

A New Bubble-Point-Pressure Correlation for the Binary LiBr/H₂O Solution¹

K. Murakami,^{2,3} H. Sato,² and K. Watanabe²

In accord with the increasing concern about the global environmental issues, the absorption refrigeration heat-pump systems are currently being considered very promising and attractive. For the purpose of supporting the advanced R&D technology in this area, we have developed a novel correlation to represent the bubble-point pressures of LiBr/H₂O solutions. The developed correlation covers the most extensive range of validity ever proposed: 273–483 K for temperatures, 0.05 kPa to 1.0 MPa for pressures, and 29–76 wt% LiBr for concentrations.

KEY WORDS: absorption refrigeration system; bubble-point pressures; LiBr aqueous solution; LiBr/H₂O solution; vapor pressure.

1. INTRODUCTION

In accord with increasing concern about global environmental issues, absorption refrigeration/heat-pump systems become more and more attractive since they do not require refrigerants such as chlorofluorocarbons (CFCs) and/or even hydrochlorofluorocarbons (HCFCs), which are being expected to be phased out shortly due to their contribution to the stratospheric ozone depletion and global warming.

The absorption refrigeration systems with LiBr/H₂O solution are dominantly being applied in most large-scale buildings and related constructions in Japan. H₂O acts as the refrigerant, while the LiBr/H₂O solution acts as an absorbent in these applications.

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² Department of Mechanical Engineering, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan.

³ To whom correspondence should be addressed.

For advanced engineering design of the absorption refrigeration systems with LiBr/H₂O solution, it is important to have reliable information about the thermodynamic properties of such working fluids. The bubble-point pressure of LiBr/H₂O solutions is one of the most essential thermodynamic properties and there exist several reported sets of measured data, including those reported recently.

In the present study, therefore, we have aimed at correlating the bubble-point pressures, by a simple function, but to cover the widest range of parameters ever attempted; in temperature, pressure and concentration.

2. BUBBLE-POINT-PRESSURE CORRELATION

Table I summarizes the experimentally available information about the bubble-point pressure of LiBr/H₂O solution. Most of these are measurements in rather limited ranges of temperature, pressure, and/or concentration of LiBr, except our own recent measurements [7], which covered a wide range of concentrations down to 20 wt% LiBr. It should be noted that all of the reported data have been converted to the new temperature scale ITS-90, which is used throughout the present paper. Each study [1-6] has also reported a bubble-point-pressure correlation exclusively on the basis of their own measurements, which implies a limit range of applicability to engineering design of each of these correlations.

The correlations developed by Pennington [1], Matsuda *et al.* [3], and Iyoki and Uemura [4] have a common functional form expressing the logarithmic values of bubble-point pressure, P , as a quadratic function of reciprocal of the solution temperature, T , with three coefficients given as a quadratic function of mass fraction, w , of LiBr in LiBr/H₂O solution. On the other hand, a correlation developed by McNeely [8] is the one most widely used in the engineering community, although detailed information about the input measured data is not given. McNeely has actually correlated the solution temperature, T , as a linear function of saturation temperature of water, T' , while two coefficients are given as a cubic function of w . His correlation is valid for the range of temperatures from 278 to 448 K and of concentrations from 45 to 70 wt% LiBr. The same functional form has also been applied in a recent correlation proposed by Feurecker *et al.* [6].

Another recent correlation developed by Lénard *et al.* [5] expressed a pressure ratio, P/P_w , empirically as a complicated function of T and x_w , water mole fraction defined on an ionized basis in the LiBr/H₂O solution.

For the present study, a novel semiempirical model, suitable for correlating the bubble-point pressures of LiBr/H₂O solutions over an extended range of temperature and concentration, has been developed. It should be

Table I. Reported Measurements of Bubble-Point Pressures for LiBr-H₂O Solutions

First author	Ref. No.	Year	Experimental method	Temperature (K)		Pressure (kPa)		Mass conc. (wt%)		No. of data points
				Range	Uncertainty	Range	Uncertainty	Range	Uncertainty	
Pennington	1	1955	Static still	303	± 0.05	0.3-1.1		50-61	± 0.3	11
				303-427	± 0.05	0.3-100		50-60	± 0.3	25
Boryta	2	1975	Static still	273-348	± 0.05	0.2-21	± 0.028	40-60	± 0.12	15
				298-448	± 0.1	0.2-84	± 0.028	40-70	± 0.12	17
Matsuda	3	1980	Gas transport	273-345		0.05-7	± 0.0014	44-58	± 0.1	119
				373-455	± 0.01	10-282	± 0.07	38-70	± 0.04	39
Iyoki	4	1989	Static still	398-483	± 0.1	110-1000	± 1.5	43-65	± 0.45	24
				318-462	± 0.15	4.5-180	--	40-75		76
Feurecker	6	1994	Ebulliometry	283-413	± 0.02	0.5-316	± 0.10	20-60	± 0.10	44
Murakami	7	1994	Bubble-point							

noted, however, that P varies by more than four orders of magnitude over the range from 0.05 kPa at about 274 K and 58 wt% LiBr to 1 MPa at about 483 K and 44 wt% LiBr. This makes it difficult to represent P as a simple function of T and x , mole fraction of LiBr.

Based upon the well-known Raoult's law, the present correlation has been developed. The bubble-point pressure of LiBr/H₂O solutions show negative deviation from Raoult's law, given below:

$$P = xP_{\text{LiBr}} + (1 - x)P_w \quad (1)$$

where P denotes the bubble-point pressure of solutions, x the mole fraction of LiBr, and P_{LiBr} and P_w represent the vapor pressure of pure LiBr and water, respectively. Since the normal melting-point temperature of pure LiBr is 822 K, the first term on the right-hand side of Eq. (1) is practically

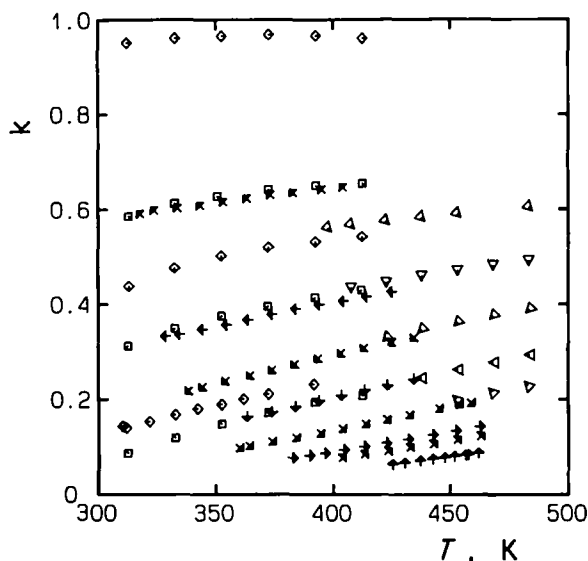


Fig. 1. Temperature dependence of the value k , Eq. (3). Lénard et al. [5]: (∇) 65.2 wt% LiBr; (\triangleleft) 60.8 wt% LiBr; (\triangle) 54.9 wt% LiBr; (∇) 4.4 wt% LiBr; (\triangleleft) 43.8 wt% LiBr. Feurecker et al. [6]: (\uparrow) 75.97 wt% LiBr; (\times) 72.44 wt% LiBr; (\rightarrow) 70.26 wt% LiBr; (\times) 65.37 wt% LiBr; (\downarrow) 60.22 wt% LiBr; (\leftarrow) 55.43 wt% LiBr; (\leftarrow) 50.36 wt% LiBr; (\times) 40.35 wt% LiBr. Murakami et al. [7]: (\square) 60.2 wt% LiBr; (\diamond) 57.9 wt% LiBr; (\square) 49.9 wt% LiBr; (\diamond) 45.3 wt% LiBr; (\square) 39.9 wt% LiBr; (\diamond) 29.9 wt% LiBr.

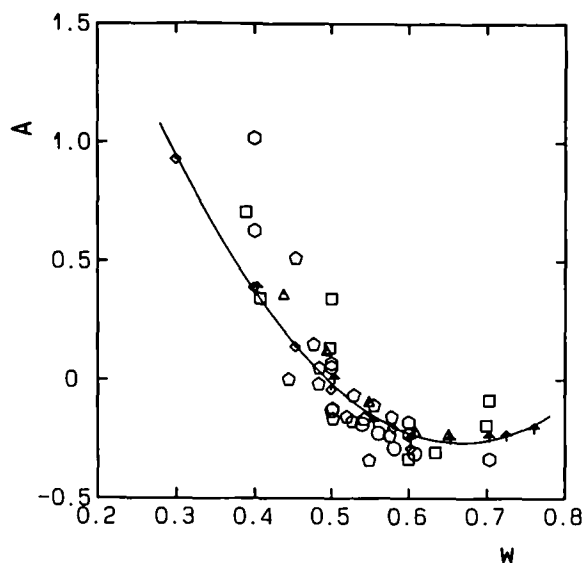


Fig. 2. Concentration dependence of coefficient A , Eq. (4). (○) Pennington [1]; (◊) Boryta et al. [2]; (◻) Matsuda et al. [3]; (◻) Iyoki and Uemura [4]; (△) Lénard et al. [5]; (♣) Feuerecker et al. [6]; (◇) Murakami et al. [7].

small enough to be disregarded. Therefore, in the present study, we have expressed P in Eq. (1) simply by a following relation;

$$P = k(1 - x) P_w \quad (2)$$

by introducing a coefficient k ($0 < k \leq 1$). Note that $k = 1$ corresponds to the Raoult's law.

Figure 1 illustrates a plot of k vs temperature along different w isopleths. The experimental data reported by three recent investigators [5-7] are included in Fig. 1 and it becomes clear that the values k depend almost linearly on T along each isopleth.

$$k = A(w) + B(w)T \quad (3)$$

It should be noted, however, that the solid lines in Fig. 1 are the calculated results of our correlation. Two coefficients, $A(w)$ and $B(w)$, in Eq. (3) have been correlated as quadratic functions of the mass fraction, w , of LiBr, as follows:

$$A(w) = 3.72068 - 11.9569w + 8.96407w^2 \quad (4)$$

$$B(w) = -0.00362512 + 0.0167468w - 0.0147492w^2 \quad (5)$$

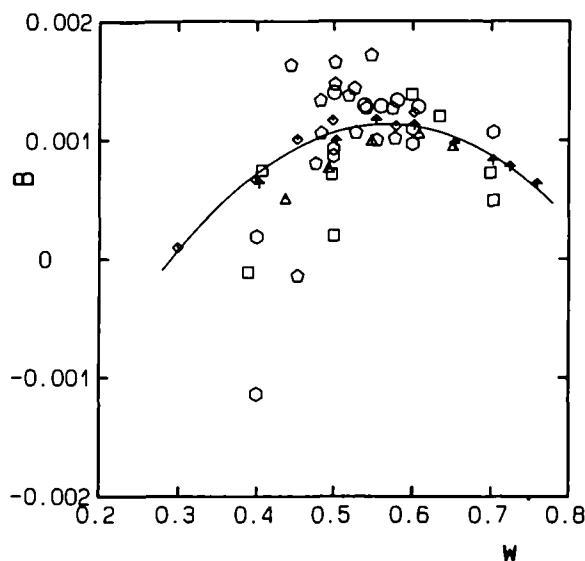


Fig. 3. Concentration dependence of coefficient B , Eq. (5).
 (□) Pennington [1]; (○) Boryta et al. [2]; (◇) Matsuda et al. [3]; (□) Iyoki and Uemura [4]; (△) Lénard et al. [5];
 (♣) Feuerecker et al. [6]; (◇) Murakami et al. [7].

In the present determination of Eqs. (4) and (5), we have used the data by Murakami et al. [7], Feuerecker et al. [6], and two isopleths of 65.2 and 60.8 wt% LiBr by Lénard et al. [5] as a set of input data. A comparison of Eqs. (4) and (5) with all of the reported measurements is shown in Figs. 2 and 3, respectively. Taking into account the molecular masses of LiBr and H_2O , we obtain the following relation:

$$1 - x = \frac{(1 - w)/18.054}{(w/86.85) + [(1 - w)/18.054]} \quad (6)$$

By combining Eqs. (2)–(6), we can finally compute the bubble-point pressures of LiBr/ H_2O solutions. The vapor pressures of H_2O are those calculated from the internationally recommended IAPWS correlation [9]. The range of application for the correlation are of temperatures from 273 to 483 K, of pressures from 0.05 kPa to 1.0 MPa, and of concentrations from 29 wt% to 76 wt% LiBr.

3. DISCUSSION

Figure 4 shows the absolute deviation of the bubble-point pressures reported [1–7] from the present correlation. Since the bubble-point

pressures for lower temperatures below 350 K are small, the absolute deviations of the data including Matsuda et al. [3], which were not used as input data sets become small significantly as shown in Fig. 4.

A similar comparison is given in Fig. 5, but with a relative percentage deviation plot. Simply due to the reason mentioned above, the deviations of data at lower temperatures appear significant up to about $\pm 10\%$ but they become slightly better for available data at higher temperatures. The reported data by Matsuda et al. [3] are available in a very narrow range of temperatures as shown in Table I and their data gave A and B values that deviate from Eqs. (4) and (5) as shown in Figs. 2 and 3, but they agree fairly well with the develop correlation, with about $+10$ to -7% at temperatures below 345 K. It also becomes clear from Fig. 5 that the data by Pennington [1] agree reasonably well with the present correlation, except for few points, while those reported by Boryta et al. [2] show the largest scatter. Among the recent data sets reported, however, those by Feurecker et al. [6] and Murakami et al. [7] behave in a similar manner but those by Lénard et al. [5] agree satisfactorily well with the proposed correlation.

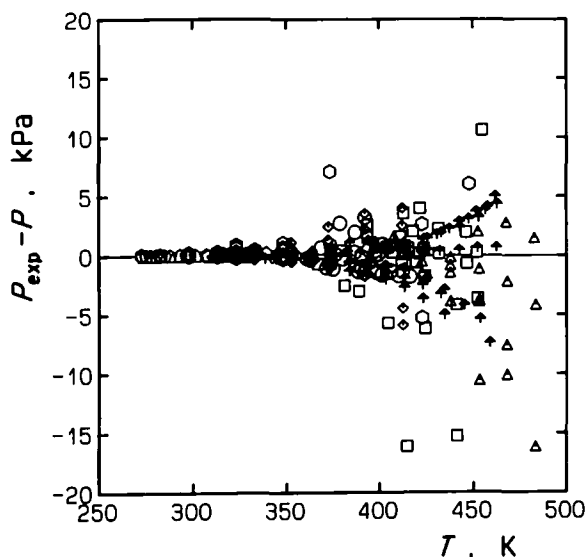


Fig. 4. Absolute deviation of the bubble-point pressures reported from the present correlation. Pennington [1]; (○) Boryta et al. [2]; (◇) Matsuda et al. [3]; (□) Iyoki and Uemura [4]; (△) Lénard et al. [5]; (▲) Feurecker et al. [6]; (◇) Murakami et al. [7].

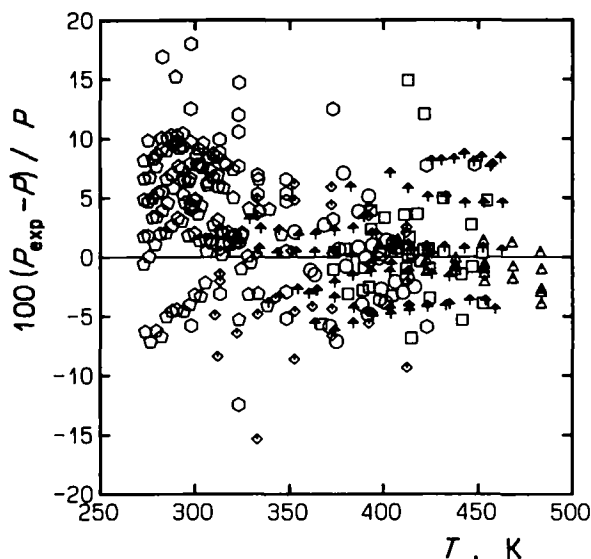


Fig. 5. Relative deviations of the bubble-point pressures reported from the present correlation. (○) Pennington [1]; (○) Boryta et al. [2]; (○) Matsuda et al. [3]; (□) Iyoki and Uemura [4]; (△) Lénard et al. [5]; (↑) Feurecker et al. [6]; (◇) Murakami et al. [7].

We have also examined the correlation developed by McNeely [8] by comparing it with the present correlation in Fig. 6. Although his correlation has been developed to cover a limited range of temperatures and concentrations, as already discussed, we have also examined his correlation along different isopleths outside his effective range. The solid curves in Fig. 6 denote the compared results for the isopleths within the range of validity, whereas those given by dashed curves are the extrapolated isopleths.

For example, the maximum positive deviation of about 25 kPa at 448 K along the 45 wt% LiBr isopleth is equivalent to about 6% in relative deviation from the present correlation, while the maximum negative deviation of about -10 kPa at 448 K along the 70 wt% LiBr isopleths is equivalent to about -15% in percentage deviation. This fact implies that the correlation by McNeely which is currently being applied worldwide should be superseded by the present correlation, since the availability of data covering a wide range of temperatures and concentrations has been improved significantly due to recent measurements [5-7].

We have also found a very interesting feature regarding the coefficients, A and B in Eqs. (4) and (5), in our process of developing Eq. (3).

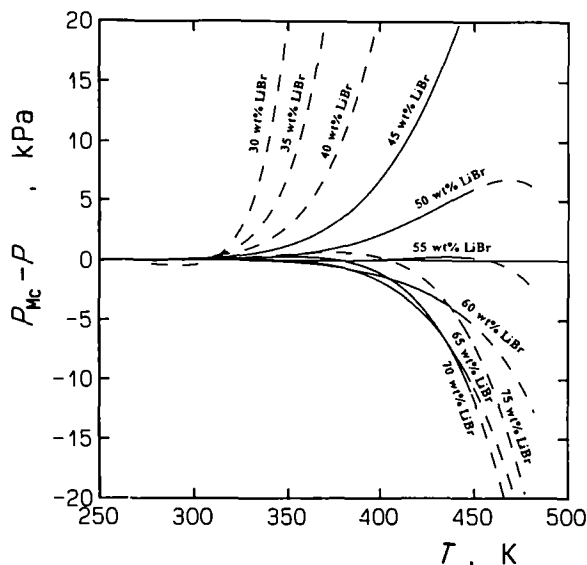


Fig. 6. Comparison of McNecly's correlation with the present correlation.

Namely, we have noticed that k in Eq. (3) becomes unity with a consistent value of $w = 0.291$ if we assign $B = 0$. On the other hand, a condition $A = 1$ provides again the consistent value of $w = 0.291$ when k becomes unity. This fact is also confirmed by observing that the isopleth calculated for 29.9 wt% LiBr has a positive inclination as clearly shown in Fig. 1 but the isopleth of 29.1 wt% LiBr would probably give a constant $k = 1$ value for any temperature. Physically speaking, it would be reasonable to predict that the so-called "absorption" phenomena would not appear for a concentration lower than 29.1 wt% LiBr in the LiBr/H₂O solutions. In other words, the intermolecular forces of different substances are feebler than that of similar substances for lower concentrations beyond 29.1 wt% LiBr.

4. CONCLUSION

We have reported the bubble-point-pressure correlation for LiBr/H₂O solutions on the basis of critically evaluated experimental data. The developed semiempirical correlation contains only six numerical constants, and it covers the widest range of parameters ever proposed: temperatures from 273 to 483 K, pressures from 0.05 kPa to 1.0 MPa, and concentrations from 29 wt% to 76 wt% LiBr.

NOMENCLATURE

k	A coefficient defined by Eq. (2) to represent the pressure ratio
P	Bubble-point (kPa)
P_{exp}	Measured bubble-point pressure (kPa)
P_{LiBr}	Vapor pressure of LiBr (kPa)
P_{Mc}	Calculated bubble-point pressures from McNeely's correlation
P_{w}	Vapor pressures of H ₂ O (kPa)
T	Temperature (K)
w	Mass fraction of LiBr in LiBr/H ₂ O solution
x	Mole fraction of LiBr in LiBr/H ₂ O solution

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