Densities, Viscosities, and Surface Tensions of the (Water + Lithium Bromide + Lithium Nitrate + Lithium Iodide + Lithium Chloride) System

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Measurements of the thermophysical properties of the (water + lithium bromide + lithium nitrate + lithium iodide + lithium chloride) system ($LiBr/LiNO_3/LiI/LiCl$ = 5:1:1:2 by mole) were performed as functions of concentration and temperature. Densities, viscosities, and surface tensions were measured at concentrations from (50.0 to 65.0) mass % and temperatures from (283.15 to 333.15) K. Regression equations for densities, viscosities, and surface tensions were obtained with least-squares methods. The average absolute deviations of the calculated values from the experimental data were 0.05%, 0.90%, and 0.30%, respectively.

Introduction

Recently, LiBr-based working fluids have been extensively studied for air-cooled absorption refrigerators and heat pumps. For proper design of absorption machines, the thermophysical properties of the working fluids are needed. Solubility and vapor pressure data are required for the construction of the $P-T-X$ diagram, which gives primary information on the absorption cycle in the system. Heat capacity, density, viscosity, and surface tension data are also required to understand heat- and mass-transfer mechanisms for the optimum design of those machines.

The (water + lithium bromide + lithium nitrate + lithium iodide + lithium chloride) system has been proposed as a possible working fluid for air-cooled absorption chillers (Okano et al., 1993). Okano et al. discussed the heat- and mass-transfer characteristics of this fluid with the molar lithium salt ratio 100:25:75:41 ($LiBr/LiNO_3/LiI/LiCl$). However, the procedure used to determine an optimal ratio of lithium salts and any thermophysical properties of this solution was not described in their communication. We independently studied this system and found that the optimum mole ratio of $LiBr/LiNO_3/LiI/LiCl$ is 5:1:1:2 on the basis of 60.0 mass % lithium salts of the system (Koo et al., 1998). With this mole ratio, crystallization temperatures in the concentration range (58 to 70) mass % are about 30 K to 35 K lower compared with those of the (water + lithium bromide) system. More recently, solubilities, vapor pressures, and heat capacities for the system were measured in our laboratory (Koo et al., 1999a). The $P-T-X$ diagram constructed from those data showed that the working range of the absorber temperature can be extended to about 45 °C to 50 °C, which is critical for the air-cooled absorption chillers (Koo et al., 1999b).

In order to evaluate the heat- and mass-transfer characteristics of this fluid, measurements of densities, viscosities, and surface tensions for the (water + lithium bromide + lithium nitrate + lithium iodide + lithium chloride) system were performed. In this article, we report those values and their regression equations over a wide range of temperatures.

Table 1. Measured Densities ρ, Viscocities η, and Surface Tensions σ of the (H_2O + LiBr + $LiNO_3$ + LiI + LiCl) System

	$100w_T$					
T/K	= 50.0	= 55.0	= 58.0	= 60.0	= 62.5	= 65.0
			Density ρ/(kg·m^{-3})			
283.15	1497	1575	1628	1665	1710	
293.15	1496	1574	1622	1658	1705	1757
303.15	1490	1567	1616	1652	1701	1753
313.15	1485	1560	1610	1643	1692	1745
323.15	1480	1555	1604	1636	1687	1737
333.15	1473	1549	1597	1630	1679	1727
			Viscosity η(mPa·s)			
283.15	5.45	8.51	12.08	15.35	21.19	
293.15	4.47	6.84	9.44	11.63	16.33	21.63
303.15	3.58	5.41	7.21	8.81	12.02	16.68
313.15	3.00	4.40	5.79	7.00	9.26	12.58
323.15	2.58	3.58	4.66	5.46	7.16	9.33
333.15	2.18	3.09	3.69	4.36	5.60	7.19
			Surface Tension σ(mN·m^{-1})			
283.15	89.12	91.80	92.95	93.80	94.98	
293.15	88.66	91.35	92.21	93.09	94.35	95.51
303.15	87.76	90.54	91.54	92.47	93.81	94.96
313.15	86.93	89.71	90.87	91.71	92.96	94.17
323.15	86.08	88.91	90.14	91.04	92.37	93.43
333.15	85.14	88.15	89.25	90.34	91.70	92.66

Experimental Section

Materials. Solutions were prepared by using LiBr (99+%), $LiNO_3$ (99+%), LiI (99+%), and LiCl (99+%). All materials supplied by Aldrich Chemical Co. were ACS reagent grade and were used without further purification. Deionized distilled water was used to prepare the solutions. The materials were measured by using an electronic balance (Ohaus, AP201-S), accurate to ±0.05 mg.

Apparatus and Procedure. The density and viscosity measurements were carried out using a set of hydrometers

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Table 2. Coefficients of Eq 2 for the Density of the (H_2O + LiBr + $LiNO_3$ + LiI + LiCl) System

A_0	2.96670×10^{5}	B_0	-1.89916×10^{3}	C_0	3.02891×10^{0}
A_1	-1.61872×10^{4}	B_1	1.04047×10^{2}	C_1	-1.65979×10^{-1}
A_2	2.93918×10^{2}	B_2	-1.88850×10^{0}	C_2	3.01269×10^{-3}
A_3	-1.76726×10^{0}	B_3	1.13634×10^{-2}	C_3	-1.81306×10^{-5}

Table 3. Coefficients of Eq 3 for the Viscosity of the (H_2O + LiBr + $LiNO_3$ + LiI LiCl) System

A_0	3.900686×10^{2}	B_0	-2.782524×10^{5}	C_0	4.865590×10^{7}
A_1	-2.138891×10^{1}	B_1	1.518189×10^{4}	C_1	-2.643987×10^{6}
A_2	3.916588×10^{-1}	B_2	-2.767958×10^{2}	C_2	4.803123×10^{4}
A_3	-2.407118×10^{-3}	B_3	1.691270×10^{0}	C_3	-2.916775×10^{2}

and Ubbelohde type viscometers, respectively. The temperature of the cylindrical chamber in which the experimental setup was placed was controlled with a thermostat (Polyscience, model 9710) with the stability ±0.01 K. The detailed experimental procedure is given elsewhere (Koo et al., 1998).

The surface tension measurements were conducted by using a capillary-rise method. The apparatus (Fisher, No. 14-818) consists basically of a 250 mm borosilicate glass capillary tube, a larger outer glass tube, and a one-hole cork to hold the capillary inside the outer tube. The capillary tube, graduated from 0 to 10 cm in 1-mm increments, was cleaned thoroughly with chromic acid and rinsed with distilled water. The tube was rinsed with methanol and with the sample solution again. Then, the capillary was inserted into the outer tube with a proper amount of sample solution such that the lower end of the capillary was submerged. Then, the apparatus was placed into the thermostat (Polyscience, model 9710). After thermal equilibrium was reached, the solution was raised by blowing so that the capillary walls were thoroughly wetted. Then, the distance between the lower meniscus in the outer tube and the upper meniscus in the capillary was measured by means of a cathetometer. The surface tension is calculated by the following equation:

$$\sigma = (1/2)r\rho g h \qquad (1)$$

where σ is the surface tension, r is the radius of the capillary, ρ is the density of the solution, g is the acceleration of gravity, and h is the height difference between the menisci. The radius of the capillary was calibrated by measuring the surface tensions of benzene and distilled water at the temperatures (10, 25, and 50) °C. The average absolute deviations between the reference values and the data measured in the present experiments were 1.40% and 0.18%.

Results

Density. The experimental results of the densities measured are listed in Table 1. A nonlinear correlation was adopted to fit precisely the obtained data for practical application. The experimental data were fitted to a polynomial in terms of absolute temperature and salt mass fraction by a least-squares method:

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

where ρ is the density, T is the absolute temperature, and w_T is the mass fraction of lithium salts (LiBr + $LiNO_3$ + LiI + LiCl). The values of the coefficients A_n, B_n, and C_n of the equation are listed in Table 2, and the experimental data are plotted in Figure 1. The solid lines given in Figure 1 are the calculated values from the correlation. The average absolute deviation between the measured data and the calculated values from these polynomial equations was 0.05%.

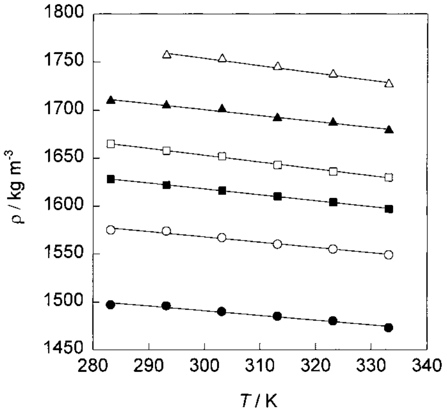

Figure 1. Densities of the (H_2O + LiBr + $LiNO_3$ + LiI + LiCl) system (LiBr/$LiNO_3$/LiI/LiCl = 5:1:1:2 by mole ratio): (●) w_T = 0.50; (○) w_T = 0.55; (■) w_T = 0.58; (□) w_T = 0.60; (▲) w_T = 0.625; (△) w_T = 0.65.

Viscosity. The experimental results of the viscosities of the system are also listed in Table 1. The experimental data were fitted to an exponential in terms of absolute temperature and salt mass fraction by a least-squares method:

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

where η is the viscosity, T is the absolute temperature, and w_T is the mass fraction of the lithium salts (LiBr + $LiNO_3$ + LiI + LiCl). The values of the coefficients A_n, B_n, and C_n of the equation are listed in Table 3, and the experimental data are plotted in Figure 2. The solid lines given in Figure 2 are the calculated values from the correlation equation (eq 3). The average absolute equation are listed in Table 3, and the experimental data are plotted in Figure 2. The solid lines given in Figure 2 are the calculated values from the correlation equation (eq 3). The average absolute deviation between the measured data and the calculated values from these polynomial equations was 0.90%.

The uncertainty of the viscosity data is affected by two factors: the uncertainty of the temperature measurement and the accuracy of the efflux time measurement. The temperature inside the cylindrical chamber with the viscosity-measuring system was monitored with a high-precision temperature-measuring system (Fluke, 2180A). The temperature was controlled to be stable within ±0.01 K during the experimental runs. The efflux time of the solution was measured three times with a stopwatch for every experimental run, and it was found that the reproducibility of the efflux time of the solution was within ±0.1%. Therefore, it is expected that the uncertainty of the

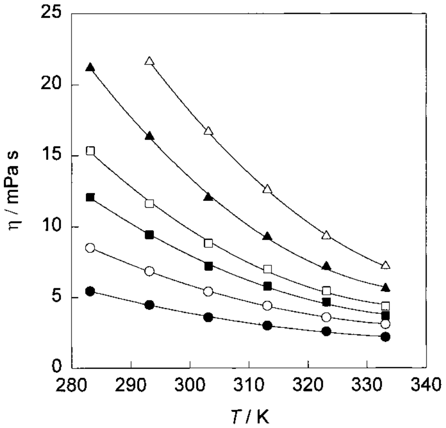

Figure 2. Viscosities of the (H_2O + LiBr + $LiNO_3$ + LiI + LiCl) system (LiBr/$LiNO_3$/LiI/LiCl = 5:1:1:2 by mole ratio): (●) $w_T = 0.50$; (○) $w_T = 0.55$; (■) $w_T = 0.58$; (□) $w_T = 0.60$; (▲) $w_T = 0.625$; (△) $w_T = 0.65$).

Table 4. Coefficients of Eq 4 for the Surface Tension of the (H_2O + LiBr + $LiNO_3$ + LiL + LiCl

A_0	-5.81495×10^3	B_0	2.01807×10^1
A_1	3.26488×10^2	B_1	-1.10353×10^0
A_2	-5.83270×10^0	B_2	1.97881×10^{-2}
A_3	3.46401×10^{-2}	B_3	-1.17498×10^{-4}

temperature measurement does not much influence the precision of the viscosity data. The solutions in the viscometer were sealed to minimize evaporation before thermal equilibration. When thermal equilibration was reached, it was unsealed and the efflux time was measured. Therefore, the vapor buoyancy effect was not cosidered here.

Surface Tension. The experimental results of the surface tensions are listed in Table 1. The experimental data were fitted to a polynomial, which is similar to the empirical formula given by Iyoki et al. (1993), in terms of absolute temperature and mass fraction of the lithium salts by a least-squares method:

$$\sigma/(\mathrm{mN{\cdot}m^{-1}}) = [\sum_{n=0}^{3}\{A_n + B_n(T/\mathrm{K})\}(100w_T)^n]^{0.85} \qquad (4)$$

Here σ is the surface tension, T is the absolute temperature, and w_T is the mass fraction of the lithium salts (LiBr + $LiNO_3$ + LiI + LiCl). The values of the coefficients A_n and B_n of the equation are listed in Table 4, and the experimental data are plotted in Figure 3. The solid lines given in Figure 3 are the calculated values from the correlation equation (eq 4). The average absolute deviation between the measured data and the calculated values from the polynomial equation was 0.30%.

Conclusions

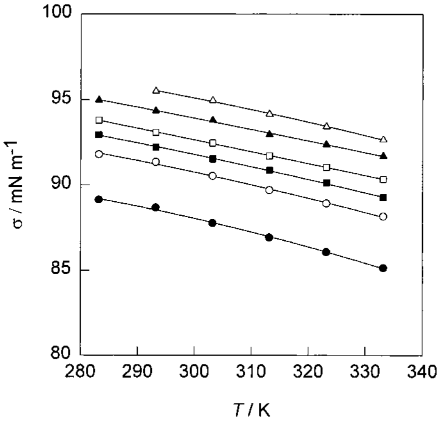

Figure 3. Surface tensions of the (H_2O + LiBr + $LiNO_3$ + LiI + LiCl) system (LiBr/$LiNO_3$/LiI/LiCl = 5:1:1:2 by mole ratio): (●) $w_T = 0.50$; (○) $w_T = 0.55$; (■) $w_T = 0.58$; (□) $w_T = 0.60$; (▲) $w_T = 0.625$; (△) $w_T = 0.65$.

The densities, viscosities, and surface tensions of the (water + lithium bromide + lithium nitrate + lithium iodide + lithium chloride) system (LiBr/$LiNO_3$/LiI/LiCl = 5:1:1:2 by mole ratio) were measured at various temperatures and concentrations. All the measured properties were correlated in terms of absolute temperature and mass fraction of the lithium salts by a least-squares method. The thermophysical properties of the proposed five-component system reported here and in a previous work (1999a) should be useful for heat- and mass-transfer calculation in the optimum design of absorption refrigerating machines and heat pumps.

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