Heat Capacities of Ethylamine + Water + Lithium Bromide from 313.15 K to 373.15 K

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Heat capacities of ethylamine + water + lithium bromide (H_2O:LiBr = 2:1 mass) were measured using a twin isoperibol calorimeter devised for high-pressure measurements in the range of temperatures from 313.15 K to 373.15 K and in the range of ethylamine concentrations from 0 to 50.3 mass %. An empirical equation of the heat capacity for this ternary system was obtained as a function of temperature by a least-squares method from experimental data. Maximum and average absolute deviations between the experimental data measured and the calculated values from this empirical equation were 0.3% and 0.1%, respectively.

Introduction

The ternary system of ethylamine + water + lithium bromide (H_2O:LiBr = 2:1 mass) was proposed in order to improve the performance characteristics and to reduce the dangerousness, toxicity, and cost of the vapor absorption machine and to lower the pressure of the ammonia + water system. Thermophysical properties (density, viscosity, surface tension, solubility, vapor pressure, vapor−liquid equilibrium, heat capacity, and enthalpy of mixing) for the working fluids are necessary for the simulation of performance and the design of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers. In our previous paper, the vapor pressure data (Iyoki et al., 1998) of this ternary system were reported. Heat capacities of ethylamine + water + lithium bromide were measured using a twin isoperibol calorimeter, devised for high-pressure measurements, at various temperatures and ethylamine concentrations. An empirical equation for the heat capacity of this ternary system was obtained as a function of absolute temperature by a least-squares method.

Experimental Section

Materials. Lithium bromide was obtained from Honjo Chemical Co., Ltd. (Japan), analytical reagent grade with a minimum purity of 99.9 mass %. The ethylamine was an aqueous solution of 70.0 mass % from Wako Pure Chemical Industries Ltd. (Japan), analytical reagent grade. All the reagents were used without further purification. The lithium bromide concentration of solution was determined by Fajans' method (Takagi, 1976) using a standardized silver nitrate solution and dichlorofluorescein as an adsorption indicator. The ethylamine concentration was determined by potentiometric titration with a potentiometric automatic titrator (Kyoto Electronics Manufacturing Co., Ltd., Japan, model AT-400). The lithium bromide solutions were titrated using a microburet of 10 mL total delivery, with divisions of 0.02 mL. All masses were determined on a direct-reading balance (mass capacity 200 g, reciprocal sensibility 1 mg). Double-distilled and degassed water was used in this work.

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Table 1. Heat Capacities of $C_2H_5NH_2$ + H_2O + LiBr (H_2O:LiBr = 2:1 mass)

	C_σ/(kJ kg^{-1} K^{-1}) at T/K			
100w	313.15	333.15	353.15	373.15
0	2.70	2.71	2.74	2.76
9.9	2.89	2.89	2.91	2.95
22.1	3.04	3.05	3.08	3.13
28.2	3.14	3.16	3.18	3.24
41.0	3.24	3.27	3.33	3.41
50.3	3.28	3.32	3.37	3.46

Apparatus and Procedure. The heat capacity of the ethylamine + water + lithium bromide system was measured with a twin isoperibol calorimeter (Tokyo Riko Co., Ltd., Japan, model HTIC-200) devised for high-pressure measurements. The experimental apparatus has been reported in our previous papers (Iyoki and Uemura, 1989; Iyoki et al., 1994). 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 sample 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 the ethylamine + water + lithium bromide system were calculated from eq 1.

$$Q = (mC_\sigma + M)\Delta T \quad (1)$$

where Q is the energy input (kJ), C_σ is the heat capacity (kJ kg^{-1} K^{-1}) of the saturated solution, M is the thermal capacity (kJ K^{-1}) of the Dewar vessel determined from measurements using pure *p*-xylene (Timmermans, 1965) of known heat capacity, m is the mass (kg) of sample solution, and ΔT is the temperature rise (K).

Results and Discussion

The heat capacities of the ternary system were measured in the range of temperatures from 313.15 K to 373.15 K

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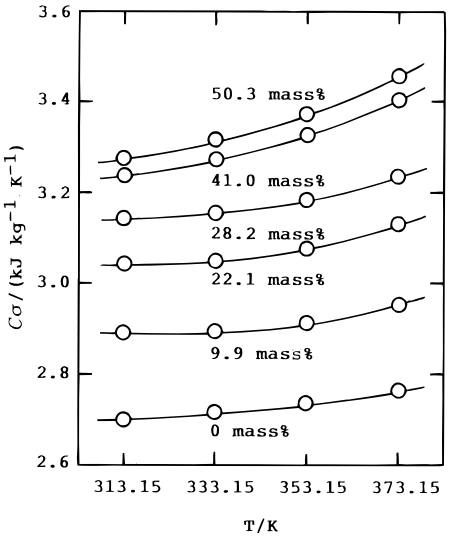

Figure 1. Heat capacities of $C_2H_5NH_2 + H_2O + LiBr$ (H_2O:LiBr = 2:1 mass).

and in the range of ethylamine concentrations from 0 to 50.3 mass %. The experimental results of 24 measurements at various temperatures and ethylamine concentrations are shown in Table 1. The experimental results were plotted in Figure 1 as heat capacity at saturated pressure. In this figure, the solid lines indicate the calculated values from eq 2. These experimental results were used to determine the constants for an empirical equation with a least-squares method. On the basis of the experimental data, eq 2 for the heat capacities of this ternary system was obtained

$$C_\sigma = \sum_{n=0}^{6} (100w)^n (A_n + B_n T + C_n T^2) \qquad (2)$$

where T is the absolute temperature (K), n is the integer exponent, and w is the ethylamine concentration (mass fraction). Values of the constants A_n, B_n, and C_n in eq 2 are shown in Table 2. The percent deviation at a given temperature and ethylamine concentration is defined as $100(C_{\sigma_{exp}} - C_{\sigma_{cal}})/C_{\sigma_{exp}}$. The percent average absolute deviation is defined as $100[\sum(|C_{\sigma_{exp}} - C_{\sigma_{cal}}|/C_{\sigma_{exp}})/N]$. N is the number of experimental data points. Maximum and average absolute deviations between the experimental data and the calculated values from eq 2 were 0.3% and 0.1%, respectively.

Table 2. Values of Coefficients A_n, B_n, and C_n in Eq 2

n	A_n	B_n	C_n
0	3.1000	-3.2394×10^{-3}	6.2500×10^{-6}
1	4.7343×10^{-1}	-2.5422×10^{-3}	3.6664×10^{-6}
2	-2.8124×10^{-2}	1.5233×10^{-4}	-2.2767×10^{-7}
3	3.4936×10^{-4}	-2.3720×10^{-6}	5.1239×10^{-9}
4	1.8883×10^{-5}	-5.7614×10^{-8}	-1.6385×10^{-11}
5	-6.0314×10^{-7}	1.9793×10^{-9}	-5.2044×10^{-13}
6	4.8849×10^{-9}	-1.4783×10^{-11}	2.2841×10^{-15}

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