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Solubilities for the Two Ternary Systems Water + Lithium Bromide + Lithium Iodide and Water + Lithium Chloride + Lithium Nitrate at Various Temperatures

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Solubilities for the water + lithium bromide + lithium iodide (salt mole ratio 4:1) and the water + lithium chloride + lithium nitrate (salt mole ratio 2.8:1) systems were measured by means of a visual polythermal method from 277.75 to 415.15 K and from 284.85 to 351.75 K, respectively. The transition point for the water + lithium bromide + lithium iodide system existed at 65.3 mass % salts and 293.85 K and at 54.2 mass % salts and 295.75 K for the water + lithium chloride + lithium nitrate system. Two solid–liquid phases for these two ternary systems were stable below and above the individual transition point. Two least-squares regression equations as a function of absolute temperatures were obtained from the individual measured solubility data for these two ternary systems. The maximum and average absolute deviations of the calculated values from the individual experimental data were 0.29 and 0.10% for the water + lithium bromide + lithium iodide system and 0.93 and 0.32% for the water + lithium chloride + lithium nitrate system, respectively.

Introduction

The analyses of absorption refrigeration and heat pump systems need extensive thermodynamic information such as heat capacities, heats of mixing, vapor pressures, solubilities, densities, viscosities, and surface tensions for working medium + absorbent systems. In the case of solutions using salts as the absorbent, the operation of the absorption refrigeration and heat pump systems is limited by the solubility curve of the absorbent. Therefore, the solubility data for the working fluids using salts as the absorbent are essential for the research and the design of absorption refrigeration and heat pump systems (*1–12*).

The water + lithium bromide + lithium iodide system was proposed in order to improve the performance characteristics of the basic water + lithium bromide system (*1*). And the water + lithium chloride + lithium nitrate system was also proposed in order to improve the performance characteristics and to reduce the corrosion caused by the basic water + lithium bromide system (*1, 13*) at the same time. In our previous papers (*14–18*), the optimum mixing ratios of absorbents used for these two ternary systems, the vapor pressure data, the heat capacity data, and the heat of mixing data for individual absorbent solutions at the optimum mixing ratios were reported.

The solubilities for these two ternary systems were measured by means of a visual polythermal method (*19–22*) over a wide range of temperatures. Two regression equations as a function of absolute temperatures were obtained by a least-squares method from the individual measured solubility data for these two ternary systems.

Table I. Solubilities of the H_2O + LiBr + LiI System (LiBr:LiI = 4:1 mol) at Various Temperatures

T/K	W^a/g	S_{exptl}/(mass %)	S_{calcd}/(mass %)	ϵ^b/%
277.75	165.3	62.3	62.3	0
278.95	166.7	62.5	62.4	0.16
285.35	171.7	63.2	63.2	0
289.15	177.8	64.0	64.0	0
291.95	183.2	64.7	64.7	0
293.85	188.2	65.3	65.4	−0.15
297.55	190.7	65.6	65.6	0
304.35	194.1	66.0	66.0	0
315.15	199.4	66.6	66.7	−0.15
317.35	202.1	66.9	66.8	0.15
336.55	217.5	68.5	68.3	0.29
354.35	234.4	70.1	70.0	0.14
381.15	269.0	72.9	73.1	−0.27
402.25	316.7	76.0	76.0	0
405.15	325.5	76.5	76.4	0.13
407.45	331.0	76.8	76.8	0
411.55	340.5	77.3	77.4	−0.13
415.15	356.6	78.1	78.0	0.13

[a] Grams of absorbent at the optimum mixing ratio per 100 g of water. [b] Deviation: $\epsilon = [(S_{\mathrm{exptl}} - S_{\mathrm{calcd}})/S_{\mathrm{exptl}}] \times 100$.

Experimental Section

Materials. The lithium bromide, lithium iodide, and lithium chloride used in this work were from the Honjo Chemical Co., Ltd. (Japan), analytical reagent grade with a minimum purity of 99.9 mass %. The analytical results of the aqueous lithium bromide, lithium iodide, and lithium chloride solutions have been described in our previous papers (*14, 16, 18*). 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 these two ternary systems were determined by Fajans' method (*23*) 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 done on a direct-reading balance (weighing capacity 200 g, reciprocal sensibility 1 mg).

The optimum mixing ratios of absorbents for these two ternary systems were determined by measuring the crystallization temperature of the individual sample solutions at constant absorbent concentration. Consequently, the optimum mixing ratios of lithium bromide and lithium iodide and of lithium chloride and lithium nitrate were found to be 4 and 1 mol and 2.8 and 1 mol, respectively (*14, 16*).

Apparatus and Procedure. The visual polythermal method used in this work has been described in detail previously (*19–22*). The apparatus used for the solubility

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Table II. Solubilities of the H_2O + LiCl + $LiNO_3$ System (LiCl:$LiNO_3$ = 2.8:1 mol) at Various Temperatures

T/K	W^a/g	S_{exptl}/(mass %)	S_{calcd}/(mass %)	ϵ^b/%
284.85	100.8	50.2	50.0	0.40
288.35	102.0	50.5	50.4	0.20
291.45	104.1	51.0	51.3	−0.59
293.25	107.0	51.7	52.0	−0.58
294.35	109.6	52.3	52.6	−0.57
294.95	111.4	52.7	52.9	−0.38
295.45	114.1	53.3	53.2	0.19
295.55	115.1	53.5	53.2	0.56
295.65	116.5	53.8	53.3	0.93
295.75	118.3	54.2	54.2	0
298.55	118.8	54.3	54.4	−0.18
303.15	120.8	54.7	54.7	0
303.55	121.7	54.9	54.8	0.18
304.25	122.2	55.0	54.8	0.36
304.75	120.8	54.7	54.9	−0.37
306.95	124.2	55.4	55.1	0.54
311.55	123.2	55.2	55.5	−0.54
321.05	131.5	56.8	56.7	0.18
323.15	133.1	57.1	57.0	0.18
323.35	132.0	56.9	57.0	−0.18
326.95	135.8	57.6	57.6	0
335.75	143.3	58.9	59.1	−0.34
336.95	146.3	59.4	59.3	0.17
338.05	147.5	59.6	59.5	0.17
341.75	153.8	60.6	60.3	0.50
344.85	153.8	60.6	60.9	−0.50
346.15	157.7	61.2	61.2	0
351.75	167.4	62.6	62.5	0.16

[a] Grams of absorbent at the optimum mixing ratio per 100 g of water. [b] Deviation: $\epsilon = [(S_{exptl} - S_{calcd})/S_{exptl}] \times 100$.

measurements consisted of a 1-L Pyrex glass vessel closed by a silicone rubber stopper and fitted with an electrically driven herical glass stirrer with the vessel and a glass stirrer shaft sealed with a glycerol seal. The experimental procedure was as follows. The assembled vessel was immersed in a thermostatic water (277.75–353.15 K) or oil (353.15–415.15 K) bath controlled to ±0.01 K. A sample solution (700 cm^3) of the desired absorbent concentration at the optimum mixing ratio was first incrementally heated to dissolve the last crystal and agitated at a temperature at least 5 K higher than the crystallization temperature, and then allowed to cool slowly to nucreate a small number of crystals. The temperature of the thermostatic bath was lowered and raised at a very slow rate—approximately 1 K/10 min. The temperature at which the first salt crystal appeared was taken as the crystallization temperature for the known absorbent solution in a polythermal run. As the results of the measurements, the temperatures at which the last crystal disappeared were in good agreement with the crystallization temperatures within 0.5 K. After the crystals were dissolved, part of the sample solution was carefully withdrawn by means of a pipet slightly hotter than the solution in order to avoid any solidification, and then the absorbent concentration of the solution was determined by Fajans' method again. The desired absorbent concentrations were in good agreement with the absorbent concentrations determined again by Fajans' method within 0.1 mass %. The solubilities of the absorbent at the optimum mixing ratio in grams per 100 g of water, used as the working medium, were calculated from the experimental data (S_{exptl}) of crystallization temperatures. The apparatus and the experimental procedure adopted were checked by using the water + lithium bromide system (*1,2*) at various crystallization temperatures, and the relative error between the measured and the published values was less than 1%.

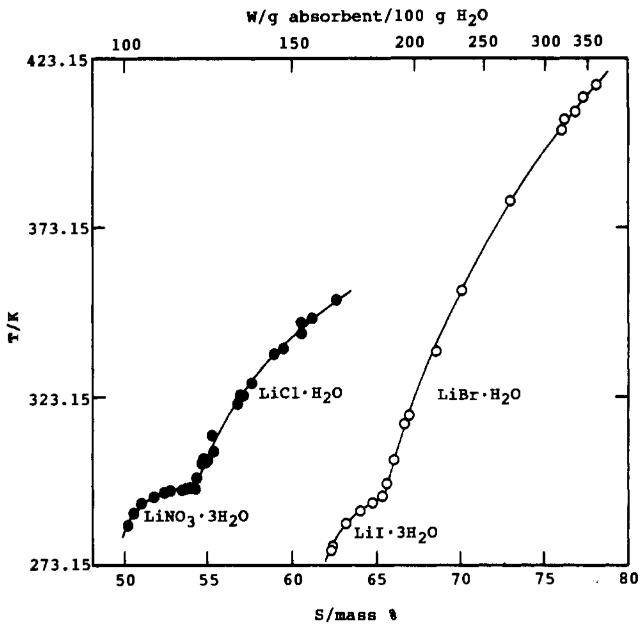

Figure 1. Solubilities of two ternary systems at various temperatures: ○, H_2O + LiBr + LiI (LiBr:LiI = 4:1 mol); ●, H_2O + LiCl + $LiNO_3$ (LiCl:$LiNO_3$ = 2.8:1 mol); —, calculated values from eq 1.

Results and Discussion

The solubilities for the water + lithium bromide + lithium iodide system (salt mole ratio 4:1) were measured from 277.75 to 415.15 K and from 284.85 to 351.75 K for the water + lithium chloride + lithium nitrate system (salt mole ratio 2.8:1). The measured mass percent solubilities (S_{exptl}) for these two ternary systems are shown in Tables I and II along with the solubilities (W) calculated from measured mass percent solubilities and the deviations between the experimental data (S_{exptl}) and the calculated values (S_{calcd}) from eq 1 derived below. The individual experimental data for these two ternary systems were regressed by a least-squares method to an equation of the following form:

$$S = \sum_{i=0}^{2} a_i T^i \tag{1}$$

where S is the solubility of the absorbent at the optimum mixing ratio in mass percent, T is the absolute temperature, and a_i are the regression coefficients. The coefficients a_i for the regression equations describing mass percent solubility of the absorbent in aqueous salt solutions are listed in Table III. The experimental data for these two ternary systems

Table III. 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) Systems in Equation 1

	a_0	a_1	a_2
	H_2O + LiBr + LiI		
277.75 K ≤ T < 293.85 K ($LiI \cdot 3H_2O$)	$6.691\,52 \times 10^2$	$-4.422\,42$	$8.056\,49 \times 10^{-3}$
293.85 K ≤ T ≤ 415.15 K ($LiBr \cdot H_2O$)	$8.906\,27 \times 10$	$-2.106\,89 \times 10^{-1}$	$4.430\,40 \times 10^{-4}$
	H_2O + LiCl + $LiNO_3$		
284.85 K ≤ T < 295.75 K ($LiNO_3 \cdot 3H_2O$)	$2.213\,76 \times 10^3$	$-1.520\,78 \times 10$	$2.672\,18 \times 10^{-2}$
295.75 K ≤ T ≤ 351.75 K ($LiCl \cdot H_2O$)	$1.798\,15 \times 10^2$	$-9.056\,00 \times 10^{-1}$	$1.626\,17 \times 10^{-3}$

were plotted in Figure 1 as a function of absolute temperatures. The solid lines shown in Figure 1 are the calculated values from eq 1 with the coefficients from Table III. As can be seen from Figure 1 and Tables I and II, an abrupt change in the solubility curve of the absorbent occurs at 65.3 mass % and 293.85 K for the water + lithium bromide + lithium iodide system and at 54.2 mass % and 295.75 K for the water + lithium chloride + lithium nitrate system. Two solid–liquid phases for these two ternary systems were stable below and above the individual transition point. Therefore, the values of coefficients a_i were divided into two temperature ranges or solubilities of $LiI\cdot 3H_2O$ and $LiBr\cdot H_2O$ and of $LiNO_3\cdot 3H_2O$ and $LiCl\cdot H_2O$ at individual transition points for these two ternary systems. The maximum and average absolute deviations between the individual experimental data and the calculated values from these regression equations were 0.29 and 0.10% for the water + lithium bromide + lithium iodide system and 0.93 and 0.32% for the water + lithium chloride + lithium nitrate system, respectively.

The solubility data for these two ternary systems are very useful for the determination of solubility limits in absorption refrigeration and heat pump systems using these solutions as working fluids.

Glossary

a_i	coefficients in eq 1
S	solubility, mass %
T	absolute temperature, K
W	solubility, g of absorbent at the optimum mixing ratio/100 g of water

Greek Letter

ϵ	deviation, %

Subscripts

calcd	calculated value from eq 1
exptl	experimental data

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