Vapor–Liquid Equilibrium Study of LiBr + H₂O and LiBr + CaCl₂ + H₂O Systems

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Vapor–liquid equilibrium (VLE) data and modeling for LiBr + H₂O and LiBr + CaCl₂ + H₂O are reported in this paper. This work focuses on the experimental determination of the boiling point of LiBr + H₂O and LiBr + CaCl₂ + H₂O solutions with vapor pressures between 6 and 101.3 kPa and the total molality of salt ranging from 0 to 21.05 mol•kg⁻¹. The procedures were carried out in a computer-controlled glass apparatus. The relationship between the boiling point and saturated vapor pressure is obtained, and Xu’s model is used to correlate and predict the VLE. By correlation of the data (literature and experimental) for LiBr + H₂O and LiBr + CaCl₂ + H₂O, the parameters are obtained. We compared the results with the ElecNRTL model and Pitzer model. The parameters for the LiBr + H₂O, CaCl₂ + H₂O, and LiBr + CaCl₂ + H₂O systems can be successfully used to calculate and predict the VLE data.

Keywords: electrolyte solution, vapor–liquid equilibrium (VLE), measurement, modeling, thermodynamics

INTRODUCTION

The vapor–liquid equilibrium (VLE) of electrolyte solutions is widely used in industries, natural processes, chemistry, and chemical engineering. LiCl, LiBr, and CaCl₂ aqueous solutions have extensive applications in the field of refrigeration, cooling, and heat transforming systems based on absorption cycles (Lan et al., 2017; Li et al., 2017). Simultaneously, the thermodynamic properties of the solutions play a key role in the absorption cycles.

Due to the strong demand for absorption and separation process design, an increasing number of researchers have studied the VLE of electrolyte systems. Massive quantities of phase equilibrium data have been reported in recent years. Some solubility isotherms of the LiCl + CaCl₂ + H₂O system have been measured (Filippov and Mikhelson, 1977; Zeng et al., 2008), and VLE data of LiCl + H₂O, CaCl₂ + H₂O, and LiCl + CaCl₂ + H₂O systems have been obtained (Xu et al., 2014, 2019a). Lan et al. (2017) and N’Tsoukpo et al. (2013) experimentally determined the saturated vapor pressure of LiBr aqueous solution with mass fractions ranging from 43.14 to 65.26 wt.% at high temperature. Chua et al. (2000) presented a thermodynamically consistent set of specific enthalpy, entropy, and heat capacity fields for a LiBr + H₂O solution. However, the phase equilibrium data of the systems containing LiBr with a wide range of pressures and temperatures are still rare.

The experimental data and thermodynamic models are equally important (Xu et al., 2019b). Significant improvements have been made in calculating thermodynamic properties using theoretical models; most models are based on the Wilson model (Wilson, 1964), NRTL model (Renon and Prausnitz, 1968), and UNIQUAC model (Abrams and Prausnitz, 1975). For electrolyte solutions, the Pitzer model (Pitzer, 1973), ElecNRTL model (Chen et al., 1982; Chen and Evans, 1986), Lu–Maurer model (Lu and Maurer, 1993; Lu et al., 1996), extended
UNIQUAC model (Thomsen et al., 1998), and Xu model (Xu et al., 2016, 2019c) have been widely utilized. The thermodynamic properties of the binary systems (CaCl₂ + H₂O and LiCl + H₂O) were simulated by the Pitzer–Simonson–Clegg (PSC) model in Li’s work (Li et al., 2015, 2016). Patek and Klomfar (2006) developed an effective formulation of the thermodynamic properties of LiBr–H₂O solutions from 273 to 500 K. Despite the aforementioned research works, thermodynamic property calculations for some electrolyte systems still face great challenges, and more accurate models over a wide range of pressures, temperatures, and concentrations are needed.

Due to the lack of VLE data for systems containing LiBr at a wide range of pressures and temperatures, in this work, VLE data of LiBr + H₂O and LiBr + CaCl₂ + H₂O systems are experimentally measured at concentrations ranging from 0 to 21.05 mol kg⁻¹ and pressures ranging from 6 to 101.3 kPa. In addition, the obtained data are used to parameterize Xu’s model (Xu et al., 2016). We expand the scope of the model, such as concentration, pressure, and temperature. Correlation and prediction of the VLE of LiBr + H₂O and LiBr + CaCl₂ + H₂O were successfully developed.

**EXPERIMENTAL SECTION**

**Materials**

Anhydrous LiBr (purity ≥ 99.5%) and anhydrous CaCl₂ (purity ≥ 99.99%) were purchased from Adamas-Beta. Distilled water (18.2 Ω cm) was used for the preparation of solutions.

**Apparatus and Procedures**

A dual circulation glass ebulliometer (40 ml) was used in the VLE measurements, as shown in Figure 1. The main experimental instruments are listed in Table 1, including a vacuum pump in the ebulliometer, a pressure controller, a heating mantle, and a temperature controller.

The reliability of the experiment has been verified in the literature (Xu et al., 2014, 2019a) (i.e., CaCl₂ + H₂O and NaCl + KCl + H₂O), as shown in Figure 2. The experimental data for the LiBr + H₂O and LiBr + CaCl₂ + H₂O systems at different molalities are listed in Tables 2–6. Each VLE experimental data in this work are averages taken after three experiments. For the systems containing LiBr, the solubility of the salt is relatively high, with a value of 21.05 mol kg⁻¹ at 298.15 K. The absorption

![Image](image_url)
is relatively strong at higher salt concentrations. The pressure (6–101.3 kPa) is an important factor for the design of absorption and separation processes.

The experimental procedures are as follows: (1) During the experiments, the sample was placed into the glass ebulliometer. When we were ready to add the sample into the ebulliometer, we filled the sample solution in the part marked 1 in Figure 1. Because of the problem of water condensation, if the part was not filled with the sample solution, the experimental results would have a large error. The sample should be added to the height of mark 2 shown in Figure 1. (2) The ebulliometer was heated by the heating mantle and was controlled by the voltage controller. (3) The operation pressure was controlled by the vacuum pump, the pressure sensor, and the control valve. (4) After the sample was added, we turned on the heater and controlled the heating voltage. Then, we stably controlled the pressure in the ebulliometer through the pressure controller. (5) The vapor H$_2$O was condensed in a spherical condenser (length 40 cm) and then returned to the mixing chamber for recirculation. The time was 0.5–1 h in the first equilibrium, and the following equilibrium time was 10–20 min. The judging standard of the VLE is an important factor. The condensate reflux of the ebulliometer was controlled at two to three drops per second and was stably refluxed for $\sim$15 min to establish an equilibrium state. (6) After the VLE was reached, we recorded the temperature and pressure.

**MODEL DESCRIPTION**

**Xu Model**

In the Xu model (Xu et al., 2016) for mixed electrolyte solution systems, the equation was based on the NRTL model:

$$
\frac{n_{\text{NRTL}}}{RT} = m_w G_{w,x} \left( \frac{\tau_{x_w G_{w,x}}}{m_w + m_x G_{x,w}} + \frac{\tau_{x,w G_{x,w}}}{m_w + m_x G_{x,w}} \right)
$$

**TABLE 2 | Experimental VLE data for temperature T, pressure P, and molality m—LiBr for the LiBr + H$_2$O system.**

| m = 21.05 mol·kg$^{-1}$ | m = 16.5 mol·kg$^{-1}$ | m = 11 mol·kg$^{-1}$ | m = 9.01 mol·kg$^{-1}$ |
|-------------------------|------------------------|---------------------|----------------------|
| T (K)                   | P (kPa)                | T (K)               | P (kPa)              | T (K)               | P (kPa)              | T (K)               | P (kPa)              |
| 319.65                  | 6.29                   | 318.35              | 6.405                | 333.15              | 6.3                  | 324.75              | 5.94                  |
| 332.25                  | 11.875                 | 329.45              | 11.33                | 345.05              | 10.955               | 338.35              | 11.085               |
| 340.85                  | 16.38                  | 337.35              | 16.265               | 354.55              | 16.61                | 347.95              | 16.405               |
| 347.15                  | 21.3                   | 343.35              | 21.365               | 360.95              | 21.185               | 354.25              | 21.495               |
| 352.05                  | 26.205                 | 347.95              | 26.21                | 366.35              | 26.225               | 359.45              | 26.05                |
| 356.45                  | 31.075                 | 352.35              | 31.295               | 371.25              | 31.235               | 363.85              | 30.94                |
| 360.45                  | 36.075                 | 356.05              | 36.2                 | 375.35              | 36.23                | 368.25              | 36.08                |
| 363.85                  | 41.23                  | 359.45              | 41.34                | 378.95              | 41.27                | 371.96              | 41.07                |
| 366.85                  | 45.98                  | 362.25              | 46.14                | 382.05              | 46.38                | 375.05              | 46.155               |
| 369.55                  | 50.96                  | 364.85              | 51.26                | 384.95              | 51.445               | 378.05              | 51.24                |
| 372.25                  | 56.165                 | 367.55              | 56.34                | 387.65              | 56.3                 | 380.85              | 56.25                |
| 374.55                  | 60.865                 | 369.95              | 61.305               | 390.05              | 61.51                | 383.45              | 61.33                |
| 376.75                  | 66.715                 | 371.95              | 66.18                | 392.45              | 66.575               | 385.55              | 66.22                |
| 378.85                  | 70.91                  | 374.05              | 70.78                | 394.65              | 71.02                | 387.55              | 71.035               |
| 380.85                  | 76.2                   | 376.15              | 75.75                | 396.55              | 75.885               | 389.75              | 76.63                |
| 382.65                  | 80.975                 | 377.85              | 81.11                | 398.05              | 81.205               | 391.45              | 81.26                |
| 384.45                  | 86.145                 | 379.85              | 86.355               | 399.95              | 86.255               | 393.25              | 86.31                |
| 386.05                  | 91.315                 | 381.45              | 91.26                | 401.95              | 91.27                | 395.15              | 91.29                |
| 387.65                  | 96.12                  | 383.05              | 96.165               | 403.25              | 96.265               | 396.75              | 96.26                |
| 389.15                  | 101.255                | 384.45              | 101.235              | 404.55              | 101.245              | 398.25              | 101.245              |

Standard uncertainties $u$ are $u(P) = 0.1$ kPa, $u(T) = 0.05$ K, $u(m) = 0.0001$ g, respectively.
**TABLE 3** | Experimental VLE data for temperature $T$, pressure $P$, and molality $m$—LiBr for the LiBr + H$_2$O system.

| $m$ (mol kg$^{-1}$) | $T$ (K) | $P$ (kPa) | $m$ (mol kg$^{-1}$) | $T$ (K) | $P$ (kPa) | $m$ (mol kg$^{-1}$) | $T$ (K) | $P$ (kPa) | $m$ (mol kg$^{-1}$) | $T$ (K) | $P$ (kPa) |
|---------------------|--------|----------|---------------------|--------|----------|---------------------|--------|----------|---------------------|--------|----------|
| 7                   | 319.65 | 6.29     | 4.8                 | 318.35 | 6.05     | 4                   | 316.95 | 6.51     | 1.5                 | 311.65 | 6.59     |
| 322.25              | 329.45 | 11.33    | 340.85              | 337.35 | 16.265   | 347.15              | 343.35 | 21.365   | 352.05              | 347.95 | 26.4     |
| 356.45              | 356.05 | 36.2     | 369.55              | 364.85 | 51.26    | 372.25              | 367.55 | 56.34    | 374.55              | 365.85 | 61.45    |
| 376.75              | 371.95 | 66.18    | 378.85              | 374.05 | 70.78    | 380.85              | 376.15 | 75.75    | 382.65              | 377.85 | 81.11    |
| 380.85              | 376.15 | 75.75    | 384.45              | 379.85 | 86.355   | 386.05              | 381.45 | 91.26    | 387.65              | 383.05 | 96.165   |
| 389.15              | 384.45 | 101.235  | 398.95              | 397.75 | 41.1     | 401.95              | 398.75 | 46.32    | 404.95              | 396.45 | 51.22    |
| 401.95              | 397.75 | 41.1     | 404.95              | 396.45 | 51.22    | 408.45              | 399.25 | 61.25    | 412.45              | 400.85 | 61.22    |
| 410.65              | 392.35 | 66.84    | 416.35              | 389.45 | 61.25    | 418.65              | 391.95 | 61.27    | 420.55              | 394.35 | 66.245   |
| 422.45              | 391.15 | 71.165   | 424.15              | 396.75 | 76.385   | 425.35              | 397.75 | 81.47    | 426.45              | 399.25 | 86.355   |
| 427.65              | 400.85 | 91.265   | 428.75              | 401.85 | 96.27    | 429.65              | 402.75 | 101.205  | 403.45              | 101.235 | 402.75   |

Standard uncertainties $u$ are $u(P) = 0.1$ kPa, $u(T) = 0.05$ K, $u(m) = 0.0001$ g, respectively.

**TABLE 4** | Experimental VLE data for temperature $T$, pressure $P$, and molality $m$—LiBr—CaCl$_2$ for the LiBr + CaCl$_2$ + H$_2$O system.

| $ma$ (mol kg$^{-1}$) | $mb$ (mol kg$^{-1}$) | $T$ (K) | $P$ (kPa) | $ma$ (mol kg$^{-1}$) | $mb$ (mol kg$^{-1}$) | $T$ (K) | $P$ (kPa) | $ma$ (mol kg$^{-1}$) | $mb$ (mol kg$^{-1}$) | $T$ (K) | $P$ (kPa) | $ma$ (mol kg$^{-1}$) | $mb$ (mol kg$^{-1}$) | $T$ (K) | $P$ (kPa) |
|----------------------|----------------------|--------|----------|----------------------|----------------------|--------|----------|----------------------|----------------------|--------|----------|----------------------|----------------------|--------|----------|
| 21.05                | 0                    | 362.25 | 6.425    | 1.5                  | 8.5                  | 369.95 | 11.29    | 384.95              | 16.265   | 403.15 | 21.29    | 427.65              | 26.31    | 428.75 | 21.24    |
| 1.5                  | 8.5                  | 362.25 | 6.425    | 1.5                  | 8.5                  | 369.95 | 11.29    | 384.95              | 16.265   | 403.15 | 21.29    | 427.65              | 26.31    | 428.75 | 21.24    |
| 3.08                 | 8.1                  | 364.95 | 7.25     | 1.5                  | 8.5                  | 369.95 | 11.29    | 384.95              | 16.265   | 403.15 | 21.29    | 427.65              | 26.31    | 428.75 | 21.24    |
| 4.12                 | 7.1                  | 364.95 | 7.25     | 1.5                  | 8.5                  | 369.95 | 11.29    | 384.95              | 16.265   | 403.15 | 21.29    | 427.65              | 26.31    | 428.75 | 21.24    |

Standard uncertainties $u$ are $u(P) = 0.1$ kPa, $u(T) = 0.05$ K, $u(m) = 0.0001$ g, respectively.
TABLE 5 | Experimental VLE data for temperature \(T\), pressure \(P\), and molality \(m\) (\(ma—\text{LiBr}, \ mb—\text{CaCl}_2\)) for the LiBr + CaCl\(_2 + \) H\(_2\)O system.

| \(ma = 5.5\) mol\(\cdot\)kg\(^{-1}\) | \(ma = 7.1\) mol\(\cdot\)kg\(^{-1}\) | \(ma = 8.85\) mol\(\cdot\)kg\(^{-1}\) | \(ma = 11\) mol\(\cdot\)kg\(^{-1}\) |
|---|---|---|---|
| \(mb = 6.1\) mol\(\cdot\)kg\(^{-1}\) | \(mb = 4.7\) mol\(\cdot\)kg\(^{-1}\) | \(mb = 4.08\) mol\(\cdot\)kg\(^{-1}\) | \(mb = 3.3\) mol\(\cdot\)kg\(^{-1}\) |
| \(T (K)\) | \(P (kPa)\) | \(T (K)\) | \(P (kPa)\) | \(T (K)\) | \(P (kPa)\) | \(T (K)\) | \(P (kPa)\) |
| 338.35 | 6.33 | 338.85 | 6.05 | 342.45 | 6.2 | 342.65 | 6.145 |
| 349.85 | 10.935 | 351.95 | 11.47 | 355.85 | 11.095 | 357.45 | 11.29 |
| 359.25 | 16.14 | 360.15 | 16.145 | 365.25 | 16.465 | 366.25 | 16.17 |
| 366.05 | 21.285 | 368.85 | 21.365 | 372.05 | 21.31 | 373.05 | 21.385 |
| 371.85 | 26.21 | 373.65 | 25.91 | 377.45 | 26.205 | 379.25 | 26.18 |
| 376.25 | 31.47 | 378.95 | 31.255 | 382.05 | 30.935 | 384.25 | 31.135 |
| 380.05 | 36.41 | 382.65 | 35.87 | 386.05 | 36.12 | 388.05 | 36.31 |
| 383.45 | 41.37 | 388.95 | 41.225 | 389.95 | 41.255 | 391.65 | 40.875 |
| 386.45 | 46.425 | 390.35 | 46.09 | 392.55 | 46.245 | 395.15 | 46.28 |
| 388.95 | 51.01 | 393.25 | 51.085 | 395.35 | 50.98 | 398.05 | 51.445 |
| 391.85 | 56.31 | 395.85 | 56.265 | 398.15 | 56.05 | 400.75 | 56.175 |
| 394.65 | 62.045 | 398.65 | 61.32 | 400.55 | 61.39 | 403.45 | 61.26 |
| 396.35 | 66.41 | 401.05 | 65.955 | 402.75 | 66.225 | 405.25 | 65.89 |
| 398.15 | 71.4 | 402.55 | 71.155 | 405.15 | 71.005 | 407.15 | 71.31 |
| 399.75 | 76.48 | 404.75 | 76.185 | 407.15 | 76.435 | 408.95 | 74.16 |
| 400.95 | 81.27 | 406.85 | 81.28 | 408.45 | 81.255 | 410.75 | 81.31 |
| 402.65 | 86.205 | 408.35 | 86.185 | 409.95 | 86.395 | 412.95 | 86.175 |
| 403.95 | 91.285 | 410.15 | 91.385 | 411.45 | 91.38 | 415.05 | 91.265 |
| 404.55 | 96.29 | 411.45 | 96.34 | 412.85 | 96.35 | 416.45 | 96.405 |
| 405.65 | 101.315 | 412.75 | 101.185 | 415.65 | 101.205 | 416.85 | 101.215 |

Standard uncertainties \(u\) are \(u(P) = 0.1\) kPa, \(u(T) = 0.05\) K, \(u(m) = 0.0001\) g, respectively.

\[
\begin{align*}
G_{w,x} &= \exp(-\alpha_{w,x}) \\
G_{x,w} &= \exp(-\alpha_{x,w}) \\
m_w &= \frac{1000}{M_s} - \sum_{i=1}^{n} (h_i m_i) \\
\tau_{w,x} &= \frac{\sum_{i=1}^{n} (\tau_{w,i} m_i)}{\sum_{i=1}^{n} (m_i)} \\
\tau_{x,w} &= \frac{\sum_{i=1}^{n} (\tau_{x,i} m_i)}{\sum_{i=1}^{n} (m_i)} \\
\tau_{w,i} &= \tau_{w,i}^{(0)} + \tau_{w,i}^{(1)} / T \\
\tau_{i,w} &= \tau_{i,w}^{(0)} + \tau_{i,w}^{(1)} / T \\
\ln a_w &= \left( \frac{\sum_{i=1}^{n} (\tau_{w,i} m_i) G_{w,x}}{\sum_{i=1}^{n} (m_i) + m_w G_{w,x}} + \frac{\sum_{i=1}^{n} (\tau_{x,i} m_i) G_{x,w}}{m_w + \sum_{i=1}^{n} (m_i) G_{x,w}} \right) \\
&\quad + m_w \left( \frac{-\sum_{i=1}^{n} (\tau_{w,i} m_i) G_{w,x}^2}{\left( \sum_{i=1}^{n} (m_i) + m_w G_{w,x} \right)^2} - \frac{\sum_{i=1}^{n} (\tau_{x,i} m_i) G_{x,w}^2}{\left( m_w + \sum_{i=1}^{n} (m_i) G_{w,x} \right)^2} \right) \\
&\text{In this model, Equation (9) is the final objective function. Five parameters } (h_i, \tau_{w,i}^{(0)}, \tau_{x,i}^{(0)}, \tau_{w,i}^{(1)}, \tau_{i,w}^{(1)}) \text{ need to be calculated in the equation. Experimental data (Tables 2–6) and the data in the literature (Xu et al., 2014, 2016) were used for correlation. } \tau_{w,i} \text{ and } \tau_{i,w} \text{ are related to the temperature, and the temperature range is between 298.15 and 440.15 K.} \\
&\text{The physical meaning of parameters } (n, m_x, m_i, m_w, h_i, n_i, \tau_{w,x}, \tau_{x,w}, \tau_{w,i}, \tau_{i,w}) \text{ in this model is shown in the NOMENCLATURE. In this model, the reference state of activity coefficients is } \gamma_i \rightarrow 1 \text{ as } x_i(=n_i/n) \rightarrow 1. \text{ Five parameters } (h_i, \tau_{w,i}^{(0)}, \tau_{x,i}^{(0)}, \tau_{w,i}^{(1)}, \tau_{i,w}^{(1)}) \text{ were fitted to the VLE data for the LiBr + CaCl}_2 + \text{H}_2\text{O system in the final equations. The 1stOpt 7.0 (7D-Soft High Technology Inc.) optimization software was chosen as the main tool for simulation calculations.} \\
&\text{RESULTS AND DISCUSSION} \\
&\text{In this work, the VLE data of the LiBr + H}_2\text{O and LiBr + CaCl}_2 + \text{H}_2\text{O systems were experimentally measured at concentrations ranging from 0 to 21.05 mol}\cdot\text{kg}^{-1} \text{ and pressures ranging from 6 to 101.3 kPa; the data are listed in Tables 2–6. Analysis and summary of the experimental data are shown in Figures 3, 4.}
\end{align*}
\]
For the study of the activity coefficient model for electrolyte solutions, we usually choose the activity coefficient of the molality concentration standard. Thus, we only need to study the activity data of water in the electrolyte solutions (Chen et al., 1982; Chen and Evans, 1986; Xu et al., 2014). The Xu model was used to correlate and predict the VLE for the LiBr + H2O and LiBr + CaCl2 + H2O systems. The applicable system of the model was extended in this work. The correlation and prediction results were used to compare the Pitzer model (Pitzer, 1973), ElecNRTL model (Chen et al., 1982; Chen and Evans, 1986), and Xu model.
and the VLE behavior of the LiBr + CaCl₂ + H₂O system was investigated.

Discussion of Experimental Results

The LiBr + H₂O and LiBr + CaCl₂ + H₂O systems were chosen to study the VLE, as shown in Tables 2–6 and Figures 3, 4. The tables and figures show that the VLE of LiBr + H₂O and LiBr + CaCl₂ + H₂O systems is similar. It is well-known that as the salt concentration increases in the LiBr + H₂O and LiBr + CaCl₂ + H₂O systems, the vapor pressure of water decreases. From Tables 2–6 and Figures 3, 4, we can see that the vapor pressure at \( m_{\text{LiBr}} = 21.05 \text{ mol kg}^{-1} \) and \( m_{\text{CaCl₂}} = 0 \text{ mol kg}^{-1} \) in the LiBr + CaCl₂ + H₂O system is lowest, and the activity at the corresponding temperature is lowest.

The VLE of the CaCl₂ + H₂O, LiBr + H₂O, LiBr + CaCl₂ + H₂O, and LiCl + CaCl₂ + H₂O systems are shown in Figures 4, 5. From the figures, it can be known that the LiBr + H₂O curve at saturated solubility (\( m = 21.05 \text{ mol kg}^{-1} \)) and normal temperature is lower than that of CaCl₂ + H₂O, LiBr + CaCl₂ + H₂O, and LiCl + CaCl₂ + H₂O. The LiBr + CaCl₂ + H₂O curve at the same concentration and temperature is lower than that of LiCl + CaCl₂ + H₂O. Therefore, the hygroscopicity of some systems containing LiBr is also relatively high, and the hygroscopicity of the LiBr + H₂O system at saturated solubility (\( m = 21.05 \text{ mol kg}^{-1} \)) is the highest.

Results of the Modeling

Correlation of the VLE

Equation (9) was used to correlate VLE data for the LiBr + H₂O and LiBr + CaCl₂ + H₂O systems. The results of the correlation for the LiBr + CaCl₂ + H₂O system are shown in Figure 6. The deviation between the literature and the calculated values for the LiBr + H₂O, CaCl₂ + H₂O, and LiBr + CaCl₂ + H₂O systems are listed in Table 8. Parameters, \( r_{1,2}^0, r_{2,1}^0, r_{3,1}^0, r_{2,3}^0, r_{2,1}^1, r_{2,1}^1, r_{1,3}^1, r_{2,1}^1, r_{2,3}^1, r_{2,1}^1, h_1, \) and \( h_2 \) were obtained from the correlation of the experimental and literature data, as listed in Table 7. For LiBr + CaCl₂ + H₂O, it can be seen from Table 8 that \( dY = 0.31 \text{ kPa} \) and \( dP = 2.55\% \). \( dY \) and \( dP \) were calculated via the

![Figure 6: Correlation of experimental VLE data for the LiBr + CaCl₂ + H₂O system. Symbols: ▲ ma = 21.05 mol kg⁻¹, mb = 0 mol kg⁻¹; ○ ma = 1.5 mol kg⁻¹, mb = 8.5 mol kg⁻¹; ▼ ma = 4.12 mol kg⁻¹, mb = 7.1 mol kg⁻¹; ● ma = 11 mol kg⁻¹, mb = 3.3 mol kg⁻¹; ★ ma = 16.5 mol kg⁻¹, mb = 1.5 mol kg⁻¹; experimental data (this work); lines: correlation of the model.](image)

| System         | Parameters | Data points | This work | Data source |
|----------------|------------|-------------|-----------|-------------|
| CaCl₂-H₂O      |            |             |           |             |
|                 |            | 5–101.3     | 322       | 0.081       |
| LiBr-H₂O       | a = 1     | 5–101.3     | 180       | 0.191       |
|                 |            |             |           | Experiment  |
| LiBr-CaCl₂-H₂O |            | 5–101.3     | 200       | 0.31        |
|                 |            |             |           | 2.55        |

\(^a dY = \left(1/N\sum|P_{\text{exp}} - P_{\text{calc}}|\right)/P_{\text{exp}} \times 100\%\), where \( N \) is the number of data points.

\(^b dP = \left(1/N\sum|P_{\text{exp}} - P_{\text{calc}}|\right)/P_{\text{exp}} \times 100\%\), where \( N \) is the number of data points.

![Figure 7: Prediction of experimental VLE data for the LiBr + CaCl₂ + H₂O system. Symbols: ▲ ma = 21.05 mol kg⁻¹, mb = 0 mol kg⁻¹; ○ ma = 1.5 mol kg⁻¹, mb = 8.5 mol kg⁻¹; ▼ ma = 4.12 mol kg⁻¹, mb = 7.1 mol kg⁻¹; ● ma = 11 mol kg⁻¹, mb = 3.3 mol kg⁻¹; ★ ma = 16.5 mol kg⁻¹, mb = 1.5 mol kg⁻¹; experimental data (this work); lines: prediction of the model.](image)

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**TABLE 7** Model parameters for the CaCl₂-H₂O, LiBr-H₂O, and LiBr-CaCl₂-H₂O systems.

| System         | Parameters | Data points | This work | Data source |
|----------------|------------|-------------|-----------|-------------|
| CaCl₂-H₂O      | CaCl₂      | Reference 4 |           |             |
| LiBr-H₂O       | LiBr       | Correlated in this work |           |             |
| LiBr-CaCl₂-H₂O | LiBr       | Correlated in this work |           |             |
| CaCl₂          |            |             |           |             |
following equations:

\[
dY = (1/N) \sum |P_{\text{exp}} - P_{\text{cal}}| \quad (10)
\]

\[
dP = (1/N) \sum |P_{\text{exp}} - P_{\text{cal}}|/P_{\text{exp}} \times 100 \quad (11)
\]

where \( N \) denotes the number of data points, and \( P_{\text{exp}} \) and \( P_{\text{cal}} \) denote experimental vapor pressure and calculated vapor pressure, respectively.

**Prediction of the VLE**

The Xu model was chosen to correlate and predict the VLE. In previous work, the model was also successfully applied to predict the VLE data in mixed electrolyte solution systems with binary parameters (Xu et al., 2016). However, the parameters of LiBr are lacking. The prediction parameters of CaCl\(_2\) were obtained from the literature (Xu et al., 2019a), the parameters of LiBr were calculated using LiBr + H\(_2\)O experimental data in this work, as listed in Table 7. The prediction result is shown in Figure 7, where \( dY = 3.1 \) kPa and \( dP = 5.96 \)%, which are worse than the correlation results.

**Comparison With Other Methods**

For the LiBr + CaCl\(_2\) + H\(_2\)O system calculation, we choose the ElecNRTL model and Pitzer model for comparison with this work. The Pitzer equation for the thermodynamic properties of electrolytes is developed on the basis of theoretical insights from improved analysis of the Debye-Hückel model. The system of equations developed in the first paper of this series is successfully applied to the available free energy data at room temperature for 227 pure aqueous electrolytes in which one or both ions are univalent. The ElecNRTL model proposed by Chen et al. (1982) is generalized to represent the excess Gibbs energy of aqueous multicomponent electrolyte systems. Using only binary parameters, the model correlates and predicts the deviation from ideality of aqueous multicomponent electrolyte systems over the entire range of temperatures and concentrations. The comparison results are shown in Table 9. Note that the results from both the ElecNRTL and Pitzer models were calculated by the software Aspen Plus 8.1 (Xu et al., 2019a).

For the LiBr + CaCl\(_2\) + H\(_2\)O system, the \( dY \) value (0.31 kPa) of this work (correlation) using the Xu model is smaller than that of the ElecNRTL model (\( dY = 4.1 \) kPa) and Pitzer model (\( dY = 2.75 \) kPa). Likewise, the \( dP \) value (2.55%) of this work (correlation) is smaller than that of the ElecNRTL model (\( dP = 8.96 \)%) and Pitzer model (\( dP = 4.51 \)%).

In this work, we expand the scope of the model based on previous work (Xu et al., 2014, 2019a). The parameters of the LiBr + H\(_2\)O system were obtained in this paper. Then, the binary parameters of LiBr + H\(_2\)O and CaCl\(_2\) + H\(_2\)O were used to predict the VLE for the LiBr + CaCl\(_2\) + H\(_2\)O system. However, the results are not satisfactory. Therefore, we recommend using the correlated parameters of LiBr + CaCl\(_2\) + H\(_2\)O in Table 8 to calculate the VLE.

**CONCLUSIONS**

In this paper, VLE data for LiBr + H\(_2\)O and LiBr + CaCl\(_2\) + H\(_2\)O systems were measured and reported. By the analysis, it is shown that the type and concentration of salt are important factors affecting the VLE. The VLE curve of the LiBr + H\(_2\)O system at saturated solubility (\( m = 21.05 \) mol\( \cdot \)kg\(^{-1}\)) and 25°C is lower than that of CaCl\(_2\) + H\(_2\)O, LiBr + CaCl\(_2\) + H\(_2\)O, and LiCl + CaCl\(_2\) + H\(_2\)O. The hygroscopicity of some systems containing LiBr is also relatively high, and the hygroscopicity of the LiBr + H\(_2\)O system at saturated solubility (\( m = 21.05 \) mol\( \cdot \)kg\(^{-1}\)) is the highest.

By correlation of the experimental data, the parameters of the LiBr + H\(_2\)O and LiBr + CaCl\(_2\) + H\(_2\)O systems were obtained in this paper. The correlation results and prediction results were compared to those of the ElecNRTL and Pitzer model. By comparison, the correlation results of the LiBr + CaCl\(_2\) + H\(_2\)O system in this work are better than those of the ElecNRTL and Pitzer models. The model can be used to successfully calculate VLE data for LiBr + H\(_2\)O and LiBr + CaCl\(_2\) + H\(_2\)O systems.

**DATA AVAILABILITY STATEMENT**

All datasets generated for this study are included in the article/supplementary material.

**AUTHOR CONTRIBUTIONS**

HW: experimental design and data processing. HC: experimental design and experimental equipment assembly. WC: experimental operation and data processing. HS: data processing and modeling. XX: overall planning of the article and modeling.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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NOMENCLATURE

- \( a \): activity
- \( G^e \): excess Gibbs energy, J\text{mol}^{-1}
- \( R \): gas constant, J\text{mol}^{-1}\text{kg}^{-1}
- \( m \): molality, mol\text{kg}^{-1}
- \( n \): mole, mol
- \( m_x \): total molality of solute, mol\text{kg}^{-1}
- \( m_w \): molar of free water, mol\text{kg}^{-1}
- \( h \): hydration numbers of the solute
- \( Z \): solvation parameters
- \( T \): temperature, K
- \( M_s \): molecular weight of water
- \( \gamma \): activity coefficients
- \( n_i \): integral molar quantity, mol
- \( \tau \): parameter
- \( i \): component \( i \)
- \( j \): component \( j \)
- \( dY \): mean absolute error, mol\text{kg}^{-1}
- \( dP \): mean relative error, %