J. Chem. Eng. Data 1993, 38, 299–301

Integral Enthalpies of Mixing for Water + Lithium Bromide + Lithium Iodide and Water + Lithium Chloride + Lithium Nitrate at 298.15 K

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Differential enthalpies of dilution and differential enthalpies of solution for water + lithium bromide + lithium iodide (salt mole ratio 4:1) and water + lithium chloride + lithium nitrate (salt mole ratio 2.8:1) were measured with a twin isoperibol calorimeter at 298.15 K. Integral enthalpies of mixing for these two ternary systems at 298.15 K were measured as a function of mass fraction, and were exothermic in both ternary systems. The results were correlated by means of Redlich–Kister-type polynomials. The average absolute deviation between the experimental and the calculated values from these equations was 0.57% for water + lithium bromide + lithium iodide and 0.52% for water + lithium chloride + lithium nitrate.

Introduction

The analyses of absorption refrigerating machines, absorption heat pumps, and absorption heat transformers require thermal and physical properties for working medium + absorbent systems. The enthalpy of mixing 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 (*1–11*).

The water + lithium bromide + lithium iodide system has been proposed to improve the performance characteristics of the basic water + lithium bromide system (*1*, *2*). An alternate, water + lithium chloride + lithium nitrate, has also been proposed to both improve the performance characteristics and reduce the corrosivity caused by the basic water + lithium bromide system (*1*, *2*, *12*). In our previous papers (*13–16*), the optimum mixing ratios of absorbents used for these two ternary systems and vapor pressure and heat capacity data of individual absorbent solutions at the optimum mixing ratios were reported.

The differential enthalpies of dilution and the differential enthalpies of solution for these two ternary systems were measured with a twin isoperibol calorimeter at 298.15 K. The values were correlated by means of Redlich–Kister-type polynomials as a function of mass fraction.

Experimental Section

Materials. All materials used in this work were analytical reagent grade. Materials used in this work, together with their suppliers and specifications, are listed in Table I. All the reagents were used without further purification. The absorbent concentrations of the lithium bromide + lithium iodide and the lithium chloride + lithium nitrate aqueous solutions were determined by Fajans' method (*17*) with use of dichlorofluorescein as an adsorption indicator. The solution was titrated by using a microburet of 10 cm^3 total delivery, with divisions of 0.02 cm^3.

The optimum mixing ratios of lithium bromide and lithium iodide and of lithium chloride and lithium nitrate were determined by measuring the crystallization temperature of sample solutions at constant mass fraction. Consequently, the most suitable mixing ratios of lithium bromide and lithium iodide and of lithium chloride and lithium nitrate were found to be 4 and 1 mol and to be 2.8 and 1 mol, respectively (*13*, *15*).

Table I. Materials Employed

material	supplier	specification (major impurity, mass %)
lithium bromide aqueous solution of 55.0 mass %	Honjo Chemical Co., Ltd. (Japan)	Ca, 0.0002; Cl, 0.01; Mg, 0.00002; SO_4, 0.01
lithium iodide aqueous solution of 56.2 mass %	Honjo Chemical Co., Ltd. (Japan)	Ca, 0.0023; Fe, 0.0001; SO_4, 0.012
lithium chloride aqueous solution of 40.0 mass %	Honjo Chemical Co., Ltd. (Japan)	Ca, 0.001; Mg, 0.00001; SO_4, 0.005
lithium nitrate	Wako Pure Chemical Industries Ltd. (Japan)	99.8+ mass %

Apparatus and Procedure. A twin isoperibol calorimeter used for this work was a commercial unit by the Tokyo Riko Co., Ltd. (Japan), model TIC-22, with an integrator, model CI-5, and with a constant-temperature circulator, model TC-100, capable of operation between 263.15 and 353.15 K with a temperature stability of ±0.01 K. This apparatus used was the same as that described in refs 7, 8, and 10. The accuracy of the measurements was ±0.1%. This 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. The assembled Dewar vessel contained a thermistor, an electric heater for calibration, a small Teflon-coated magnet, a breaker rod made of Teflon resin, and an ampule holder. The Teflon-coated magnet and ampule holder were supported by the frame of Teflon resin. The heater was made of manganin wire with an electric resistance of 100 Ω. The Dewar vessel was sealed with a Teflon O-ring. A magnetic stirrer was rotated by a synchronous motor. The pure water sample or anhydrous absorbent sample at a fixed mixing ratio was transferred into a glass ampule weighed to within 1 mg which was then flame-sealed under vacuum, reweighed, and mounted in the ampule holder of the Dewar vessel. An accurately weighed sample solution was then added to the Dewar vessel. After thermal equilibrium of both Dewar vessels was reached, the glass ampule containing about 0.1 g of sample was broken by depressing the breaker rod. The temperature inside the Dewar vessel was measured with a thermistor. The resulting temperature change of the calorimeter was recorded by a recorder. The extent of the thermal effect was determined subsequently by

0021-9568/93/1738-0299$04.00/0

Table II. Differential Enthalpies of Dilution H_d for H_2O + LiBr + LiI (LiBr:LiI = 4:1 mol) at 298.15 K

w	H_d/(kJ kg^{-1})	w	H_d/(kJ kg^{-1})	w	H_d/(kJ kg^{-1})
0.115	−3.7	0.448	−55.9	0.595	−316.4
0.197	−9.0	0.500	−103.1	0.601	−333.9
0.300	−14.2	0.550	−191.8	0.623	−402.1
0.400	−37.4	0.566	−225.0		

Table III. Differential Enthalpies of Solution H_s for H_2O + LiBr + LiI (LiBr:LiI = 4:1 mol) at 298.15 K

w	H_s/(kJ kg^{-1})	w	H_s/(kJ kg^{-1})	w	H_s/(kJ kg^{-1})
0	−504.3	0.406	−389.8	0.580	−171.6
0.102	−500.0	0.462	−333.8	0.605	−139.0
0.250	−471.8	0.528	−285.1	0.620	−98.0
0.342	−425.0	0.570	−195.1		

Table IV. Differential Enthalpies of Dilution H_d for H_2O + LiCl + $LiNO_3$ (LiCl:$LiNO_3$ = 2.8:1 mol) at 298.15 K

w	H_d/(kJ kg^{-1})	w	H_d/(kJ kg^{-1})	w	H_d/(kJ kg^{-1})
0.101	−4.5	0.335	−77.6	0.461	−225.9
0.201	−17.2	0.376	−99.5	0.482	−260.3
0.254	−32.6	0.403	−146.8	0.503	−293.7
0.301	−55.1	0.435	−192.4	0.518	−330.2

Table V. Differential Enthalpies of Solution H_s for H_2O + LiCl + $LiNO_3$ (LiCl:$LiNO_3$ = 2.8:1 mol) at 298.15 K

w	H_s/(kJ kg^{-1})	w	H_s/(kJ kg^{-1})	w	H_s/(kJ kg^{-1})
0	−597.1	0.252	−416.7	0.401	−193.9
0.101	−537.0	0.306	−354.9	0.422	−155.4
0.150	−502.3	0.335	−316.6	0.449	−106.3
0.201	−462.7	0.367	−261.5	0.501	−33.8

comparison with a known input of energy to a calibrating heater inside the Dewar vessel. The calorimeter and the experimental procedure adopted were checked by using the water + lithium bromide system (*1*, *2*) at 298.15 K, and the relative error between the measured and the published values was less than 1% over the entire absorbent range.

Results and Discussion

The differential enthalpies of dilution and the differential enthalpies of solution for water + lithium bromide + lithium iodide (salt mole ratio 4:1) at 298.15 K were measured in the range of mass fractions from 0 to 0.623 and from 0 to 0.518 for water + lithium chloride + lithium nitrate (salt mole ratio 2.8:1). The results for these two ternary systems are shown in Tables II–V. The integral enthalpies of mixing were calculated from the following equation described in ref 1:

$$H_m = (1 - w)H_d + wH_s \tag{1}$$

where H_m is the integral enthalpy of mixing, H_d is the differential enthalpy of dilution, H_s is the differential enthalpy of solution, and w is the mass fraction of absorbent at a fixed mixing ratio.

The values of the integral enthalpy of mixing were fitted to the Redlich–Kister-type polynomials:

$$H_m/(\text{kJ kg}^{-1}) = w(1 - w)\sum_{i=0}^{6} a_i(1 - 2w)^i \tag{2}$$

The values of the coefficients a_i determined by a least-squares method for these two ternary systems are shown in Table VI. The average absolute deviation between the individual experimental values and the calculated values from eq 2 was 0.57% for water + lithium bromide + lithium iodide and 0.52% for water + lithium chloride + lithium nitrate. The values of the integral enthalpy of mixing calculated from eq 2 are presented graphically in Figure 1 as a function of mass fraction. The integral enthalpies of mixing for these two ternary systems showed exothermic behavior. Crystallization of water + lithium bromide + lithium iodide and water + lithium chloride + lithium nitrate at 298.15 K occurs at mass fractions over about 0.66 and 0.54, respectively (*18*). Therefore, the integral enthalpies of mixing at mass fractions over solubility limits are not shown because of crystallization of absorbent solutions at 298.15 K. The minimum integral enthalpy of mixing for water + lithium bromide + lithium iodide occurs at 0.56 mass fraction of absorbent and 0.42 mass fraction of absorbent for water + lithium chloride + lithium nitrate. As can be seen from Figure 1, water + lithium bromide + lithium iodide shows a more exothermic integral enthalpy of mixing compared with water + lithium chloride + lithium nitrate at mass fractions over about 0.34. The integral enthalpy of mixing for water + lithium chloride + lithium nitrate is lower by about 50 kJ kg^{-1} at the minimum than the corresponding value for water + lithium bromide + lithium iodide.

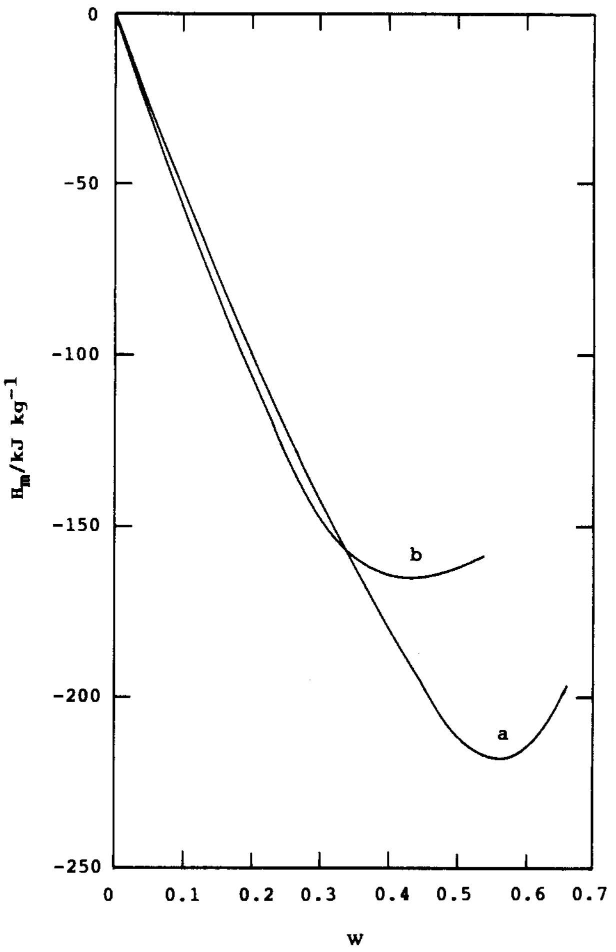

Figure 1. Calculated integral enthalpies of mixing for H_2O + LiBr + LiI (a, LiBr:LiI = 4:1 mol) and H_2O + LiCl + $LiNO_3$ (b, LiCl:$LiNO_3$ = 2.8:1 mol) at 298.15 K.

Table VI. Values of Coefficients a_i for H_2O + LiBr + LiI (LiBr:LiI = 4:1 mol) and H_2O + LiCl + $LiNO_3$ (LiCl:$LiNO_3$ = 2.8:1 mol) in Equation 2

	H_2O + LiBr + LiI	H_2O + LiCl + $LiNO_3$
a_0	$-8.391\,40 \times 10^2$	$-6.511\,78 \times 10^2$
a_1	$3.877\,77 \times 10^2$	$-1.642\,81 \times 10^2$
a_2	$5.161\,48 \times 10^2$	$-7.207\,89 \times 10$
a_3	$-1.133\,04 \times 10^3$	$5.210\,18 \times 10^2$
a_4	$-8.181\,28 \times 10$	$2.115\,53 \times 10^2$
a_5	$7.668\,53 \times 10^2$	$-4.898\,04 \times 10^2$
a_6	$-9.245\,24 \times 10$	$4.229\,35 \times 10^{-2}$

The integral enthalpy of mixing data for these two ternary systems are very useful for the research and the design of absorption refrigeration and heat pump systems.

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Received for review July 22, 1992. Accepted November 17, 1992. We gratefully acknowledge the partial support for this research by the Yazaki Memorial Foundation for Science and Technology.