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Thermal Property Measurements and Enthalpy Calculation of the Lithium Bromide + Lithium Iodide + 1,3-Propanediol + Water System

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The lithium bromide + lithium iodide + 1,3-propanediol + water [LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ mass ratio = 4] solution is being considered as a potential working fluid for an absorption chiller. Heat capacities at four temperatures, 283.15, 298.15, 313.15, and 333.15 K, were measured in the range from 50 to 70 mass%. In addition, the differential heats of dilution at 298.15 K were measured in the range from 45.3 to 71.8 mass%. Each individual data set was correlated with a proper regression equation with a high accuracy. A new enthalpy calculation method for the working fluids containing organics was proposed. The calculation method correlated the heat capacity (at various temperatures and concentrations) and the differential heat of dilution (at ambient temperature and various concentrations). The present method was applied for the construction of enthalpy–concentration (H–T–X) diagrams with high confidence.

KEY WORDS: absorption chiller; enthalpy; heat capacity; heat of dilution; LiBr/LiI/1,3-propanediol/water system; working fluid.

1. INTRODUCTION

The development of new working fluids is one of the key technologies for advanced absorption heat pumps and chillers, especially for small-scale lithium bromide-based absorption chillers. A small-scale absorption chiller can be constructed by replacing the cooling tower with a direct air-cooling system. The high absorber temperature caused by air-cooling needs a high absorbent concentration to generate a proper level of vapor pressure in the

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absorber. Thus, the conventional lithium bromide + water solution cannot meet this requirement due to the operating limitation caused by salt crystallization and, thus, cannot be used as a proper working fluid. In our previous studies [1–5], several new working fluid mixtures were proposed and their theoretical performances were evaluated through computer simulation. All of these solutions contain one of three organics such as ethanolamine, diethanolamine, and 1,3-propanediol to suppress the crystallization of the lithium bromide + water solution. To obtain the thermodynamic design data and then evaluate the theoretical performance of new working fluids, the enthalpy values of a working fluid have to be calculated by a proper thermodynamic correlation.

In this study, the lithium bromide + lithium iodide + 1,3-propanediol + water system [LiBr/LiI mole ratio = 4 and $(\mathrm{LiBr} + \mathrm{LiI})/\mathrm{HO(CH_2)_3OH}$ mass ratio = 4] was newly investigated as a promising working fluid for an air-cooled absorption chiller. The optimum mixing ratio of LiBr/LiI was proposed by Iyoki et al. [6] to give the highest solubility. The 1,3-propanediol was added to enhance salt solubilities. Two basic thermal properties, heat capacity and differential heat of dilution, were measured and used for enthalpy calculations of the solution at different temperatures and concentrations.

To calculate the enthalpy of the organic-containing solution, a new calculation procedure that thermodynamically correlates the heat capacity with the differential heat of dilution was adopted. However, several procedures for calculating the enthalpies of a working fluid for absorption chillers have been introduced, which require various types of calorimetric properties of the working fluids. One procedure [7] is to use the integral heats of mixing measured at one ambient temperature and various concentrations and the heat capacities measured at several temperatures and concentrations. The integral heat of mixing is calculated from the differential heat of dilution and the differential heat of solution. Another procedure [8] is to use the differential heat of dilution at several temperatures and concentrations and the heat capacity at several temperatures and one concentration. But the differential heats of dilution are quite difficult to measure over a wide temperature range. The other procedure [8, 9] is to use the vapor pressure at several temperatures and concentrations and the heat capacity at several temperatures and one concentration. The last procedure is applicable only when one volatile component is contained in the working fluid.

In our previous work, we proposed different types of new working fluids for absorption chillers that include suitable combinations of lithium bromide, amines, and alcohols as absorbents and water as a refrigerant. For these solutions it is very hard to measure the differential heat of solution because the solute is a mixture of salts and organics. The procedure using vapor pressure must show a certain level of deviation from the true value because another volatile organic component is contained in the solution. However, enthalpy calculations of the organic-containing working fluids have been done by neglecting the volatility of organic components [10, 11]. In this study a widely applicable and accurate method for calculating enthalpy is proposed to overcome the limitations inherent in the above procedures. On the other hand, the present method needs the differential heat of dilution at ambient temperature and the heat capacity at several temperatures and concentrations. This method can be successfully applied even to solutions containing organic additives. The resulting *H–T–X* diagrams can be effectively used with great confidence for testing a new working fluid performance and for simulating an absorption chiller cycle.

2. EXPERIMENTAL

2.1. Materials

The lithium bromide (mass fraction, 0.99+), lithium iodide (mass fraction, 0.99), and 1,3-propanediol (mass fraction, 0.98) were supplied by Aldrich Chemical Co. and used without further purification. All solutions were prepared with deionized water. The mixing mole ratio of LiBr/LiI was fixed at 4 and the mixing mass ratio $(\mathrm{LiBr}+\mathrm{LiI})/\mathrm{HO(CH_2)_3OH}$ at 4.

2.2. Heat Capacity

The experimental apparatus and procedures for the measurement of heat capacity were almost the same as those in previous studies [3, 4]. The measured heat capacity has an accuracy of $\pm 1\%$ relative error. An isoperibol solution calorimeter (CSC4300) was used to measure the heat capacities of solutions. The temperature resolution of the calorimeter was $2\,\mu\mathrm{K}$, the temperature noise level was $\pm 30\,\mu\mathrm{K}$, and the bath temperature stability was $\pm 0.0005\,\mathrm{K}$. For the measurement of heat capacity, an accurately weighed sample solution (approximate volume of $25\,\mathrm{cm}^3$) of a desired concentration was placed into the Dewar vessel. The thermistor, calibration heater, and stirring rod were immersed when the vessel was clamped on the isoperibol solution calorimeter. The stirrer and heater were then turned on to heat the sample solution to a temperature slightly lower than the final desired temperature. After 300 s passed from that point, an actual measuring process including 200 s of holding time without heating, 400 s of heating, and 200 s of holding time began. An accurate value of the added heat in the heating process was calculated by measuring the current and voltage values with a digital voltmeter. All of the measuring procedures were completely controlled by a computer, and the calculated temperature difference was used to obtain the heat capacity of the sample solution through the following equation:

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

where Q is the total amount of heat added, m is the mass of the sample solution, C_p is the heat capacity ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$) of the sample, and ε is the heat capacity ($\mathrm{kJ \cdot K^{-1}}$) of the apparatus including the Dewar vessel, stirring rod, heater, and thermistor. The value of ε was calculated by using water as a reference solution and its known heat capacity value [12] at each temperature.

2.3. Differential Heat of Dilution

An isoperibol solution calorimeter (CSC4300) was also used to measure the differential heats of dilution of solutions. The measurement was carried out through two calorimeter runs, a calibration, and actual measuring procedures. Prior to each measurement, an absorbent solution (approximately 25 $\mathrm{cm^3}$) with a fixed concentration was charged into the Dewar vessel, while accurately weighed water (approximately 0.01 g) was placed into the small cylindrical container including fragile glass covers at the top and bottom sides. The calibration was done by the same procedure followed in the heat capacity measurement. The temperature difference during the heating process was used to calculate the heat equivalent E, denoted $mC_p + \varepsilon$ in Eq. (1), which is the total heat capacity of both the sample solution and the apparatus. The actual measuring procedure was similar to the calibration procedure, but a mixing of solution and water must be taken into account instead of the heat input. The mixing was initiated by breaking the glass covers with a plunger rod. The mass of water used for dilution, m_{water} (kg), the temperature increase during the mixing process, ΔT (K), and the heat equivalent, E ($\mathrm{kJ \cdot K^{-1}}$), were used to calculate the differential heat of dilution, H_d ($\mathrm{kJ \cdot kg^{-1}}$), at the experimental concentration and temperature,

$$H_d = \Delta T E / m_{\mathrm{water}} \tag{2}$$

3. PROPERTY DATA AND REGRESSIONS

The measured properties for the lithium bromide + lithium iodide + 1,3-propanediol + water [LiBr/LiI mole ratio = 4 and (LiBr + LiI)/ $\mathrm{HO(CH_2)_3OH}$ mass ratio = 4] system are reported in Tables I and II. The

Table I. Heat Capacities of the $LiBr + LiI + HO(CH_2)_3OH + H_2O$ [LiBr/LiI Mole Ratio = 4, $(LiBr + LiI)/HO(CH_2)_3OH$ Mass Ratio = 4] System at Various Concentrations and Temperatures

T (K)	C_p ($kJ \cdot kg^{-1} \cdot K^{-1}$)
70.0 mass%	
283.15	1.75
298.15	1.76
313.15	1.78
333.15	1.80
65.0 mass%	
283.15	1.89
298.15	1.90
313.15	1.92
333.15	1.94
60.0 mass%	
283.15	2.01
298.15	2.03
313.15	2.05
333.15	2.06
55.0 mass%	
283.15	2.16
298.15	2.17
313.15	2.20
333.15	2.21
50.0 mass%	
283.15	2.33
298.15	2.34
313.15	2.36
333.15	2.36

Table II. Differential Heat of Dilution of the $LiBr + LiI + HO(CH_2)_3OH + H_2O$ [LiBr/LiI Mole Ratio = 4:1 and $(LiBr + LiI)/HO(CH_2)_3OH$ Mass Ratio = 4:1] System at Various Concentrations and 298.15 K

X (mass%)	H_d ($kJ \cdot kg^{-1}$)	X (mass%)	H_d ($kJ \cdot kg^{-1}$)
45.3	29.9	64.5	199.0
49.4	42.0	69.1	306.0
55.3	65.9	67.0	255.7
59.4	110.0	71.8	376.7
61.8	141.5		

data were correlated by Eqs. (3) and (4) for the heat capacity and the differential heat of dilution, respectively.

$$C_p = \sum_{i=0}^{3} (A_i + B_i T)\, X^i \tag{3}$$

$$H_d = (a + bX)/(1 + cX + dX^2) \tag{4}$$

where T is the absolute temperature in K, X is the absorbent ($LiBr + LiI + HO(CH_2)_3OH$) concentration in mass%, and A_i, B_i, a, b, c, and d are regression parameters. The resulting parameters determined by least-squares method are listed in Table III. The deviations of the calculated data sets from the measured results were expressed by the average absolute deviation (AAD).

Heat capacities were measured at four temperatures, 283.15, 298.15, 313.15, and 333.15 K, and for the absorbent concentration range of 50 to 70 mass%. The measured data set was fitted by a simple polynomial, Eq. (3). To extend the enthalpy calculation to higher temperatures, a first-order polynomial expressed in temperature was selected for regression. Figure 1 shows that the solution heat capacity decreases with an increase in the absorbent concentration due to the amount of water and increases slightly with an increase in temperature.

The differential heats of dilution were measured at 298.15 K for the absorbent concentration range of 45.3 to 71.8 mass%. To check the

Table III. Values of Coefficients for Least-Squares Representations[a]

Equation (3)			
i	*A*	*B*	AAD (%)[b]
0	2.57935×10^{1}	-5.70428×10^{-2}	0.18
1	-1.08431	2.72921×10^{-3}	
2	1.64983×10^{-2}	-4.24677×10^{-5}	
3	-8.53155×10^{-5}	2.18902×10^{-7}	

Equation (4)				
a	*b*	*c*	*d*	AAD[b]
8.73147×10^{-2}	1.00054×10^{-1}	-2.66554×10^{-2}	1.81037×10^{-4}	2.8

[a] Each set of parameters is valid only for the corresponding experimental composition range.
[b] AAD (%) $= (100/\mathrm{NP}) \sum_{i=1}^{\mathrm{NP}} |(\mathrm{Value}_i^{\mathrm{exp.}} - \mathrm{Value}_i^{\mathrm{calc.}})/\mathrm{Value}_i^{\mathrm{exp.}}|$. AAD $= (1/\mathrm{NP}) \sum_{i=1}^{\mathrm{NP}} |(\mathrm{Value}_i^{\mathrm{exp.}} - \mathrm{Value}_i^{\mathrm{calc.}})|$. NP = number of data points.

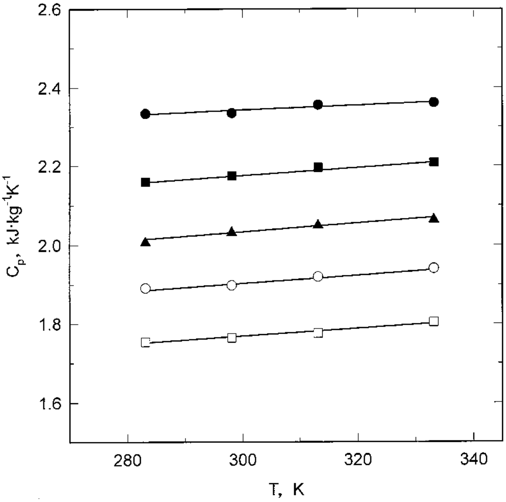

Fig. 1. Heat capacities of the $LiBr + LiI + HO(CH_2)_3OH + H_2O$ [LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ mass ratio = 4] system: ●, 50.0 mass%; ■, 55.0 mass%; ▲, 60.0 mass%; ○, 65.0 mass%; □, 70.0 mass%; ——, calculated by Eq. (3).

validity of the apparatus and measuring procedures, the differential heats of dilution of the lithium bromide + water solution were measured and found to be in good agreement with the average absolute deviation of 3 $kJ \cdot kg^{-1}$ from literature data [7]. The differential heats of dilution of the new working fluid were measured and fitted by Eq. (4). The results are plotted in Fig. 2.

4. ENTHALPY CALCULATION

The enthalpy–concentration (*H–T–X*) diagram of a working fluid is very important for the detailed design of an absorption chiller, especially for the calculation of the energy balance. The enthalpy of a solution mixture is generally represented by a function of temperature, pressure, and concentration. The enthalpy under any conditions can be calculated by using several relevant thermodynamic properties with the proper reference states. In this study the pressure dependence of the solution enthalpy was neglected because an absorption chiller is operated under the low-pressure state.

Considering an isothermal evaporation of water from a solution of mass m_0 at a temperature T_1, the differential mass change in the solution

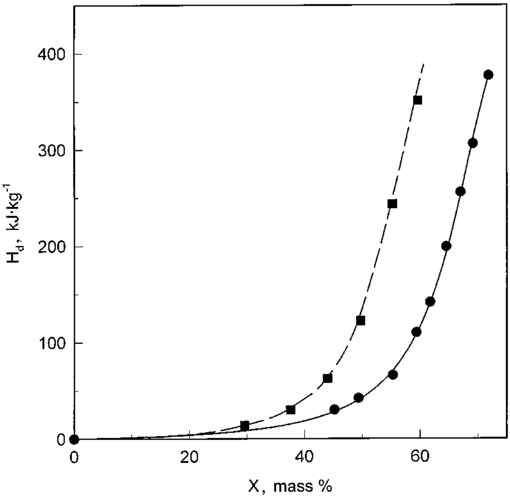

Fig. 2. Differential heats of dilution of the $LiBr + LiI + HO(CH_2)_3OH + H_2O$ [LiBr/LiI mole ratio = 4 and $(LiBr + LiI)/HO(CH_2)_3OH$ mass ratio = 4] system at 298.15 K: - - -, $LiBr + H_2O$ system (smoothed line) [7]; ■, $LiBr + H_2O$ system (measured in this study); ●, $LiBr + LiI + HO(CH_2)_3OH + H_2O$ system of this study; ——, calculated by Eq. (4).

is *dm* and the differential mass change of water vapor is *dm*. The heat balance is thus expressed as

$$\int_{m_0}^{m} \Delta H \, dm + \int_{m_0}^{m} H^{\text{vapor}}(-dm) + Hm = H_0 m_0 \tag{5}$$

Here, ΔH is the latent heat of vaporization of water in the solution at T_1, H^{vapor} is the enthalpy of water vapor at T_1, and H is the enthalpy of the solution at T_1 with respect to the arbitrary state H_0. If the solution concentration is denoted $X = 100m_s/m$, where m_s is the absorbent mass, then $H(T_1, X)$ is given by

$$H(T_1, X) = \frac{X}{X_0} H_0(T_1, X_0) + X \int_{X_0}^{X} \frac{\Delta_{\text{vap}} H(T_1, X) - H^{\text{vapor}}(T_1, P)}{X^2} \, dX \tag{6}$$

Equation (6) gives the enthalpy–concentration relationship under isothermal conditions. If the reference state of solution for zero enthalpy is set to

T_0 and X_0 (mass%), the enthalpy at the reference concentration is then given by

$$H_0(T_1, X_0) = \int_{T_0}^{T_1} C_p(T, X_0)\, dT \tag{7}$$

When only one volatile component exists in solution, $\Delta_{\text{vap}}H$ can be successfully estimated by the vapor pressure data at various concentrations and temperatures [9]. The enthalpy at any temperature and concentration needs two additional properties, the heat capacity at one reference concentration and the enthalpy of superheated water vapor. This calculation procedure has been commonly used to obtain the enthalpy of a working fluid of an absorption heat pump [8]. If experimental results for the differential heat of dilution are available at various temperatures, the enthalpy can be calculated by using the differential heat of dilution, the heat capacity at one concentration, and the enthalpy of liquid water [13] using Eq. (8).

$$H(T_1, X) = \frac{X}{X_0} H(T_1, X_0) + X \int_{X_0}^{X} \frac{H_d(T_1, X) - H^{\text{water}}(T_1)}{X^2}\, dX \tag{8}$$

However, the differential heat of dilution is somewhat difficult to measure, particularly in the high-temperature region. As a secondary choice for solving this problem, Eq. (6) has been directly adopted even for a solution containing two volatile components (water and organic), but the volatality of the organic component is completely neglected [10, 11]. However, these problems can be easily overcome by calculating only one enthalpy isotherm at a relatively low temperature at which accurate measurements of the differential heats of dilution are possible at several absorbent concentrations. The enthalpy at an arbitrary temperature is directly calculated from the following equation:

$$H(T, X_1) = H(T_1, X_1) + \int_{T_1}^{T} C_p^{\text{sol}}(T, X_1)\, dT \tag{9}$$

In this enthalpy calculation, 273.15 K was selected as a reference temperature for both the solution and the liquid water, and 60 mass% as a reference concentration of the solution. Therefore, the enthalpies of liquid water and 60 mass% solution were taken as zero at 273.15 K. The solution enthalpy is expressed by the following equation:

$$H(T, X) = \sum_{i=1}^{3} (C_i + D_i T + E_i T^2)\, X^i \tag{10}$$

Table IV. Values of Coefficients for Enthalpy Calculations at Various Temperatures and Concentrations by Eq. (10)

i	C_i	D_i	E_i
0	-5.29997×10^{3}	2.57878×10^{1}	-2.85144×10^{-2}
1	2.16235×10^{2}	-1.08400	1.36423×10^{-3}
2	-3.36293	1.64929×10^{-2}	-2.12273×10^{-5}
3	1.81780×10^{-2}	-8.52842×10^{-5}	1.09414×10^{-7}

where H is the solution enthalpy in $\mathrm{kJ\cdot kg^{-1}}$, X is the absorbent concentration in mass%, and T is the solution temperature in K. The parameters C_i, D_i, and E_i are listed in Table IV, and the calculated enthalpy isotherms are plotted against the absorbent concentration (in mass%) in Fig. 3.

To check the validity of the calculation procedure, the enthalpies of the lithium bromide + water solution were calculated by the same kinds of thermodynamic properties [7, 14] and procedures over the concentration range of 40 to 60 mass% at 323.15, 373.15, and 423.15 K. The calculated results and literature [15] values are compared in Fig. 4. The calculated results showed good agreement, with average absolute deviations of 0.3% (323.15 K), 1.0% (373.15 K), and 1.8% (423.15 K) from literature values when the same reference state was used (enthalpies of water and 50 mass% solution at 0°C are zero). Larger deviations in the higher-temperature

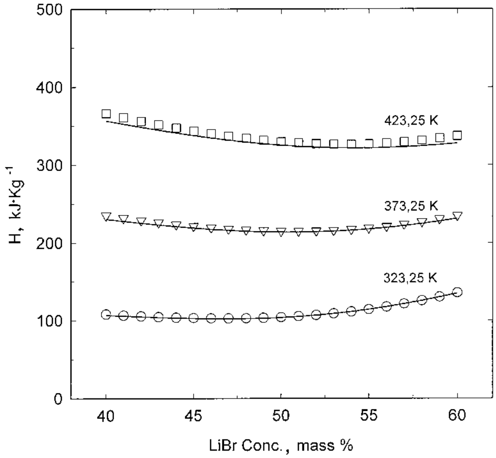

Fig. 3. Enthalpy diagram of the $\mathrm{LiBr + LiI + HO(CH_2)_3OH + H_2O}$ [LiBr/LiI mole ratio = 4 and $\mathrm{(LiBr + LiI)/HO(CH_2)_3OH}$ mass ratio = 4] system.

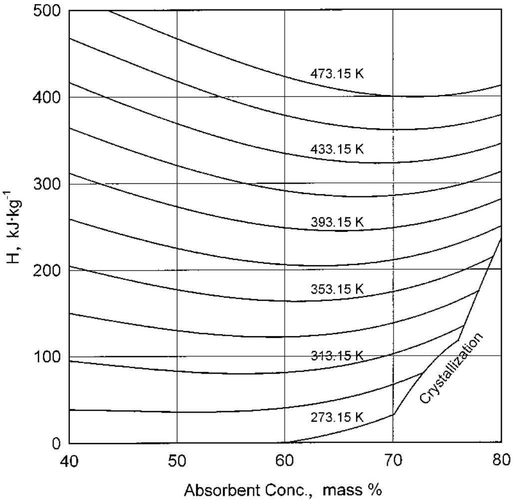

Fig. 4. Calculated enthalpies of the $LiBr + H_2O$ system and their comparison with literature values [12]. Data sources for calculation: heat capacity, Loewer [14]; differential heat of dilution, Uemura and Hasaba [7].

region are because the high-temperature heat capacity values were extrapolated from low-temperature data for both the literature results and these calculations.

5. CONCLUSIONS

A new working fluid of the lithium bromide + lithium iodide + 1,3-propanediol + water [LiBr/LiI mole ratio = 4 and (LiBr + LiI)/$HO(CH_2)_3OH$ mass ratio = 4] system is being considered for an absorption chiller. The thermal properties of the heat capacities and differential heats of dilution were accurately measured, and the data set of each property was correlated with a proper regression equation. The calculated results show good agreement with measured values. Enthalpy–concentration (*H*–*T*–*X*) diagrams of the new working fluid were constructed by using the measured thermal data. To calculate the enthalpy of the working fluid, a new calculation procedure that correlates the heat capacity with the differential heat of dilution was adopted because conventional methods cannot be applied to the organic-containing working fluid. The measured data sets and the correlated results can be used to give the required thermodynamic design data for a detailed system design.

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