International Journal of Thermophysics, Vol. 18, No. 6, 1997

Note

Solubilities and Vapor Pressures of the Lithium Bromide + Calcium Nitrate + Water System

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Received April 15, 1997

Solubilities and vapor pressures of the lithium bromide + calcium nitrate + water system [$LiBr/Ca(NO_3)_2$ mass ratio = 1.0] were measured in various absorbent (lithium bromide + calcium nitrate) concentration and temperature ranges. Solubilities were measured by a visual polythermal method in the temperature range from 282.55 to 343.45 K and the experimental values were correlated with two least-squares regression equations as a function of temperature. The average absolute deviation between the experimental and the calculated solubilities was 0.23%. Vapor pressures were measured by the boiling point method in the temperature range from 334.65 to 385.85 K and in the absorbent concentration range from 44.9 to 70.3 mass%. The experimental values were correlated with an Antoine-type equation and the overall average absolute deviation was found to be 1.06%.

KEY WORDS: absorption heat pump; calcium nitrate [$Ca(NO_3)_2$]; lithium bromide (LiBr); solubility; vapor pressure.

1. INTRODUCTION

The absorption heat pump has received growing attention in past years from the areas of refrigeration and air-conditioning, especially in the aspects of saving energy and protecting the environment. Recently, a number of papers [1–5] dealing with the development of new working fluids used in the air-cooled absorption heat pump have appeared, because the air-cooled absorption heat pump uses only a cooling fan instead of a cooling tower and thus the equipment cost is low. There are many additional problems in the construction of the air-cooled absorption cycle with new

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working fluids. The most serious problem is the crystallization of the working fluid, because the high absorber temperature caused by air-cooling requires a high concentration of the working fluid in order to maintain a low vapor pressure in the absorber. In this work, the lithium bromide + calcium nitrate + water [LiBr/Ca$(NO_3)_2$ mass ratio = 1.0] system is proposed to achieve a higher solubility than the lithium bromide + water solution [6] used as a typical absorbent in the absorption heat pump. In this study, crystallization temperatures were measured at a constant absorbent concentration in order to find the optimum mixing ratio of lithium bromide and calcium nitrate. The solubilities and vapor pressures under a fixed condition [LiBr/Ca$(NO_3)_2$ mass ratio = 1.0] were measured at various temperatures and concentrations, respectively. Each set of results was correlated with the proper equation.

2. EXPERIMENTS

2.1. Materials

Lithium bromide (99 + %) was supplied by Aldrich Chemical Co. and calcium nitrate tetrahydrate (99%) was supplied by Sigma Chemical Co. All materials were used without further purification. All solutions were prepared with deionized water.

2.2. Apparatus and Method

Solubilities and vapor pressures were measured by a visual polythermal method [7, 8] and the boiling point method [9], respectively. The experimental apparatuses and procedures were almost the same as those described previously [10, 11]. The apparatus for the solubility measurements consisted of a glass vessel with an internal volume of 50 cm^3, a thermistor thermometer capable of reading to 0.01 K, a constant-temperature bath, a circulator for both cooling and heating, and two stirrers. Each sample solution of a desired absorbent concentration at a given mixing ratio was accurately prepared by weighing each component with a precision balance. The sample solution, with an approximate volume of 30 cm^3, was placed in the vessel and stirred well. The solution was first incrementally heated above the crystallization temperature to dissolve all the crystals. Then the solution temperature was lowered slowly to nucleate a small amount of crystals. The temperature of the solution was lowered and then raised at a very slow rate, less than 0.1 $K \cdot min^{-1}$, with the aid of the constant-temperature bath and circulator. Through a series of dissolving and nucleation procedures, the temperature at which the last crystal disappeared was taken as the crystallization temperature for a given solution in this polythermal run. The apparatus for vapor-pressure measurements consisted primarily of an equilibrium vessel with an internal volume of 500 cm^3, a constant-temperature bath, a condenser, a U-tube mercury manometer capable of reading to 0.05 mm, a K-type thermocouple with a reading accuracy of 0.4%, and two stirrers. A sample solution of a desired absorbent concentration was prepared. The sample solution, with an approximate volume of 250 cm^3, was placed in the vessel and evacuated to a pressure sightly higher pressure than the vapor pressure of the solution. The sample solution was then heated and stirred well with a magnetic stirrer to prevent superheating. After thermal equilibrium was reached, the temperature of the sample solution and the pressure of the apparatus were measured.

3. RESULTS AND DISCUSSION

3.1. Optimum Mixing Ratio

The optimum mixing ratio of lithium bromide and calcium nitrate was determined by measuring the crystallization temperatures of sample solutions at a constant absorbent (lithium bromide + calcium nitrate)

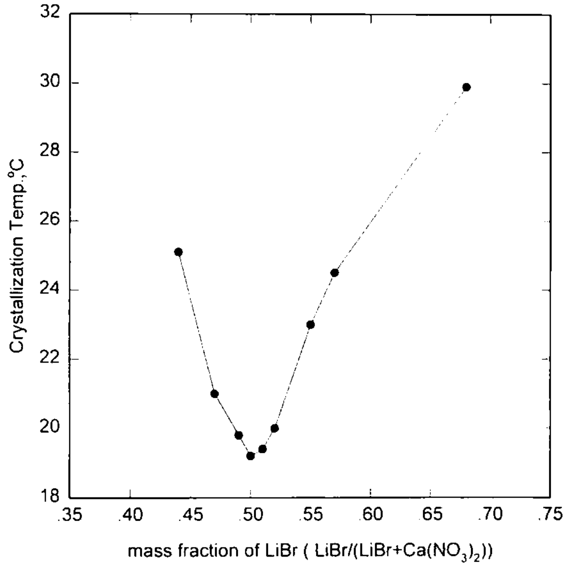

Fig. 1. Relationship between mixing ratio and crystallization temperatures (absorbent concentration = 65 wt%).

concentration (65 wt%). The crystallization temperatures were observed by changing the mass fraction of lithium bromide a fixed absorbent concentration and are shown in Fig. 1. The most suitable mixing ratio of lithium bromide and calcium nitrate was found to be 1:1 by mass.

3.2. Solubility and Vapor Pressure

The solubilities of the lithium bromide + calcium nitrate + water [LiBr/ $Ca(NO_3)_2$ mass ratio = 1.0] system were measured in the temperature range from 282.55 to 343.45 K. The measured values are listed in Table I and were correlated with the following equation:

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

where S is the solubility represented by the mass percentage of absorbent (lithium bromide + calcium nitrate), T the absolute temperature in K, and A_i the equation parameters. The A_i parameters were determined by the least-squares method and the results are listed in Table II. The average absolute deviation between experimental and calculated values was 0.23%.

Table I. Solubilities of the LiBr + $Ca(NO_3)_2$ + H_2O [LiBr/$Ca(NO_3)_2$ Mass Ratio = 1.0] System at Various Temperatures

T (K)	S (mass%)
282.55	63.5
289.95	64.5
291.25	64.8
291.85	64.9
292.35	65.0
294.35	65.7
297.45	66.5
298.65	67.0
300.75	68.0
304.15	69.1
307.55	70.0
308.75	70.2
309.65	70.4
312.15	70.4
319.95	70.5
325.15	71.0
332.15	72.0
343.45	73.4

Table II. Values of Coefficients A_i for the LiBr + $Ca(NO_3)_2$ + H_2O [LiBr/$Ca(NO_3)_2$) Mass Ratio = 1.0] System in Eq. (1)

	A_0	A_1	A_2
$282.55 \leqslant T(K) \leqslant 309.65$	3.60743×10^2	-2.26460	4.28834×10^{-3}
$309.65 \leqslant T(K) \leqslant 343.45$	3.17909×10^2	-1.60387	2.59764×10^{-3}

The experimental and calculated results were plotted in Fig. 2. This figure shows that a large solubility enhancement was obtained compared to the basic lithium bromide + water solution and this result can assist in extending the operation range of the absorption cycle. The vapor pressures of the system were measured in the temperature range from 334.65 to 385.85 K and in the concentration range from 44.9 to 70.3 mass%. The experimental results are listed in Table III and these values were correlated with an Antoine-type equation which expresses vapor pressure as a function of temperature and concentration:

$$\log P = \sum_{i=0}^{4} [A_i + \{1000B_i/(T - 43.15)\}]X^i \tag{2}$$

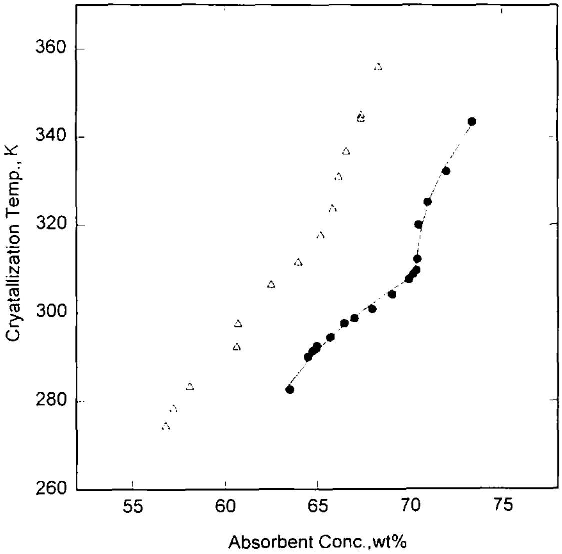

Fig. 2. Solubilities S of LiBr + $Ca(NO_3)_2$ + H_2O system: (●) LiBr + Ca(No$_3$)$_2$ + H_2O system; (△) LiBr + H_2O system [6]; (——) calculated.

Table III. Vapor Pressures of the LiBr + Ca(NO$_3$)$_2$ + H$_2$O [LiBr/Ca(NO$_3$)$_2$ Mass Ratio = 1.0] System at Various Concentrations

T (K)	P (kPa)	T (K)	P (kPa)
$X = 44.9$ mass%		$X = 49.8$ mass%	
334.65	10.87	337.65	10.26
341.55	15.09	344.45	14.17
348.25	20.19	357.45	25.10
359.85	32.72	363.65	32.23
366.45	42.31	370.75	41.60
$X = 55.0$ mass%		$X = 60.1$ mass%	
336.15	7.30	340.05	6.00
341.25	9.55	347.95	9.07
351.15	14.92	353.25	11.47
357.55	19.59	363.15	17.33
366.36	28.17	370.85	23.07
$X = 65.1$ mass%		$X = 70.3$ mass%	
347.05	5.76	349.15	3.91
358.35	9.59	357.65	5.61
369.15	15.46	366.35	8.40
378.25	22.22	375.85	12.37
385.15	28.88	385.85	18.73

where P is the vapor pressure in kPa, A_i and B_i are the regression parameters, T is the absolute temperature in K, and X is the mass concentration of absorbent. The A_i and B_i parameters were determined by the least-squares method, and the results are shown in Table IV. The average absolute deviation between the experimental data and the calculated values was found to be 1.06%. The experimental and calculated results are plotted

Table IV. Values of A_i and B_i for the LiBr + Ca(NO$_3$)$_2$ + H$_2$O [LiBr/Ca(NO$_3$)$_2$ Mass Ratio = 1.0] System in Eq. (2)

i	A_i	B_i
0	-1.55477×10^{2}	4.92889×10^{1}
1	1.17157×10^{1}	-3.68421
2	-3.14080×10^{-1}	9.90136×10^{-2}
3	3.71130×10^{-3}	-1.17318×10^{-3}
4	-1.63111×10^{-5}	5.15986×10^{-6}

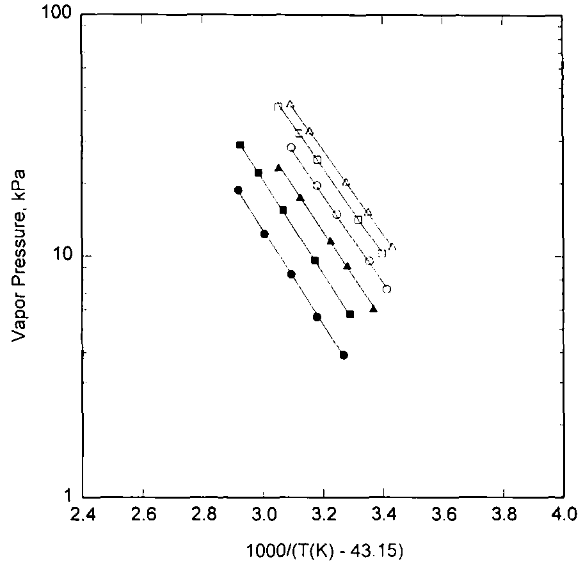

Fig. 3. Vapor pressures of the $LiBr + Ca(NO_3)_2 + H_2O$ system at various mass percentages: (△) $X = 44.9$ mass%; (□) $X = 49.8$ mass%; ( ) $X = 55.0$ mass%; (▲) $X = 60.1$ mass%; (■) $X = 65.1$ mass%; (●) $X = 70.3$ mass%; (——) calculated.

in Fig. 3, which shows that the $\log P$ versus $1000/(T - 43.15)$ relation at a given concentration is linear over the pressure and temperature ranges considered.

4. CONCLUSION

Solubilities and vapor pressures of the lithium bromide + calcium nitrate + water system [$LiBr/Ca(NO_3)_2$ mass ratio = 1.0] were measured at various absorbent concentrations and temperature ranges as a possible new working fluid for the absorption heat pump. All the properties measured were correlated with proper regression equations and the calculated values showed a good agreement with the experimental values. The good solubility enhancement of the lithium bromide + calcium nitrate + water system compared to the basic lithium bromide + water solution indicates that the operation range of the absorption heat pump can be extended using this proposed solution. In order to evaluate the overall performance of the solution more closely, other thermodynamic and transport properties should be extensively determined and carefully cross-checked.

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