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Heat Capacity for the Water + Lithium Chloride + Lithium Nitrate System at Temperatures from 283.15 to 433.15 K

Shigeki Iyoki,* Hirokazu Tanaka, Yutaka Kuriyama, and Tadashi Uemura

Department of Chemical Engineering, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan

Heat capacities of the water + lithium chloride + lithium nitrate (salt mole ratio 2.8:1) system were measured in the range of temperatures from 283.15 to 433.15 K and in the range of absorbent concentrations from 9.1 to 63.5 mass %. The measurements of heat capacity were made with two separate experimental apparatus for individual temperatures below 343.15 K and above 353.15 K. An empirical formula for this ternary system was obtained as a function of absolute temperature by a least-squares method from these experimental data. Maximum and average absolute deviations between these experimental data measured with two apparatus and the calculated values from this empirical formula were 0.97% and 0.35%, respectively.

Introduction

Extensive thermodynamic properties (density, viscosity, surface tension, solubility, vapor pressure, heat capacity, and enthalpy of mixing) for the working medium + absorbent system are necessary for the research and the design of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers. The heat capacity data for working fluids are one of the most important basic properties for the research and the design of absorption refrigeration and heat pump systems (*1–10*). The heat capacity data for working fluids at high temperatures are particularly essential for the design of absorption heat transformers.

The ternary system of water + lithium chloride + lithium nitrate (salt mole ratio 2.8:1) was proposed in order to simultaneously improve the performance characteristics and reduce the corrosivity caused by the basic water + lithium bromide system (*1*, *11*). In our previous papers, the optimum mixing ratio (*12*) of the lithium chloride and lithium nitrate and the density (*13*), viscosity (*13*), surface tension (*13*), solubility (*14*), vapor pressure (*12*), and enthalpy of mixing data (*15*) for aqueous lithium chloride + lithium nitrate solutions at the optimum mixing ratio were reported.

The heat capacities of this ternary system at the optimum mixing ratio were measured with two separate experimental apparatus at temperatures from 283.15 to 433.15 K. The measurements of heat capacity at temperatures below 343.15 K were made with a usual experimental apparatus. At temperatures above 353.15 K measurements were made with a special apparatus devised for high-temperature measurements. An empirical formula for the heat capacity of this ternary system was obtained as a function of absolute temperature by a least-squares method from these experimental data measured with two separate experimental apparatus.

Experimental Section

Materials. The lithium chloride used in this work was from Honjo Chemical Co., Ltd. (Japan), analytical reagent grade with a minimum purity of 99.9 mass %. The lithium nitrate used in this work was from Wako Pure Chemical Industries Ltd. (Japan), analytical reagent grade with a minimum purity of 99.8 mass %. All the reagents were used without further purification. The absorbent concentrations of aqueous lithium chloride + lithium nitrate solutions were determined by Fajans' method (*16*) with use of standardized aqueous silver nitrate solution and dichlorofluorescein as an adsorption indicator. The absorbent solution was titrated by using a microburet of 10-mL total delivery, with divisions of 0.02 mL. All weighings were made on a direct-reading balance (weighing capacity 200 g, reciprocal sensibility 1 mg). Double-distilled and degassed water was used in this work.

The optimum mixing ratio of lithium chloride and lithium nitrate was determined by measuring the crystallization temperature of sample solutions at constant absorbent concentration. Consequently, the most suitable mixing ratio of lithium chloride and lithium nitrate was found to be 2.8 and 1 mol, respectively (*12*).

Apparatus and Procedure. The heat capacities of aqueous lithium chloride + lithium nitrate solutions for temperatures below 343.15 K were measured with a twin isoperibol calorimeter (Tokyo Riko Co., Ltd., Japan, model TIC-22I, experimental apparatus 1), and with a constant-temperature circulator (Tokyo Riko Co., Ltd., Japan, model TC-100), capable of operation between 263.15 and 353.15 K with a temperature stability of ±0.01 K. The experimental apparatus has been reported in our previous paper (*9*). This twin isoperibol calorimeter consisted of two Dewar vessels of the same size in a constant-temperature bath made of an aluminum block. The aluminum block was wrapped with a tube in which water of constant temperature from the circulator was circulated. The Dewar vessel was made of Pyrex glass. Each Dewar vessel was equipped with a heater, a thermistor, and a stirrer paddle. The Dewar vessel was sealed with a Teflon O-ring. The temperature inside the Dewar vessel was measured with a thermistor. The temperature difference of the sample solution before and after heating was recorded by a two-pen-type recorder. The heat capacities of aqueous lithium chloride + lithium nitrate solutions for temperatures below 343.15 K were calculated from eq 1,where Q

$$Q = (mC_p + M)\Delta T \qquad (1)$$

is the energy input (kJ), m is the mass of the sample solution (kg), M is the thermal capacity (kJ K^{-1}) of the Dewar vessel determined from measurements using pure water (*17*) (experimental apparatus 1) or pure *p*-xylene (*18*) (experimental apparatus 2), and ΔT is the temperature rise (K).

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Table 1. Heat Capacities of the H_2O + LiCl + $LiNO_3$ System (LiCl:$LiNO_3$ = 2.8:1 mol) Measured with Experimental Apparatus 1[a]

	C_p/(kJ·kg^{-1}·K^{-1}) at *T*/K				
100*w*	283.15	298.15	308.15	323.15	343.15
9.1	3.786	3.785	3.784	3.783	3.792
16.3	3.489	3.508	3.511	3.513	3.524
22.1	3.289	3.309	3.309	3.324	3.329
30.3	3.054	3.056	3.084	3.101	3.110
34.6	2.984	2.960	2.961	2.990	2.997
40.5	2.861	2.852	2.855	2.882	2.903
44.3	2.794	2.773	2.785	2.815	2.819
50.5		2.676	2.673	2.710	2.719
55.2				2.643	2.659

[a] *w* is the mass fraction of salt.

Table 2. Heat Capacities of the H_2O + LiCl + $LiNO_3$ System (LiCl:$LiNO_3$ = 2.8:1 mol) Measured with Experimental Apparatus 2[a]

	C_p/(kJ·kg^{-1}·K^{-1}) at *T*/K				
100*w*	353.15	373.15	393.15	413.15	433.15
22.1	3.353	3.348	3.371	3.405	3.441
30.3	3.088	3.110	3.156	3.174	3.232
40.5	2.873	2.897	2.954	2.938	3.024
50.3	2.716	2.725	2.775	2.779	2.816
56.6	2.628	2.643	2.659	2.684	2.715
63.5			2.582	2.586	2.610

[a] *w* is the mass fraction of salt.

Table 3. Values of Coefficients a_i, b_i, and c_i in Eq 3

i	a_i	b_i	c_i
0	5.44815	-7.99032×10^{-3}	1.25726×10^{-5}
1	-6.16831×10^{-2}	9.94168×10^{-5}	-1.42985×10^{-7}
2	1.82561×10^{-4}	-1.31368×10^{-6}	1.90473×10^{-9}
3	1.07026×10^{-5}	5.32122×10^{-8}	-8.02826×10^{-11}
4	-2.14508×10^{-7}	-1.03849×10^{-9}	1.60566×10^{-12}
5	1.48497×10^{-9}	9.69484×10^{-12}	-1.52169×10^{-14}
6	-3.29204×10^{-12}	-3.46401×10^{-14}	5.48834×10^{-17}

The heat capacities of aqueous lithium chloride + lithium nitrate solutions for temperatures above 353.15 K were measured with a twin isoperibol calorimeter (Tokyo Riko Co., Ltd., Japan, model HTIC-200, experimental apparatus 2) devised for high-temperature measurements. The experimental apparatus has been reported in our previous paper (*10*). This twin isoperibol calorimeter consisted of two Dewar vessels of the same size in a constant-temperature bath made of an aluminum block. The Dewar vessel was made of type 316 stainless steel. The interior stainless steel surface of the Dewar vessel was coated with Teflon resin to prevent corrosion caused by absorbent solutions at high temperatures. Each Dewar vessel was equipped with a heater, a copper–constantan thermocouple, and a stirrer paddle. The Dewar vessel was sealed with a Teflon O-ring. The temperature inside the Dewar vessel was measured with a copper–constantan thermocouple. The temperature difference of the sample solution before and after heating was recorded by a two-pen-type recorder. The heat capacities of aqueous lithium chloride + lithium nitrate solutions for temperatures above 353.15 K were calculated from eq 1.

Results and Discussion

The thermodynamic definition of the heat capacity of solutions in absorption refrigeration and heat pump systems is given by eq 2,where C_σ is the variation in the enthalpy of a saturated liquid with temperature and C_P represents the change in enthalpy with temperature at constant pressure (*19*). The two forms of the liquid heat capacity of C_σ and C_P are in close numerical agreement in the range of this work. Therefore, no correction was made. The heat capacity data obtained in this work give C_σ and C_P. However, under these circumstances, C_σ equals C_P.

$$C_\sigma = \mathrm{d}H_\sigma/\mathrm{d}T = C_P + [V_\sigma - T(\partial V/\partial T)_P](\mathrm{d}P/\mathrm{d}T)_\sigma \quad (2)$$

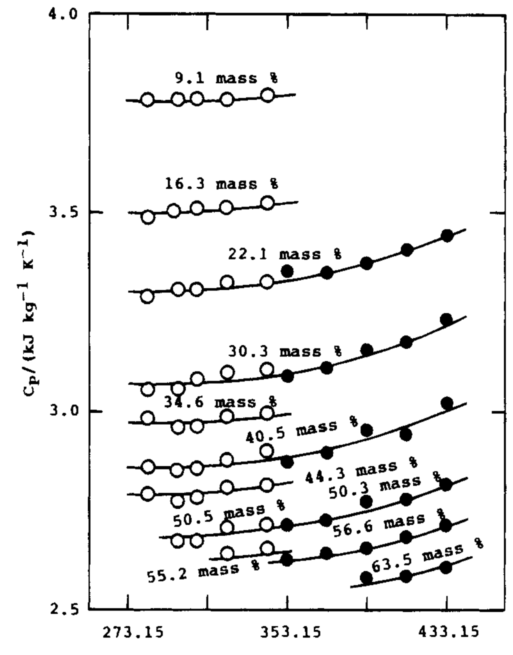

Figure 1. Heat capacities of the H_2O + LiCl + $LiNO_3$ system (LiCl:$LiNO_3$ = 2.8:1 mol) measured with experimental apparatus 1 and 2: ○, experimental apparatus 1; ●, experimental apparatus 2; —, calculated values from eq 3.

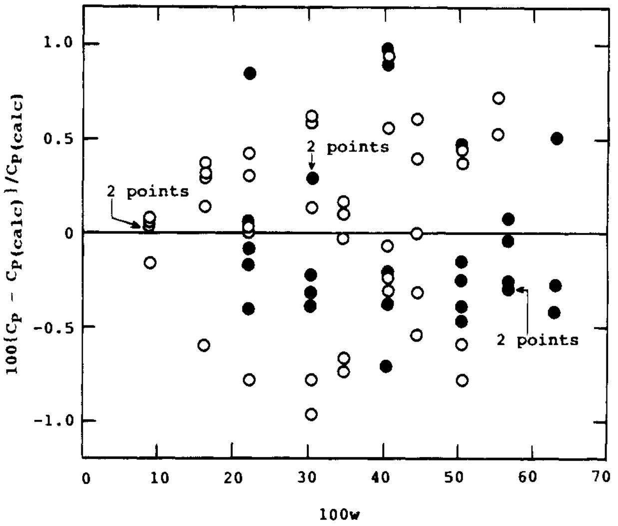

Figure 2. Percent deviations between experimental data measured with experimental apparatus 1 and 2 and calculated values from eq 3: ○, experimental apparatus 1; ●, experimental apparatus 2.

The heat capacities of aqueous lithium chloride + lithium nitrate solutions from 283.15 to 343.15 K were measured with apparatus 1 with a range of absorbent concentrations from 9.1 to 55.2 mass %. The experimental results of 41 measurements for this ternary system at the optimum mixing ratio are shown in Table 1. The heat capacities of aqueous lithium chloride + lithium nitrate solutions from 353.15 to 433.15 K were measured with apparatus 2 with a range of absorbent concentrations from 22.1 to 63.5 mass

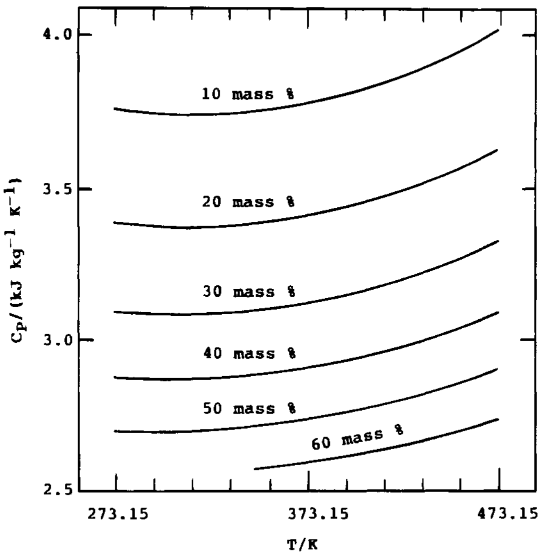

Figure 3. Calculated values of heat capacity from eq 3 for the $H_2O + LiCl + LiNO_3$ system ($LiCl:LiNO_3$ = 2.8:1 mol).

%. The experimental results of 28 measurements for this ternary system at the optimum mixing ratio are shown in Table 2. The experimental data were used to determine the coefficients for the following empirical formula by a least-squares method:

$$C_p/(\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}) = \sum_{i=0}^{6} (100w)^i (a_i + b_i T + c_i T^2) \qquad (3)$$

where w is the mass fraction of salt. Values of the coefficients a_i, b_i, and c_i in eq 3 are given in Table 3. The experimental results are plotted in Figure 1. In this figure, the solid lines indicate the calculated values from eq 3 with the coefficients from Table 3. The maximum and average absolute deviations between the results measured with experimental apparatus 1 and the calculated values from eq 3 were 0.97% and 0.34%, respectively. The maximum and average absolute deviations between the results measured with experimental apparatus 2 and the calculated values from eq 3 were 0.97% and 0.36%, respectively. The percent deviations between all the results and the values calculated from eq 3 are shown in Figure 2 for various absorbent concentrations. Figure 3 shows a graph of the calculated values from eq 3 for the heat capacity of this ternary system at the optimum mixing ratio.

The heat capacity data of this ternary system are very useful for the research and the design of these absorption refrigeration and heat pump systems. In particular, the heat capacity data measured at high temperatures are also useful for the design of absorption heat transformers.

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