Vapor Pressures of the Aqueous Desiccants

Tsair-Wang Chung* and Chung-Ming Luo

Chemical Engineering Department, Chung Yuan Christian University,
Chungli, Taiwan 32023, Republic of China

The vapor pressures of the aqueous desiccants lithium chloride, lithium bromide, calcium chloride, ethylene glycol, propylene glycol, and their mixtures were measured at their typical operating concentrations and at temperatures from 298 K to 313 K. The experimental data were fitted to an Antoine type of equation, $\ln[P(\mathrm{kPa})] = A - B/[T(\mathrm{K}) + C]$, where A, B, and C are constants and are concentration dependent. Vapor pressure data were further used to predict the effectiveness of dehumidification in liquid desiccant dehumidifiers.

Introduction

Liquid desiccants in absorption dehumidification systems are aqueous solutions of either inorganic salts, such as lithium chloride, lithium bromide, and calcium chloride, or organic compounds, such as ethylene glycol and propylene glycol. The liquid desiccants work on the principle of absorption and have the property of absorbing moisture from air. When the vapor pressure of the inlet liquid desiccant is lower than that of the air stream, dehumidification takes place.

Various thermodynamic properties of inorganic salt solutions, such as the fugacity, the osmotic coefficient, and the activity of water, are directly dependent on the salt concentration and can be used to calculate the vapor pressure of the salt solutions. Johnson and Furter (*1*) tried to relate the theoretical significance of the salt effect in the vapor−liquid equilibrium. They studied 18 alcohol + water + salt systems. The equilibrium data for part of the salt-free systems were compared with the data in Perry and Chilton's Handbook (*2*), and the agreement is extremely good. Because there were no data available for comparison with their data on these binary-solvent salt systems at that time, they assumed that the data for the systems containing salt were as consistent as the data for salt-free systems. A correlation of the salt effect in alcohol + salt and water + salt systems was obtained by Rousseau et al. (*3*). The fugacity was used to take into account the vapor pressure in their correlation. Their model was also useful in evaluating other similar systems that contain an added nonvolatile component and for comparing the behavior with those of the original salt-free systems. Boone et al. (*4*) recommended a procedure to correlate the vapor−liquid equilibrium behavior of binary-solvent salt systems. Equilibrium data were successfully correlated using vapor pressure data and activity coefficients. Most of the above correlations were collected in the book by Horvath (*5*). Thermodynamic data related to the inorganic salt solutions have been compiled by Robinson and Stokes (*6*), Harned and Owen (*7*), Wu and Hamer (*8*), International Critical Tables (*9*), and the CRC Handbook (*10*) and were most useful as graphical correlations for the activity coefficients of Meissner and Tester (*11*). Experimental osmotic coefficients and activity coefficients for various solutions were also presented by Robinson and Stokes (*6*). These thermodynamic parameters can be predicted by several semiempirical equations from models by Renon and Prausnitz (*12*), Abrams and Prausnitz (*13*), and Chen et al. (*14*−*16*). Since the osmotic coefficients and activity coefficients at room temperature for most salt solutions are available in the literature, the transition of these parameters into vapor pressure is more direct than predictions of the activity coefficients by the above correlations.

The vapor pressures of the organic desiccant solutions are rare in the open literature. Although some technical reports from industry (*17*) provided part of the vapor pressure data for the aqueous organic desiccant solutions, the accuracy of the data was unknown. Actually, the experimental data for most of the vapor pressures of the organic desiccants or the mixed solutions are very few in the literature, and the prediction methods are limited. Therefore, a device for measuring the vapor pressure of the desiccant solutions has been designed and built in this study. The vapor pressures of the potential desiccant solutions at the typical concentrations employed in liquid desiccant dehumidifiers were obtained at temperatures from 298 K to 313 K. The relationship between the vapor pressure and the effectiveness of dehumidification under different operating conditions and using different working solutions was also tested.

Experimental Section

Materials. Lithium chloride (99%) and lithium bromide (99+%) were supplied by Lahcaster Synthesis Ltd.; triethylene glycol (99.9%), dipropylene glycol (99.9%), and tripropylene glycol (98.0%) were supplied by Tokyo Kasei Kogyo Co., Ltd.; calcium chloride (95%) was supplied by Showa Chemical Company; diethylene glycol (99.87%) was supplied by Tedia Company, Inc.; tetraethylene glycol (99.5%) was supplied by Janssen Chemica; and propylene glycol (99%) was supplied by Acros Organics; and all were used without further purification. The concentrations of the desiccant solutions in this study were adjusted by reverse osmosis water.

Apparatus and Procedure. The vapor pressure measurement apparatus was modified from the design of Yamamoto et al. (*18*) for measuring the gas solubility in liquids. Therefore, this apparatus can be used to measure both

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* To whom correspondence should be addressed. E-mail: twchung@mbox.cycu.edu.tw.

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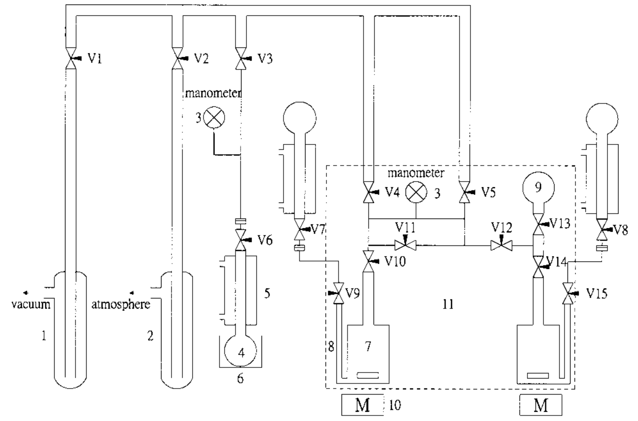

Figure 1. Schematic diagram of the vapor pressure and solubility measurement apparatus: (1) liquid nitrogen trap; (2) mercury bubbler; (3) manometer; (4) degassing flask; (5) condenser; (6) liquid nitrogen tank; (7) equilibrium cell; (8) capillary; (9) gas flask; (10) magnetic stir; (11) water bath; (V1−V15) needle valves.

Table 1. Experimental Vapor Pressures of Aqueous Salt Solutions

salt	concn (mass %)	vapor pressure (kPa) 298.15 K	303.15 K	308.15 K	313.15 K
LiCl[a]	35		2.20		2.79
	40		1.79		2.41
	40[c]	1.48	1.74	2.13	2.41
	44		1.47		2.10
LiBr[a]	31		3.11		3.67
	38		2.90		3.47
	40[c]	2.45	2.82	3.08	3.35
	44		2.57		3.14
$CaCl_2$[b]	35		2.78		3.36
	40		2.55		3.13
	40[c]	2.10	2.53	2.86	3.14
	43		2.20		2.80

[a] Patil et al. (1990). [b] Patil et al. (1991). [c] This work.

vapor pressure and solubility data. Figure 1 is a schematic flow diagram of the apparatus where the parts are described below the figure. The most important procedure to operate this vapor pressure measurement apparatus is the degassing of the liquid samples using liquid nitrogen in a standard procedure. Good results can be obtained from this procedure, but it is necessary to repeat the procedure at least three times (thawing then freezing).

Several methods of criteria for determination of degassing are available in the literature. One method is to compare the vapor pressure with the literature data. For aqueous salt solutions the vapor pressure data are available in the literature (*19,20*). The most adequate concentration for dehumidification usage is about 40 mass %; therefore, the data of the vapor pressures of liquid samples at 40 mass % are obtained in this study to compare with the literature data in Table 1. Since good agreement of these data was obtained, the degassing method in this study was considered adequate.

The step-by-step operating procedure for measuring the vapor pressure by using the apparatus is provided below:

(1) After degassing, the system (exclusive of flask 4) was brought to atmospheric pressure with air by opening valve V6. (2) The degassing device was disconnected and reversed to connect valve V7 as shown in Figure 1. (3) The valves V2, V3, V5, and V10 were closed, and the system was evacuated through valves V1, V4, V7, V8, and V9 again. (4) Valve V4 was closed and valve V6 was opened; therefore, the liquid sample was flowed through the capillary tube to the equilibrium cell [7]. (5) With valve V7 closed, the solvent was stirred magnetically in the constant-temperature bath [11]. The system was allowed to come to equilibrium for about 2 h, and the vapor pressure of the liquid sample at the specific temperature was measured.

Results and Discussion

The vapor pressures of the potential desiccant solutions at typical concentrations for the dehumidification applications were determined at different operating temperatures and listed in Table 2. Since the vapor pressures of the organic glycols are almost zero from 298 K to 313 K and the presence of the inorganic salts in water results in water vapor pressure depression, the water vapor is the only vapor-phase component of both aqueous organic and inorganic desiccant solutions. The variation of the vapor pressure is not linear with the change of the temperature. For salt solutions 40 mass % LiCl is the best choice to be a liquid desiccant because the vapor pressure of LiCl is lower than those of the other two desiccants. If compared with those of the organic desiccants, the vapor pressures of the aqueous glycol are lower than that of LiCl at similar temperatures. However, the viscosities of the glycol are much higher than that of the aqueous salt solutions and the pumping cost is higher also. The corrosion problem is serious in the systems using the salt desiccants. Both types of desiccants have certain advantages and disadvantages. Therefore, in commercial dehumidifiers both types of desiccants are used widely.

The evidence as to whether ions are present in the solution is usually determined by their colligative properties, such as freezing point depression, boiling point elevation, or osmotic pressure. The approaches to the vapor pressures of salt solutions by using their colligative properties were collected in the book by Horvath (*5*). However, for aqueous organic solutions this kind of approach was rare in the literature. Therefore, data on the vapor pressures of the aqueous desiccant solutions at different temperatures were correlated by an Antoine type equation

$$\ln[P(\mathrm{kPa})] = A - B/[T(\mathrm{K}) + C] \tag{1}$$

where P and T denote the vapor pressure and temperature, and A, B, and C are adjustable parameters. The constants in the Antoine equation are provided in Table 3. These constants are obtained from the regression of the data in Table 2 for each desiccant solution.

The performance of the liquid desiccant dehumidifier is usually evaluated by the effectiveness of dehumidification, the mass transfer coefficient, or the height of a transfer unit (*18*). However, the most direct and obvious parameter for presenting the system performance is the effectiveness. The effectiveness of dehumidification is determined as the ratio of the change in moisture content of air leaving the system to the maximum possible change in the moisture content under a given operating condition. Therefore, the effectiveness of dehumidification ϵ can be expressed as

$$\epsilon = \frac{W_{\mathrm{in}} - W_{\mathrm{out}}}{W_{\mathrm{in}} - W_{\mathrm{equ}}} \tag{2}$$

where W_{in} and W_{out} are the water content (kg H_2O/kg dry air) of the inlet and outlet air, respectively. W_{equ} is the water content of the air which is at equilibrium with the desiccant solution at a particular concentration and temperature.

Table 2. Experimental Vapor Pressures of the Potential Desiccant Solutions Measured in This Study

	vapor pressure (kPa)			
desiccant solutions	298.15 K	303.15 K	308.15 K	313.15 K
aqueous LiCl solution (40 mass %)	1.48	1.74	2.13	2.41
aqueous LiBr solution (40 mass %)	2.45	2.82	3.08	3.35
aqueous $CaCl_2$ solution (40 mass %)	2.10	2.53	2.86	3.14
aqueous diethylene glycol solution (95 mass %)	1.53	2.01	2.38	2.66
aqueous triethylene glycol solution (95 mass %)	1.70	2.10	2.47	2.78
aqueous tetraethylene glycol solution (95 mass %)	1.70	2.15	2.50	2.83
aqueous propylene glycol solution (95 mass %)	1.46	1.97	2.32	2.61
aqueous dipropylene glycol solution (95 mass %)	2.17	2.56	2.87	3.14
aqueous tripropylene glycol solution (95 mass %)	2.05	2.42	2.72	2.98
40 mass % LiCl + triethylene glycol[a]	1.67	1.97	2.35	2.69
40 mass % LiBr + triethylene glycol[a]	2.61	2.95	3.25	3.52
40 mass % $CaCl_2$ + triethylene glycol[a]	*b*	*b*	*b*	*b*
40 mass % LiCl + propylene glycol[a]	2.05	2.41	2.73	3.02
40 mass % LiCl + 40 mass % LiBr[a]	2.12	2.37	2.71	3.04

[a] 1 to 1 volume ratio. [b] Crystals were observed.

Table 3. Constants in the Antoine Equation $\ln(P/\mathrm{kPa}) = A - B/(T/\mathrm{K} + C)$

desiccant solution	*A*	*B*	*C*
aqueous LiCl solution (40 mass %)	10.65	3042.04	−1.44
aqueous LiBr solution (40 mass %)	1.80	25.58	−269.63
aqueous $CaCl_2$ solution (40 mass %)	8.81	2386.40	−1.19
aqueous diethylene glycol solution (95 mass %)	11.22	3176.23	−2.24
aqueous triethylene glycol solution (95 mass %)	10.46	2937.35	−1.36
aqueous tetraethylene glycol solution (95 mass %)	10.63	2974.82	−2.31
aqueous propylene glycol solution (95 mass %)	1.49	15.45	−284.27
aqueous dipropylene glycol solution (95 mass %)	8.24	2207.72	−1.30
aqueous tripropylene glycol solution (95 mass %)	8.27	2233.49	−1.59
40 mass % LiCl + triethylene glycol[a]	10.42	2928.16	−2.43
40 mass % LiBr + triethylene glycol[a]	7.10	1823.02	−0.75
40 mass % $CaCl_2$ + triethylene glycol[a]	*b*	*b*	*b*
40 mass % LiCl + propylene glycol[a]	8.60	2333.04	−1.51
40 mass % LiCl + 40 mass % LiBr[a]	8.36	2259.58	−1.25

[a] 1 to 1 volume ratio. [b] Crystals were observed.

The correlation of effectiveness is modified from the correlation of Ullah et al. (*22*). This correlation can be used to predict the performance of liquid desiccant dehumidifiers, since the driving force in liquid desiccant dehumidifiers is the vapor pressure difference between the inlet air and the liquid desiccant. The lower the vapor pressure of the liquid desiccant is, the drier the outlet air is. Therefore, one of the most important parameters used in this correlation is the vapor pressure of the desiccant solution. The detailed development of the correlation was provided in the report of Chung (*23*).

$$\epsilon = \frac{1 - \left\{\dfrac{0.024\left(\dfrac{G_{\mathrm{in}}}{L_{\mathrm{in}}}\right)^{0.6}\exp\left[1.057\left(\dfrac{T_{G_{\mathrm{in}}}}{T_{L_{\mathrm{in}}}}\right)\right]}{(aZ)^{-0.185}X^{0.638}}\right\}}{1 - \left\{\dfrac{0.192\exp\left[0.615\left(\dfrac{T_{G_{\mathrm{in}}}}{T_{L_{\mathrm{in}}}}\right)\right]}{X^{-21.498}}\right\}} \qquad (3)$$

where X is defined as a function of the vapor pressure depression of the desiccant solution to the vapor pressure of pure water ($(P_{\mathrm{water}} - P_{\mathrm{soln}})/P_{\mathrm{water}}$), a is the surface area-to-volume ratio of packings in m^2/m^3, and Z is the packing height in m. $T_{G_{\mathrm{in}}}$ and $T_{L_{\mathrm{in}}}$ denote the inlet temperatures of the air and the liquid, respectively. G_{in} and L_{in} represent the inlet mass flow rates of air and liquid, respectively. It should be noted that eq 3 is a function of the properties of the liquid desiccant and the packing and column geometries. Therefore, the correlation can be extended to predict other systems. The vapor pressure data obtained in this study were used in eq 3 to predict systems with different packings and desiccant solutions from those of Chung et al. (*24*−*26*), Sadasivam and Balakrishnan (*27*), and Gandhidasan et al. (*28*). The test results in Figure 2 show that about 80% of the data points fall within ±10% deviation, and the average value of errors between the predicted and experimental data was about 9.96%. Therefore, this study not only proves that the vapor pressure of a desiccant solution is one of the important parameters for predicting the system effectiveness but also provides the important data of vapor pressure for the potential desiccant solutions.

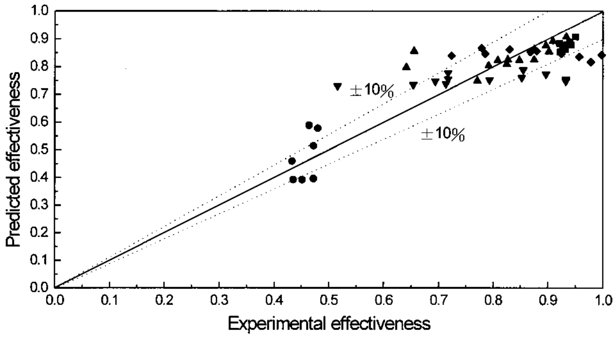

Figure 2. Comparison of predicted and experimental effectiveness for different desiccants and packings: (■) Polypropylene Flexi rings−TEG (Chung et al., 1995); (●) Plastic Pall rings−LiCl (Chung, 1997); (▲) Polypropylene Jaeger Tri-Packs−TEG (Chung et al., 1995); (▼) Ceramic Berl Saddles−LiCl (Sadasivam and Balakrishnan, 1994).

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