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Heat Capacities of the Water + Lithium Bromide + Ethanolamine and Water + Lithium Bromide + 1,3-Propanediol Systems

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Heat capacities of the water + lithium bromide + ethanolamine (LiBr/$H_2N(CH_2)_2OH$ mass ratio = 3.5) and water + lithium bromide + 1,3-propanediol (LiBr/$HO(CH_2)_3OH$ mass ratio = 3.5) systems were measured by using an isoperibol solution calorimeter at four temperatures (283.15, 298.15, 313.15, and 333.15 K) and absorbent (LiBr + $H_2N(CH_2)_2OH$ and LiBr + $HO(CH_2)_3OH$) concentration ranges of (29.2 to 70.7)% and (30.7 to 68.3)%, respectively. The measured values were fitted with a simple equation by a least-squares method and the average absolute deviations between experimental and calculated values were 0.21% for the water + lithium bromide + ethanolamine system and 0.15% for the water + lithium bromide + 1,3-propanediol system, respectively.

Introduction

Various new working fluids for absorption heat pumps have been developed to improve the performance characteristics of the conventional lithium bromide + water system or satisfy specific conditions for various types of heat pumps (Hihara, 1993). A general procedure for checking the validity of a new working fluid includes the measurements of various basic thermodynamic properties of the solution (Uemura, 1993). These properties are essential to evaluating the performance of the working fluid and for optimal design of a desired type of heat pump. In the previous studies we measured 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). Two systems consisting of water as refrigerant and the others as absorbents were suggested as the possible working fluids for air-cooled cycle operation. Ethanolamine and 1,3-propanediol were added to suppress the crystallization of the solutions, and therefore the addition of these two organics can offer operation ranges wide enough for the air-cooled cycle operation. In this work heat capacities of these two systems were measured at various concentration and temperature conditions and were fitted with a simple equation. The heat capacity data of electrolyte solutions are generally used to construct the enthalpy−concentration chart together with several other properties (McNeely, 1979), and this chart is quite often used calculate the amount of heat required or transferred in each unit of the heat pump.

Experiment

Materials. 1-Butanol (99.5%), 1-propanol (99.9%), ethylene glycol (99+%), *p*-xylene (99+%), lithium bromide (99+%), ethanolamine (99+%), 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. An isoperibol solution calorimeter (CSC 4300) was used to measure heat capacities of sample solutions. The calorimeter consists of three parts. One is the main body primarily including a constant temperature bath, a thermistor, a calibration heater with 100 Ω resistor, and a stirring rod made of glass. Another part is Dewar vessel for containing the sample solution, and the other is a computer set for the control of the whole measuring process. The temperature resolution of the calorimeter was 2 μ °C, the temperature noise level was ±30 μ °C, and the bath temperature stability was ±0.0005 K. An accurately weighted sample solution (25 cm^3) of a desired concentration was placed into the Dewar vessel. The thermistor, calibration heater, and stirring rod were immersed when the Dewar vessel was clamped on the main body of the isoperibol solution calorimeter. The stirrer and heater were then turned on to heat up the sample solution to a slightly lower (0.15 K) temperature than desired. After 300 s passed from that point, an actual measuring process which consisted of 200 s of holding time without heating, 400 s of heating, and 200 s of holding time sequentially started. The amount of heat added was set to 10 mcal s^{-1} in the heating process, and the accurate value of the added heat was calculated through measuring the current and voltage values with a built-in digital voltmeter. The measuring procedure was completely controlled by a computer, and the temperature difference during the heating process was also calculated by the computer using the temperature data set recorded with time. The temperature difference value was used to calculate the heat capacity of the sample solution with the following equation

$$Q = (mC_p + \epsilon)\Delta T \tag{1}$$

where Q is the total amount of heat added, m is the mass of the sample solution, C_p is the heat capacity (in kJ kg^{-1} K^{-1}) of the sample, and ϵ is the heat capacity (in kJ K^{-1}) of the apparatus including the Dewar vessel, stirring rod, heater, and thermistor. The value of ϵ was calculated by the experimental result using water as a sample solution and its known heat capacity value at each temperature

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Table 1. Heat Capacities of H_2O (1) + LiBr (2) + $H_2N(CH_2)_2OH$ (3) (w_2/w_3 = 3.5) and H_2O (1) + LiBr (2) + $HO(CH_2)_3OH$ (4) (w_2/w_4 = 3.5) Systems

	C_p/kJ kg^{-1} K^{-1}	
T/K	LiBr + $H_2N(CH_2)_2OH + H_2)$	LiBr + $HO(CH_2)_3OH + H_2O$
	$w_{2+3} = 0.292$	$w_{2+4} = 0.307$
283.15	3.06	3.02
298.15	3.07	3.05
313.15	3.10	3.05
333.15	3.11	3.07
	$w_{2+3} = 0.403$	$w_{2+4} = 0.405$
283.15	2.69	2.66
298.15	2.70	2.69
313.15	2.72	2.72
333.15	2.75	2.74
	$w_{2+3} = 0.499$	$w_{2+4} = 0.506$
283.15	2.36	2.32
298.15	2.39	2.36
313.15	2.41	2.39
333.15	2.45	2.42
	$w_{2+3} = 0.605$	$w_{2+4} = 0.608$
283.15	2.06	2.04
298.15	2.10	2.08
313.15	2.13	2.10
333.15	2.17	2.15
	$w_{2+3} = 0.707$	$w_{2+4} = 0.683$
298.15	1.83	1.88
313.15	1.87	1.91
333.15	1.91	1.96

considered. The experimental apparatus and procedures were checked first with three pure substances (1-butanol, 1-propanol, and ethylene glycol) at 298.15 K, and all the measured heat capacities showed good agreement with the literature (Zegers and Somsen, 1984; Parks and Kelley, 1925) values within 1% relative error. The experimental apparatus and procedures were tested with the heat capacity data of pure *p*-xylene at three different temperatures and with the heat capacity data of the LiBr + H_2O aqueous solution at various temperatures and concentrations. The experimental heat capacity data of the *p*-xylene and LiBr + H_2O system also showed good agreement with those in the literature (Corruccini and Ginnings,1947; ASHRAE, 1989) within 1% relative error.

Results and Discussion

Heat capacities of the water + lithium bromide + ethanolamine (LiBr/$H_2N(CH_2)_2OH$ mass ratio = 3.5) and water + lithium bromide + 1,3-propanediol (LiBr/$HO(CH_2)_3$ OH mass ratio = 3.5) systems were measured at four temperatures (283.15, 298.15, 313.15, and 333.15 K) and concentration ranges of (29.2 to 70.7)% and (30.7 to 68.3)%, respectively. The experimental results are listed in Table 1 and plotted in Figures 1 and 2 and are simply fitted with the following equation

$$C_p/\mathrm{kJ\ kg^{-1}\ K^{-1}} = \sum_{i=0}^{3}[(a_i + b_iT + c_iT^2)(100w)^i] \quad (2)$$

where C_p is the heat capacity, 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. The parameters a_i, b_i, and c_i were determined by a least-squares method and are listed in Table 2. The average absolute deviations between the experimental and calculated values were 0.21% for the water + lithium bromide + ethanolamine system and 0.15% for the water + lithium bromide + 1,3-propanediol system. The heat capacity of the solutions decreased with increasing absorbent concentration at the same temperature and slightly increased with increasing temperature at the same concentration. The temperature effect on the heat capacity of the solution became less at lower concentrations.

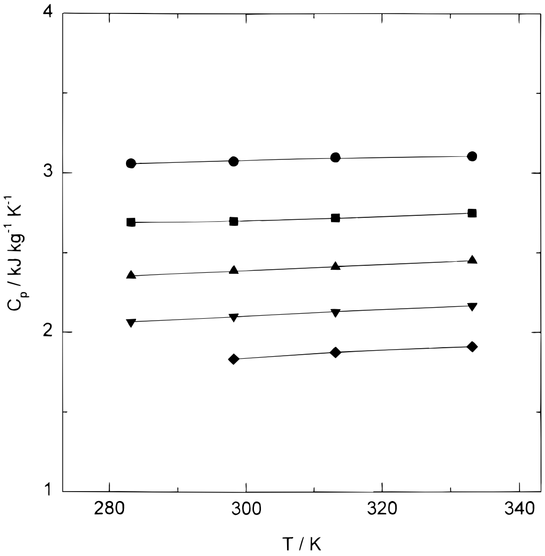

Figure 1. Heat capacities of the H_2O (1) + LiBr (2) + $H_2N(CH_2)_2$-OH (3) (w_2/w_3 = 3.5) system: (●) $w_{2+3} = 0.292$; (■) $w_{2+3} = 0.403$; (▲) $w_{2+3} = 0.499$; (▼) $w_{2+3} = 0.605$; (◆) $w_{2+3} = 0.707$.

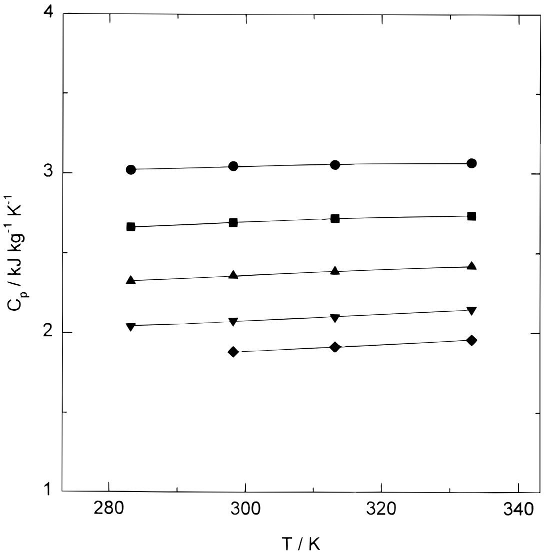

Figure 2. Heat capacities of the H_2O (1) + LiBr (2) + $HO(CH_2)_3$-OH (4) (w_2/w_4 = 3.5) systems: (●) $w_{2+4} = 0.307$; (■) $w_{2+4} = 0.405$; (▲) $w_{2+4} = 0.506$; (▼) $w_{2+4} = 0.608$; (◆) $w_{2+4} = 0.683$.

Table 2. Values of a_i, b_i, and c_i for Least-Squares Representation by Equation 2

	H_2O + LiBr + $H_2N(CH_2)_2OH$	H_2O + LiBr + $HO(CH_2)_3OH$
a_0	-3.82624×10	2.26523
a_1	2.75275	2.18262×10^{-1}
a_2	-5.80310×10^{-2}	-1.16369×10^{-2}
a_3	3.82253×10^{-4}	1.28712×10^{-4}
b_0	2.70014×10^{-1}	1.52974×10^{-2}
b_1	-1.77827×10^{-2}	-1.80602×10^{-3}
b_2	3.68858×10^{-4}	7.59334×10^{-5}
b_3	-2.42095×10^{-6}	-8.19097×10^{-7}
c_0	-4.27412×10^{-4}	-2.78971×10^{-5}
c_1	2.81813×10^{-5}	3.07439×10^{-6}
c_2	-5.82845×10^{-7}	-1.22269×10^{-7}
c_3	3.82093×10^{-9}	1.30347×10^{-9}

Conclusions

For two systems of water + lithium bromide + ethanolamine (LiBr/$H_2N(CH_2)_2OH$ mass ratio = 3.5) and water

+ lithium bromide + 1,3-propanediol (LiBr/HO$(CH_2)_3$OH mass ratio = 3.5) heat capacities were measured at various concentrations and temperatures and were fitted with a simple equation. Both systems were found to be possibly used as new working fluids for an air-cooled absorption chiller. For the practical application of the selected solutions to real working fluids, additional studies on the corrosion problem, heat and mass transfer characteristics, cost evaluation, and so on should be further carried out.

Literature Cited

ASHRAE. *Handbook of Fundamentals*; American Society of Heating, Refrigerating, and Air Conditioning Engineers: Atlanta, 1989.

Corruccini, R. J.; Ginnings, D. C. The Enthalpy, and Specific Heat of Liquid *p*-Xylene from 0 to 300°. The Heat of Fusion. *J. Am. Chem. Soc.* **1947**, *69*, 2291−2294.

Hihara, E. Current Status of Thermophysical Property Research on New Working Fluid. *Reito* **1993**, *68*, 693−698.

Kim, J.-S.; Park, Y.; Lee, H. Solubilities and Vapor Pressures of the Water + Lithium Bromide + Ethanolamine System. *J. Chem. Eng. Data* **1996a**, *41*, 279−281.

Kim, J-S.; Park, Y.; Lee, H. Densities and Viscosities of the Water + Lithium Bromide + Ethanolamine System. *J. Chem. Eng. Data* **1996b**, *41*, 678−680.

McNeely, L. A. Thermodynamic Properties of Aqueous Solutions of Lithium Bromide. *ASHRAE Trans.* **1979**, *3*, 413−434.

Park, Y.; Kim, J.-S.; Lee, H. Physical Properties of the Lithium Bromide + 1,3-Propanediol + Water System. *Int. J. Refrig.* **1996**, submitted for publication.

Parks, G. S.; Kelley, K. K. Thermal Data on Organic Compounds. II. The Heat Capacities of Five Organic Compounds. The Entropies and Free Energies of Some Homogeneous Series of Aliphatic Compounds. *J. Am. Chem. Soc.* **1925**, *47*, 2089−2097.

Uemura, T. Working Medium-Absorbent Systems for Absorption Refrigerating Machine, Absorption Heat Pump and Heat Transformer. *Reito* **1993**, *68*, 699−709.

Zegers, H. C.; Somsen, G. Partial Molar Volumes and Heat Capacities in (Dimethylformamide + an n-Alkanol). *J. Chem Thermodyn.* **1984**, *16*, 225−235.

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