

# Solubilities, Vapor Pressures, Densities, and Viscosities of the (Water + Lithium Bromide + Lithium Iodide + Lithium Chloride) System

Kee-Kahb Koo\* and Hyung-Rae Lee

Department of Chemical Engineering, Sogang University, C.P.O. Box 1142, Seoul 100-611, Korea

Siyoung Jeong

Department of Mechanical Engineering, Sogang University, C.P.O. Box 1142, Seoul 100-611, Korea

Young-Sam Oh, Dal-Ryung Park, and Young-Soon Baek

R & D Center, Korea Gas Corporation, Ansan 425-150, Korea

---

Measurements of thermophysical properties of the (water + lithium bromide + lithium iodide + lithium chloride) system (LiBr:LiI:LiCl = 4.5:1:2 by mole ratio) were performed as functions of concentration and temperature. Solubilities were measured by a visual polythermal method at temperatures from (248.59 to 350.46) K. Regression equations were obtained with a least-squares method, and the average absolute deviations of the calculated values from the experimental data were 0.10% (solution temperature < 284.59 K) and 0.12% (temperature  $\geq$  284.59 K), respectively. The vapor pressures were measured by a boiling point method at lithium salts concentrations from (50.0 to 70.0) mass % and temperatures from (318.36 to 455.75) K. The experimental data were correlated with an Antoine-type equation. The average absolute deviation of the calculated values from the experimental data was 1.83%. Densities and viscosities were measured at concentrations from (50.0 to 64.0) mass % and temperatures from (283.15 to 333.15) K. Regression equations for densities and viscosities were obtained with a least-squares method, and the average absolute deviations of the calculated values from the experimental data were 0.08% and 0.87%, respectively.

---

## Introduction

Extensive thermophysical properties of working fluids are required for the proper design of absorption refrigerators and heat pumps. Extension of the absorption cycle to improve the performance of those machines is often limited by crystallization of the absorbent, which is a function of concentration and pressure in the absorber. Therefore, precise solubility and vapor pressure data for the working fluid are essential. The density and viscosity data are also very important for the optimum design of those machines.

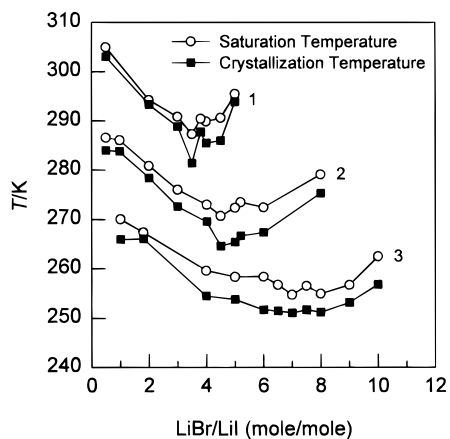
Solubilities and vapor pressures of the (water + lithium bromide + lithium iodide) system were measured by Iyoki et al. (1990, 1993). However, the vapor pressure of this system is considered to be higher than that expected for a working fluid. In the present study, to suppress vapor pressure without loss of solubility, LiCl was selected. In this article, determination procedure on the optimum mole ratio of the lithium salts is introduced using the solubility data of (water + lithium bromide + lithium iodide) and (water + lithium bromide + lithium iodide + lithium chloride) systems. Second, solubilities, vapor pressures, densities, and viscosities for the (water + lithium bromide + lithium iodide + lithium chloride) system are reported over a wide range of temperatures, and the values are correlated.

## Experimental Section

**Materials.** LiBr (99+%), LiI (99+%), and LiCl (99+%) used in this work were supplied by Aldrich Chemical Co. All the reagents were used without further purification. All solutions were prepared with deionized distilled water.

**Experimental Setup and Procedure.** The visual polythermal method used in this work was detailed elsewhere (Clynnne and Potter II, 1979). The solubility apparatus consists of an equilibrium cell and a thermostat (Lauda, RM20S), which is stabilized to  $\pm 0.01$  K. The cell is a 100 mL Pyrex glass vessel with a triple-jacket. The inner cell is for solution. The heating media from the thermostat is circulated through the middle jacket. The outer jacket of the cell was hermetically sealed under vacuum to prevent fogging on the surface of the cell during experiments at lower temperatures and allows us to observe easily the formation or melting of crystals. This configuration is also effective for keeping a constant temperature by preventing the heat loss from the wall.

The experimental procedure is as follows: the sample solution of about 30 mL in the cell is cooled to crystallize with a cooling rate of 1 K/min and make a rough estimation of the crystallization temperature. Then sample solution is heated with controlled heating rate as crystals are molten. When a few crystals remain, the heating rate is controlled to be 0.003 K/min. At this heating rate, the melting point of the last crystal of salt is taken to be the equilibrium saturation temperature. At the temperature



**Figure 1.** Crystallization and saturation temperatures with LiBr/LiI mole ratio in the (H<sub>2</sub>O + LiBr + LiI) system: 1, 100 w<sub>T</sub> = 62.5; 2, 100 w<sub>T</sub> = 60.0; 3, 100 w<sub>T</sub> = 58.0.

10 K higher than the equilibrium saturation temperature, the solution is kept about 1 h to dissolve all clusters that may remain. Then the solution is cooled again. As the temperature of solution approaches to the expected crystallization temperature, the cooling rate is controlled to be 0.1K/min. Finally the crystallization temperature is determined when the first crystal forms.

The determination of vapor pressure was made using the boiling point method (Scatchard et al., 1938, 1940). The experimental setup consists of 500 mL round flask (as the equilibrium still), a condenser, mercury manometer, and vacuum pump. The equilibrium still with sample solution (about 250 mL) is placed in the thermostat equipped with cooler and heater. With this assembly the thermostat was found to be stable within  $\pm 0.01$  K during experimental runs.

A solution of a desired absorbent concentration is poured into the equilibrium still, which is placed in the thermostat. A coolant of 0 °C is supplied to condenser, and the system is evacuated to a desired degree of pressure. Then the solution in the still is heated by controlling the temperature of the thermostat. When thermal equilibrium is reached, the temperature is measured and the vapor pressure is determined by the reading of manometer.

Using a set of hydrometers, the density measurements were carried out. The sample solution with a proper hydrometer was first placed in the cylindrical chamber located in the constant-temperature bath. The bath temperature was controlled by a thermostat (Polyscience, model 9710). When the solution temperature was equilibrated with that of thermostat, the value of the specific gravity was obtained from the meniscus of solution with the hydrometer by using a cathetometer.

The viscosity measurements were carried out by using a set of Ubbelohde type viscometers. The solution in the viscometer was sealed to minimize evaporation, and the viscometer was placed in the thermostat at the desired temperature. After thermal equilibration, the efflux time of the solution was measured three times by stopwatch for every experimental run. The reproducibility of efflux time measurement was within  $\pm 0.1\%$ . Finally, viscosity was calculated by the following equation:

$$\frac{\eta_{\text{Sol}}}{\eta_{\text{H}_2\text{O ref}}} = \frac{\rho_{\text{Sol}} t_{\text{Sol}}}{\rho_{\text{H}_2\text{O ref}} t_{\text{H}_2\text{O ref}}} \quad (1)$$

Here  $\eta$  is viscosity,  $t$  is time, and  $\rho$  is density.

**Table 1.** Solubilities of the (H<sub>2</sub>O + LiBr + LiI + LiCl) System

<i>T</i> /K	100 w <sub>T</sub>	<i>T</i> /K	100 w <sub>T</sub>
248.59	56.0	292.71	63.0
261.60	57.8	297.09	63.5
268.75	59.0	304.54	64.0
271.87	59.7	312.99	65.0
274.42	60.0	324.71	66.0
280.38	61.0	334.92	67.0
284.59	62.0	346.51	68.2
289.60	62.5	350.46	68.6

**Table 2.** Coefficients of Eq 2 for (H<sub>2</sub>O + LiBr + LiI + LiCl) System

<i>A<sub>n</sub></i>	<i>T</i> < 284.59 (K)	<i>A<sub>n</sub></i>	<i>T</i> ≥ 284.59 (K)
<i>A</i> <sub>0</sub>	$8.24786 \times 10^1$	<i>A</i> <sub>0</sub>	$2.90878 \times 10^1$
<i>A</i> <sub>1</sub>	$-3.44180 \times 10^{-1}$	<i>A</i> <sub>1</sub>	$1.30130 \times 10^{-1}$
<i>A</i> <sub>2</sub>	$9.55868 \times 10^{-4}$	<i>A</i> <sub>2</sub>	$-4.99417 \times 10^{-5}$

**Table 3.** Vapor Pressures of the (H<sub>2</sub>O + LiBr + LiI + LiCl) System

<i>T</i> /K	<i>P</i> /kPa	<i>T</i> /K	<i>P</i> /kPa	<i>T</i> /K	<i>P</i> /kPa
100 w <sub>T</sub> = 50.0					
318.36	2.27	325.23	2.13	336.57	-2.27
332.03	4.67	339.88	4.53	350.73	-4.67
340.05	6.93	347.90	6.93	358.73	-6.93
350.33	11.33	358.49	11.33	368.64	11.33
360.08	17.60	369.69	17.87	378.70	17.60
370.38	27.60	380.64	27.46	390.04	27.06
381.61	41.60	392.40	42.40	401.81	42.13
389.68	55.73	398.85	54.80	415.93	69.06
396.76	68.66	407.05	70.26	430.20	101.19
402.31	82.53	413.63	84.79		
408.34	101.60	418.64	101.46		
100 w <sub>T</sub> = 65.0					
347.95	2.27	402.75	16.67		
361.35	4.67	413.89	27.73		
370.04	6.93	426.65	41.60		
380.50	11.36	439.90	64.39		
390.95	17.60	446.34	78.79		
401.90	27.20	455.75	102.39		
413.42	40.53				
423.84	57.86				
430.56	71.33				
436.43	84.53				
442.52	101.99				
100 w <sub>T</sub> = 70.0					

Figure 1 shows the crystallization temperatures and equilibrium saturation temperatures in the (water + lithium bromide + lithium iodide) system with (58.0, 60.0, and 62.5) mass % absorbent (lithium salts). As the mole ratio of LiBr/LiI increased, crystallization temperatures decreased and reached a minimum and then increased slowly as the LiBr/LiI ratio increased. Crystallization temperatures were found to drop about 15–20 K compared with those of the (water + lithium bromide) system. In the (water + lithium bromide + lithium iodide) system, the optimum mole ratio at 60.0 mass % is about 4.5 as can be seen from Figure 1.

Addition of LiCl was observed to suppress vapor pressure as expected. However, the solubility was found to decrease when the LiCl/LiI ratio was bigger than 2 (not shown here). Therefore, the optimum mole ratio of LiBr:LiI:LiCl was determined to be 4.5:1:2 based on 60.0 mass % lithium salts of the (water + lithium bromide + lithium iodide + lithium chloride) system.

## Results and Discussion

**Solubility.** The solubilities for the system (LiBr:LiI:LiCl = 4.5:1:2 by mole ratio) were measured by a visual

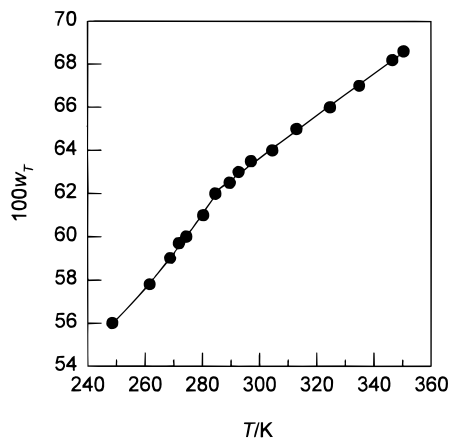


Figure 2. Solubilities of the (H<sub>2</sub>O + LiBr + LiI + LiCl) system (LiBr:LiI:LiCl = 4.5:1:2 by mole ratio).

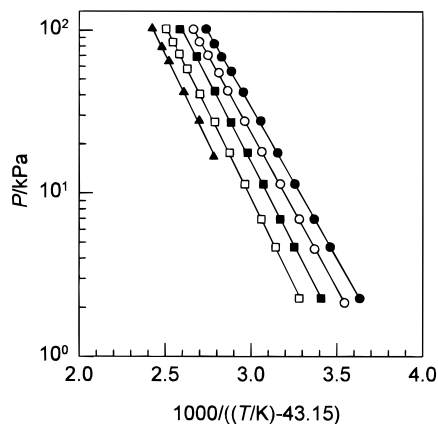


Figure 3. Vapor pressures of the (H<sub>2</sub>O + LiBr + LiI + LiCl) system (LiBr:LiI:LiCl = 4.5:1:2 by mole ratio): ● ( $w_T = 0.50$ ); ○ ( $w_T = 0.55$ ); ■ ( $w_T = 0.60$ ); □ ( $w_T = 0.65$ ); ▲ ( $w_T = 0.70$ ).

polythermal method at temperatures from (248.59 to 350.46) K. The experimental data are listed in Table 1 and regressed by a least-squares method with the following equation

$$S = \sum_{n=0}^2 A_n T^n \quad (2)$$

where  $S$  is the solubility represented by the mass percent of absorbent (lithium salts),  $100w_T$ ,  $T$  is the absolute temperature, and  $A_n$  are the coefficients. The calculated values of the coefficients are listed in Table 2. The experimental data and calculated values are plotted in Figure 2. The average absolute deviation between experimental and calculated values is 0.10% when the solution temperature is smaller than 284.59 K and 0.12% when the solution temperature is larger than 284.59 K.

**Vapor Pressure.** The vapor pressures of the (water + lithium bromide + lithium iodide + lithium chloride) system (LiBr:LiI:LiCl = 4.5:1:2 by mole ratio) were measured at concentrations from (50.0 to 70.0) mass % and temperatures from (318.36 to 455.75) K. Experimental results are listed in Table 3 and are presented in Figure 3 against the reciprocal of the temperature. As can be seen from Figure 3, the  $\log P$  against  $1000/(T - 43.15)$  relation for the given concentrations was linear over the pressure and temperature range. The vapor pressures were correlated with an Antoine-type equation that expresses vapor pressure as a function of temperature and concentration

Table 4. Coefficients of Eq 3 for the (H<sub>2</sub>O + LiBr + LiI + LiCl) System

$A_0$	$3.32636 \times 10^2$	$B_0$	$-9.19579 \times 10^4$
$A_1$	$-2.14306 \times 10^1$	$B_1$	$5.88479 \times 10^3$
$A_2$	$5.24677 \times 10^{-1}$	$B_2$	$-1.42457 \times 10^2$
$A_3$	$-5.66454 \times 10^{-3}$	$B_3$	$1.51666 \times 10^0$
$A_4$	$2.27751 \times 10^{-5}$	$B_4$	$-6.01141 \times 10^{-3}$

Table 5. Densities  $\rho/\text{kg}\cdot\text{m}^{-3}$  of the (H<sub>2</sub>O + LiBr + LiI + LiCl) System

	$100w_T$					
	50.0	55.0	58.0	60.0	62.5	64.0
283.15	1513	1596	1647	1690		
293.15	1510	1592	1642	1681	1727	
303.15	1504	1585	1638	1676	1721	
313.15	1499	1579	1631	1671	1713	1750
323.15	1494	1574	1625	1665	1706	1742
333.15	1488	1567	1619	1657	1700	1735

Table 6. Coefficients of Eq 4 for the (H<sub>2</sub>O + LiBr + LiI + LiCl) System

$A_0$	$2.44536 \times 10^5$	$B_0$	$-1.51263 \times 10^3$	$C_0$	$2.33654 \times 10^0$
$A_1$	$-1.31828 \times 10^4$	$B_1$	$8.19377 \times 10^1$	$C_1$	$-1.26597 \times 10^{-1}$
$A_2$	$2.37114 \times 10^2$	$B_2$	$-1.47275 \times 10^0$	$C_2$	$2.27526 \times 10^{-3}$
$A_3$	$-1.41362 \times 10^0$	$B_3$	$8.78624 \times 10^{-3}$	$C_3$	$-1.35740 \times 10^{-5}$

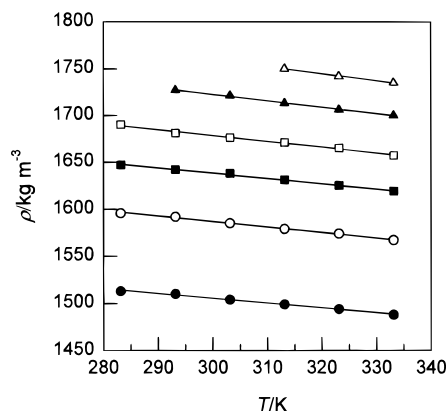


Figure 4. Densities of the (H<sub>2</sub>O + LiBr + LiI + LiCl) system (LiBr:LiI:LiCl = 4.5:1:2 by mole ratio): ● ( $w_T = 0.50$ ); ○ ( $w_T = 0.55$ ); ■ ( $w_T = 0.58$ ); □ ( $w_T = 0.60$ ); ▲ ( $w_T = 0.625$ ); △ ( $w_T = 0.64$ ).

as follows

$$\log(P/\text{kPa}) = \sum_{n=0}^4 [A_n + \{B_n/((T/K) - 43.15)\}](100w_T)^n \quad (3)$$

where  $P$  is the vapor pressure,  $T$  is the absolute temperature, and  $w_T$  is the mass fraction of the lithium salts (LiBr + LiI + LiCl). The coefficients  $A_n$  and  $B_n$  determined by the least-squares method are listed in Table 4. The average absolute deviations of the calculated values from the experimental data were 1.80%.

**Density.** The densities for the system were measured in the range of temperatures from (283.15 to 333.15) K and in the range of absorbent concentrations from (50.0 to 64.0) mass %. Experimental results are listed in Table 5. The experimental data were fitted to polynomial equations as a function of absolute temperature by a least-squares method

$$\rho/\text{kg}\cdot\text{m}^{-3} = \sum_{n=0}^3 [A_n + B_n/(T/K) + C_n(T/K)^2](100w_T)^n \quad (4)$$

where  $\rho$  is the density,  $T$  is the absolute temperature, and

**Table 7. Viscosities  $\eta/\text{mPa}\cdot\text{s}$  of the ( $\text{H}_2\text{O} + \text{LiBr} + \text{LiI} + \text{LiCl}$ ) System**

T/K	$100w_T$					
	50.0	55.0	58.0	60.0	62.5	64.0
283.15	5.22	8.11	11.18	14.59		
293.15	4.31	6.54	8.83	11.06	14.00	
303.15	3.51	5.22	6.94	8.56	11.16	
313.15	3.09	4.29	5.62	6.87	8.72	10.35
323.15	2.73	3.50	4.49	5.46	6.79	7.98
333.15	2.50	3.06	3.65	4.36	5.37	6.26

**Table 8. Coefficients of Eq 5 for the ( $\text{H}_2\text{O} + \text{LiBr} + \text{LiI} + \text{LiCl}$ ) System**

$A_0$	$1.321\ 504 \times 10^3$	$B_0$	$-8.438\ 289 \times 10^5$	$C_0$	$1.355\ 424 \times 10^8$
$A_1$	$-6.894\ 528 \times 10^1$	$B_1$	$4.419\ 346 \times 10^4$	$C_1$	$-7.124\ 179 \times 10^6$
$A_2$	$1.203\ 648 \times 10^0$	$B_2$	$-7.745\ 670 \times 10^2$	$C_2$	$1.253\ 119 \times 10^5$
$A_3$	$-7.043\ 891 \times 10^{-3}$	$B_3$	$4.548\ 235 \times 10^0$	$C_3$	$-7.376\ 570 \times 10^2$

$w_T$  is the mass fraction of lithium salts (LiBr + LiI + LiCl). The values of coefficients  $A_n$ ,  $B_n$ , and  $C_n$  of the equation are listed in Table 6, and experimental data are plotted in Figure 4. The solid lines given in Figure 4 are the calculated values from the equation. The average absolute deviation between the measured data and the calculated values from these polynomial equations was 0.08%.

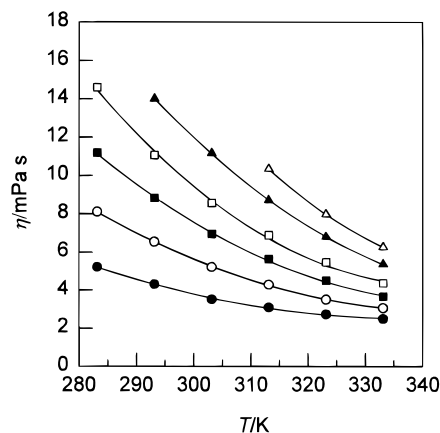
**Viscosity.** The viscosities for the system were measured in the range of temperatures from (283.15 to 333.15) K and in the range of absorbent concentrations from (50.0 to 64.0)%. Experimental results are listed in Table 7. The experimental data were fitted to polynomial equations as a function of absolute temperature by a least-squares method

$$\log(\eta/\text{mPa}\cdot\text{s}) = \sum_{n=0}^3 [A_n + B_n/(TK) + C_n(TK)^2](100w_T)^n \quad (5)$$

where  $\eta$  is the viscosity,  $T$  is the absolute temperature, and  $w_T$  is the mass fraction of the lithium salts (LiBr + LiI + LiCl). The values of coefficients  $A_n$ ,  $B_n$ , and  $C_n$  of the equation are listed in Table 8, and experimental data are plotted in Figure 5. The solid lines given in Figure 5 are the calculated values from the equation. The average absolute deviation between the measured data and the calculated values from these polynomial equations was 0.87%.

## Conclusions

Solubilities, vapor pressures, densities and viscosities of the (water + lithium bromide + lithium iodide + lithium

**Figure 5.** Viscosities of the ( $\text{H}_2\text{O} + \text{LiBr} + \text{LiI} + \text{LiCl}$ ) system (LiBr:LiI:LiCl = 4.5:1:2 by mole ratio): ● ( $w_T = 0.50$ ); ○ ( $w_T = 0.55$ ); ■ ( $w_T = 0.58$ ); □ ( $w_T = 0.60$ ); ▲ ( $w_T = 0.625$ ); △ ( $w_T = 0.64$ ).

chloride) system (LiBr:LiI:LiCl = 4.5:1:2 by mole ratio) were measured at various temperatures and concentrations. The optimum mole ratio of lithium salts was determined by solubility measurements on the (water + lithium bromide + lithium iodide) and on the (water + lithium bromide + lithium iodide + lithium chloride) systems.

All the measured properties were correlated with the proper equations. The calculated values from the correlation equations were in good agreement with the experimental data. The properties reported in the present work would be useful for the optimum design of absorption refrigerating machines and heat pumps.

## Literature Cited

- Clyne, M. A.; Potter, R. W., II. Solubility of Some Alkali and Alkaline Earth Chlorides in Water at Moderate Temperature. *J. Chem. Eng. Data* **1979**, *24*, 338–340.
- Iyoki, S.; Iwasaki, S.; Uemura, T. Vapor Pressure of the Water–Lithium Bromide–Lithium Iodide System. *J. Chem. Eng. Data* **1990**, *35*, 429–433.
- 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.
- Scatchard, G.; Raymond, C. L.; Gilman, H. H. Vapor–Liquid Equilibrium (I). *J. Am. Chem. Soc.* **1938**, *60*, 1275–1287.
- Scatchard, G.; Wood, S. E.; Mochel, J. M. Vapor–Liquid Equilibrium (V). *J. Am. Chem. Soc.* **1940**, *62*, 712–716.

Received for review March 6, 1998. Accepted May 15, 1998.

JE980063L