nishiyama, 1993), and solar powered absorption chiller (Iyoki and Uemura, 1981; Matsuda and Choi, 1993). A general procedure for checking the usefulness of a possible working fluid includes the measurements of various physical and thermal properties of the solution. The investigation of operation range, cycle simulation, and optimum design of the heat pump thus comes to be possible from a knowledge of their properties (Iyoki and Uemura, 1990). In previous studies several physical properties of the water + lithium bromide + ethanolamine system (Kim et al., 1996a,b) and the lithium bromide + 1,3-propanediol + water system (Park et al., 1996) were measured. In these two systems water was used as refrigerant and the others as absorbent. Ethanolamine and 1,3-propanediol were added to suppress the crystallization of the solutions, and two systems were found to have wide enough operation ranges for the air-cooled cycle absorption. In this work the water + lithium bromide + lithium nitrate + 1,3-propanediol system ($LiBr/LiNO_3$ mole ratio = 4, ($LiBr + LiNO_3$)/$HO(CH_2)_3OH$ mass ratio = 3.5) was selected as a potential working fluid pair, and four basic physical properties (solubility, vapor pressure, density, and viscosity) were measured over extensive temperature and concentration ranges. Lithium nitrate was added as a corrosion inhibitor at an optimum mole ratio proposed by Iyoki et al. (1993), and 1,3-propanediol, as an anticrystallization additive. Each set of the experimental results was correlated.

Experiment

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

Apparatus and Procedure. The visual polythermal method and the boiling point method were used to measure the solubilities and vapor pressures, respectively. The experimental apparatus and procedures were almost the same as those of the previous work (Kim et al., 1996a). The solubility measuring apparatus primarily consisted of a Pyrex glass vessel (50 cm^3), a thermistor thermometer (Cole Parmer, 08502−16) capable of reading to 0.01 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. After a series of dissolving and nucleation procedures of the small amount of crystals, the temperature at which the last crystal disappeared was taken as the crystallization temperature in each run. The vapor pressure measuring apparatus primarily consists of an 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), and two stirrers. A sample solution (approximately 250 cm^3) of a desired absorbent concentration was first placed in the vessel, and the system was evacuated to a slightly higher pressure than the expected vapor pressure of the sample solution at the initial temperature. Then the sample solution was heated and stirred well with a magnetic stirrer to prevent superheating. After thermal equilibrium was reached, the temperature of the sample solution and the pressure were measured. More detailed

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* Email: hlee@hanbit.kaist.ac.kr.

S0021-9568(96)00233-6 CCC: $14.00

Table 1. Mass Fraction Solubilities w_{2+3+4} for H_2O (1) + LiBr (2) + $LiNO_3$ (3) + $HO(CH_2)_3OH$ (4) with $LiBr/LiNO_3$ Mole Ratio = 4 and (LiBr + $LiNO_3$)/$HO(CH_2)_3OH$ Mass Ratio = 3.5 at Various Temperatures

T/K	w_{2+3+4}	T/K	w_{2+3+4}
285.55	0.680	315.25	0.707
294.05	0.686	319.65	0.712
303.45	0.695	320.85	0.715
305.35	0.699	322.25	0.718
305.45	0.699	325.05	0.722
306.25	0.702	329.15	0.728
309.25	0.703	338.25	0.740
312.85	0.704	346.65	0.750

descriptions of the experimental apparatus and procedure have been given (Kim et al., 1996a).

Densities and viscosities were measured by using a set of hydrometers (Alla) and five Ubbelohde-type viscometers which were well calibrated in accordance with ASTM published standards (Witeg). Each hydrometer was capable of reading to 0.001 g cm^{-3} and was used together with a cylinder-type sample vessel clamped in the constant temperature bath. Each viscometer has a different capillary diameter (Capillary No. 0C, 0B, 1, 1C, and 2) and the efflux time of a sample solution through the capillary was accurately measured and converted to the viscosity value by the following equation:

$$\eta = tK\rho \tag{1}$$

where η is the absolute viscosity, t is the efflux time, K is the given constant for the calculation of kinematic viscosity (tK), and ρ is the density at the same condition. All the sample solutions with the specified concentrations were prepared before measurement by weighing each component with a precision balance. The temperature was measured by a thermistor thermometer (Cole Parmer, 08502−16) and was controlled within ±0.05 K with a constant temperature bath. The experimental apparatus and procedures were checked in previous work (Kim et al., 1996b) and the relative errors from the literature values were less than 0.1% for the density measurement and were less than 1% for the viscosity measurement.

Results and Discussion

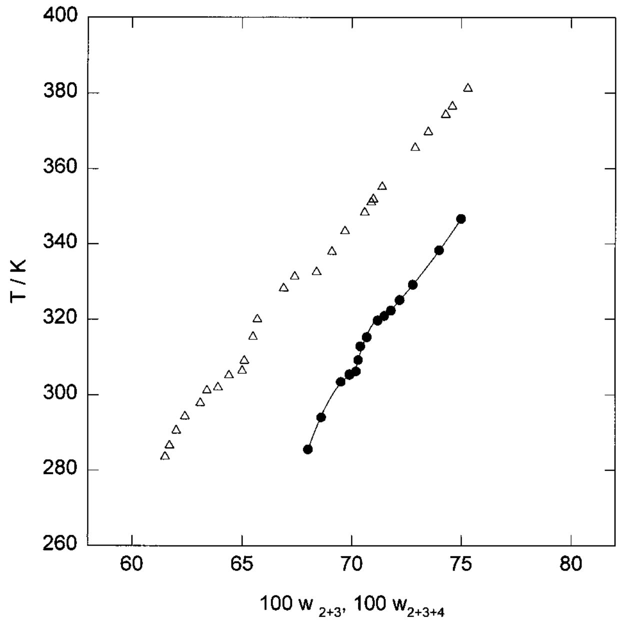

Figure 1. Mass fraction solubilities w_{2+3} and w_{2+3+4} of the H_2O (1) + LiBr (2) + $LiNO_3$ (3) and H_2O (1) + LiBr (2) + $LiNO_3$ (3) + $HO(CH_2)_3OH$ (4) systems at various temperatures: (△) H_2O + LiBr + $LiNO_3$ (Iyoki, 1993); (●) H_2O + LiBr + $LiNO_3$ + $HO(CH_2)_3OH$ ($LiBr/LiNO_3$ mole ratio = 4 and (LiBr + $LiNO_3$)/$HO(CH_2)_3OH$ mass ratio = 3.5); (—) calculated.

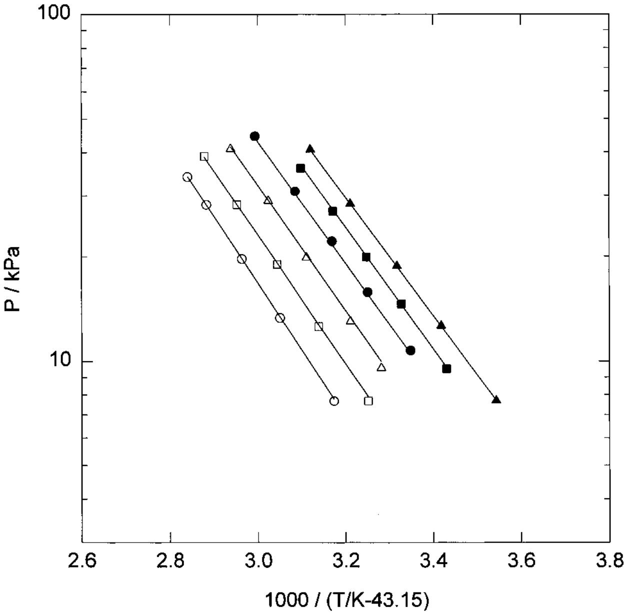

Figure 2. Vapor pressures of the H_2O (1) + LiBr (2) + $LiNO_3$ (3) + $HO(CH_2)_3OH$ (4) system ($LiBr/LiNO_3$ mole ratio = 4 and (LiBr + $LiNO_3$)/$HO(CH_2)_3OH$ mass ratio = 3.5) at various mass fractions: (▲) $w_{2+3+4} = 0.460$; (■) $w_{2+3+4} = 0.513$; (●) $w_{2+3+4} = 0.563$; (△) $w_{2+3+4} = 0.611$; (□) $w_{2+3+4} = 0.658$; (○) $w_{2+3+4} = 0.696$; (—) calculated.

The solubilities of the water + lithium bromide + lithium nitrate + 1,3-propanediol system ($LiBr/LiNO_3$ mole ratio = 4, (LiBr + $LiNO_3$)/$HO(CH_2)_3OH$ mass ratio = 3.5) were measured in the temperature range (285.55 to 346.65) K and in the concentration range (68.0 to 75.0) mass %, and the results are listed in Table 1. The measured values were correlated with the following equation:

$$100w = \sum_{i=0}^{2} a_i (T/\mathrm{K})^i \tag{2}$$

where w is the solubility represented by the mass fraction of absorbent (LiBr + $LiNO_3$ + $HO(CH_2)_3OH$), T is the absolute temperature, and a_i represents the regression parameters. The parameters a_i were determined by a least-squares method, and the results are listed in Table 2. The overall average absolute deviation between experimental and calculated values was found to be 0.04%. These measured and calculated solubility results were plotted in Figure 1 along with the solubility of the lithium bromide + lithium nitrate + water system. The solubility curve of the lithium bromide + lithium nitrate + 1,3-propanediol + water system shifted a little right by adding 1,3-proanediol, but the trend of the curve was similar to that of the system not containing 1,3-propanediol. The vapor

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

	a_0	a_1	a_2
$285.55 \le T/\mathrm{K} \le 306.25$	3.30939×10^{2}	−1.87304	3.33447×10^{-3}
$306.25 \le T/\mathrm{K} \le 320.85$	7.22973×10^{2}	−4.24675	6.90732×10^{-5}
$320.85 \le T/\mathrm{K} \le 346.65$	-3.44125×10	5.12162×10^{-1}	-5.66636×10^{-4}

Table 3. Vapor Pressures of the H_2O (1) + LiBr (2) + $LiNO_3$ (3) + $HO(CH_2)_3OH$ (4) System (LiBr/$LiNO_3$ Mole Ratio = 4 and (LiBr + $LiNO_3$)/$HO(CH_2)_3OH$ Mass Ratio = 3.5) at Various Mass Fractions of Absorbent w_{2+3+4}

T/K	P/kPa	T/K	P/kPa
$w_{2+3+4} = 0.460$		$w_{2+3+4} = 0.513$	
325.35	7.690	334.65	9.513
335.65	12.63	343.65	14.61
344.55	18.75	351.05	19.92
354.55	28.40	358.45	27.04
363.65	40.80	365.95	36.04
$w_{2+3+4} = 0.563$		$w_{2+3+4} = 0.611$	
341.75	10.73	347.85	9.562
350.75	15.79	354.55	13.02
358.65	22.13	364.55	19.88
367.25	30.91	373.85	28.99
377.15	44.56	383.45	40.98
$w_{2+3+4} = 0.658$		$w_{2+3+4} = 0.696$	
350.65	7.917	358.25	7.675
361.75	12.71	370.95	13.34
371.65	19.22	380.55	19.71
381.85	28.34	389.95	28.26
390.55	38.79	395.15	34.05

Table 4. Values of A_i, B_i, and AAD for Least-Squares Representation by Eq 3

A_0	-2.22548×10^{3}	B_1	-5.31371×10^{1}
A_1	1.61716×10^{2}	B_2	1.39429
A_2	-4.23702	B_3	-1.61266×10^{-2}
A_3	4.89233×10^{-2}	B_4	6.92739×10^{-5}
A_4	-2.10079×10^{-4}	AAD[a]	1.40%
B_0	7.36471×10^{2}		

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

pressures of the system were measured in the temperature range (325.35 to 395.15) K and in the concentration range (46.0 to 69.6) mass %. The experimental results are listed in Table 3, and these values were correlated with an Antoine-type equation which expresses vapor pressure as a function of temperature and concentration:

$$\log(P/\mathrm{kPa}) = \sum_{i=0}^{4} [A_i + \{1000B_i/(T/\mathrm{K} - 43.15)\}](100w)^i \tag{3}$$

where P is the vapor pressure, A_i and B_i are the regression parameters, T is the absolute temperature, and w is the mass fraction of absorbent (LiBr + $LiNO_3$ + $HO(CH_2)_3OH$). The parameters A_i and B_i were determined by a least-squares method, and the results are shown in Table 4. The overall average absolute deviation between the experimental and calculated values was found to be 1.40%. The experimental and calculated results were plotted in Figure 2, and the figure shows that the log P versus 1000/(T/K − 43.15) relation at a given concentration is linear over the pressure and temperature ranges considered.

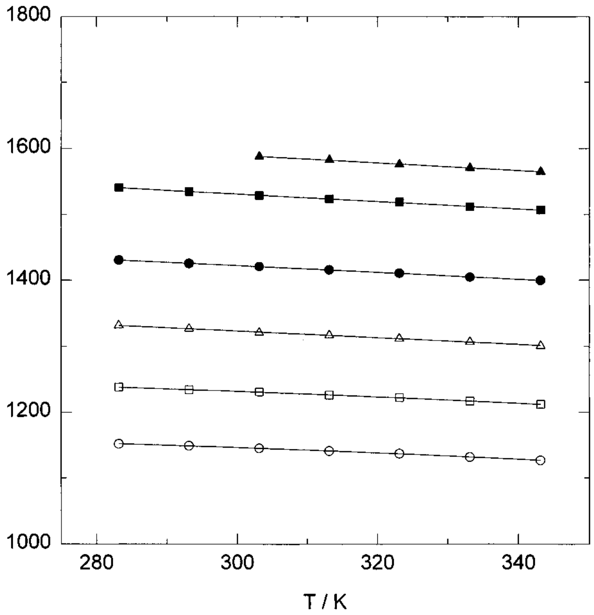

Figure 3. Densities of the H_2O (1) + LiBr (2) + $LiNO_3$ (3) + $HO(CH_2)_3OH$ (4) system (LiBr/$LiNO_3$ mole ratio = 4 and (LiBr + $LiNO_3$)/$HO(CH_2)_3OH$ mass ratio = 3.5) at various mass fractions: (○) $w_{2+3+4} = 0.243$; (□) $w_{2+3+4} = 0.355$; (△) $w_{2+3+4} = 462$; (●) $w_{2+3+4} = 0.563$; (■) $w_{2+3+4} = 0.657$; (▲) $w_{2+3+4} = 0.703$; (—) calculated.

The densities and viscosities of the system were measured at seven different temperatures between (283.15 and 343.15) K in the concentration range (24.3 to 70.3) mass %. The experimental results are listed in Table 5 and were correlated with the following equations:

$$\rho/\mathrm{kg\ m^{-3}} = \sum_{i=0}^{3} [(a_i + b_i T/\mathrm{K} + c_i (T/\mathrm{K})^2)(100w)^i] \tag{4}$$

$$\log(\eta/\mathrm{mPa{\cdot}s}) = \sum_{i=0}^{4} [(a_i + b_i/(T/\mathrm{K}) + c_i/(T/\mathrm{K})^2)(100w)^i] \tag{5}$$

where ρ is the density, η is the absolute viscosity, a_i, b_i, and c_i are the regression parameters, T is the absolute temperature in K, and w is the mass fraction of absorbent (LiBr + $LiNO_3$ + $HO(CH_2)_3OH$). The parameters a_i, b_i, and c_i were determined by a least-squares method, and the

Table 5. Densities and Viscosities of the H_2O (1) + LiBr (2) + $LiNO_3$ (3) + $HO(CH_2)_3OH$ (4) System (LiBr/$LiNO_3$ Mole Ratio = 4 and (LiBr + $LiNO_3$)/$HO(CH_2)_3OH$ Mass Ratio = 3.5) at Various Mass Fractions of Absorbent w_{2+3+4}

	T/K						
$100w_{2+3+4}$	283.15	293.15	303.15	313.15	323.15	333.15	343.15
				ρ/kg m^{-3}			
24.3	1152	1149	1145	1141	1137	1132	1127
35.5	1238	1234	1231	1226	1222	1217	1212
46.2	1332	1327	1321	1317	1312	1307	1301
56.3	1431	1426	1421	1416	1411	1405	1400
65.7	1541	1535	1529	1524	1519	1512	1507
70.3			1588	1583	1576	1571	1565
				η/mPa·s			
24.3	2.11	1.62	1.29	1.06	0.888	0.811	0.705
35.5	2.96	2.26	1.80	1.47	1.23	1.04	0.903
46.2	4.74	3.59	2.81	2.29	1.92	1.61	1.39
56.3	9.71	7.01	5.38	4.26	3.67	2.91	2.43
65.7	31.8	21.3	15.2	11.3	8.61	6.80	5.53
70.3			30.6	21.4	15.7	11.9	9.28

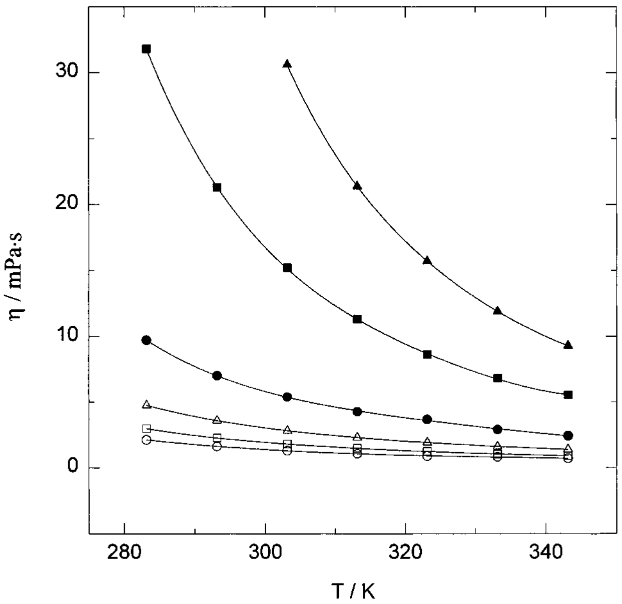

Figure 4. Viscosities of the H_2O (1) + LiBr (2) + $LiNO_3$ (3) + $HO(CH_2)_3OH$ (4) system (LiBr/$LiNO_3$ mole ratio = 4 and (LiBr + $LiNO_3$)/$HO(CH_2)_3OH$ mass ratio = 3.5) at various mass fractions: (○) $w_{2+3+4} = 0.243$; (□) $w_{2+3+4} = 0.355$; (△) $w_{2+3+4} = 462$; (●) $w_{2+3+4} = 0.563$; (■) $w_{2+3+4} = 0.657$; (▲) $w_{2+3+4} = 0.703$; (—) calculated.

Table 6. Values of a_i, b_i, and c_i for Least-Squares Representation by Eqs 4 and 5

eq 4		eq 5	
a_0	8.72052×10^{2}	a_0	5.27614×10^{1}
a_1	6.76476	a_1	−4.69906
a_2	1.16208×10^{-1}	a_2	1.53712×10^{-1}
a_3	-3.51710×10^{-4}	a_3	-2.19142×10^{-3}
b_0	8.76733×10^{-1}	a_4	1.15278×10^{-5}
b_1	1.13873×10^{-2}	b_0	-3.32782×10^{4}
b_2	-9.97744×10^{-4}	b_1	2.90627×10^{3}
b_3	7.07307×10^{-6}	b_2	-9.56273×10
c_0	-1.86250×10^{-3}	b_3	1.37602
c_1	-2.72725×10^{-5}	b_4	-7.30994×10^{-3}
c_2	1.67235×10^{-6}	c_0	5.23921×10^{6}
c_3	-1.19702×10^{-8}	c_1	-4.49888×10^{5}
		c_2	1.49381×10^{4}
		c	-2.17277×10^{2}
		c_4	1.17082

results are listed in Table 6. The average absolute deviations between the experimental and the calculated values were 0.02% for density measurement and 0.79% for viscosity measurement, respectively. The experimental and calculated results of density and viscosity measurements were plotted in Figures 3 and 4, respectively.

Conclusions

As an alternative working fluid for absorption heat pump, the water + lithium bromide + lithium nitrate + 1,3-propanediol system (LiBr/$LiNO_3$ mole ratio = 4, (LiBr + $LiNO_3$)/$HO(CH_2)_3OH$ mass ratio = 3.5) was selected and four physical properties (solubility, vapor pressure, density, and viscosity) were measured at various absorbent concentrations and temperatures. The measured properties were correlated with the proper equations. The properties considered in this work are necessary for the design of the absorption heat pump, but several other properties such as heat capacity and heat of mixing are to be measured in order to evaluate the performance characteristic of the working fluid.

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Received for review July 9, 1996. Accepted October 29, 1996.®

JE960233Z

® Abstract published in *Advance ACS Abstracts,* December 1, 1996.