Vapor–Liquid Equilibria Study of the LiCl + CaCl₂ + H₂O System

Xianzhen Xu,*† Yan Wang,‡ Xiangyu Sun,‡ and Yu Zhou‡

†Shandong Sino-Japanese Center for Collaborative Research of Carbon Nanomaterials, College of Chemistry and Chemical Engineering and ‡College of Applied Technology, Department of Chemical Engineering, Qingdao University, Qingdao 266071, China

ABSTRACT: Vapor–liquid equilibrium (VLE) data are measured and reported for the LiCl + CaCl₂ + H₂O system. The experimental procedures were carried out with pressures between 6 and 101.3 kPa in a computer-controlled glass apparatus. We obtained the relationship between solubility of salt and vapor pressure by analyzing and summarizing the results. Then, a modified NRTL model based on the hypothesis of hydration was used in this paper. By correlation of literature and experimental data for LiCl + H₂O, CaCl₂ + H₂O, and LiCl + CaCl₂ + H₂O (pressure spanning from 5 to 101.3 kPa), some parameters were modified for improving the accuracy of the calculation. Meanwhile, the model was successfully applied to predict the VLE data in LiCl + CaCl₂ + H₂O systems with the modified binary parameters.

1. INTRODUCTION

Crystallization, separation, and purification of electrolyte solutions are the key roles in technology and industrial fields. Vapor–liquid equilibrium (VLE) is widely used in chemical engineering and industries, which plays a fundamental role in chemical engineering.

Massive amounts of data with respect to phase equilibrium are reported in recent years, whereas corresponding thermodynamic models have been developed to calculate thermodynamic properties for electrolyte and nonelectrolyte systems. Because of the strong demand for separation process design, more researchers studied VLE on electrolyte systems. However, most of the data were concentrated in normal pressure (101.3 kPa) and room temperature (298.15 K). Up to now, some solubility isotherms of LiCl + CaCl₂ + H₂O system have been measured,1−4 whereas VLE of LiCl + H₂O and CaCl₂ + H₂O binary systems has been obtained.5 Nevertheless, VLE data for systems composed of LiCl + CaCl₂ + H₂O are still rare. For nonelectrolyte solutions, thermodynamic models such Wilson’s model,6 NRTL model,7 and UNIQUAC model8 are well established. For thermodynamic property calculation of electrolyte solutions, Pitzer’s model,9 ElecNRTL model10,11 Lu–Maurer’s model12,13 extended UNIQUAC model14 and Xu’s model15 have been widely utilized. In recent years, some scholars18−20 have done some research on the electrolyte solution systems. Despite the aforementioned research works, the calculation of VLE for mixed electrolyte systems is still confronted with great challenges.

In this paper, VLE data of the system composed of LiCl + CaCl₂ + H₂O are elaborately determined with a pressure varying from 10 to 101.3 kPa. The obtained data in binary systems5,15 are used to parameterize the modified NRTL model. By this means, a complete VLE diagram of the LiCl + CaCl₂ + H₂O system at various pressures and model parameters is obtained.

2. MODEL DESCRIPTION

2.1. Xu’s Model. In Xu’s model5,15 the excess Gibbs energy was expressed by the NRTL term7

\[
\frac{n_iG_{NRTL}}{RT} = m_xm_w \left( \frac{\tau_{w,x}G_{w,x}}{m_x + m_wG_{w,x}} + \frac{\tau_{x,w}G_{x,w}}{m_w + m_xG_{x,w}} \right)
\]

(1)

\[
G_{w,x} = \exp(-\alpha \tau_{w,x})
\]

(2)

\[
G_{x,w} = \exp(-\alpha \tau_{x,w})
\]

(3)

\[
m_w = \frac{1000}{M_i} \sum_{i=1}^{n} \left( h_i m_i \right)
\]

(4)

where \(n\) is the number of species of solute in electrolyte solution, \(m_i\) is the total molality of solute, \(m_i\) is the molality of solute, \(m_w\) is the molar of free water, \(h_i\) is the hydration numbers of the solute, \(n_i\) is the molar of solute and solvent, and \(M_i\) is the molecular weight of water. \(\tau_{w,x}\) and \(\tau_{x,w}\) are the water-entity term and the entity-water term, respectively:

\[
\tau_{w,x} = \sum_{i=1}^{n} \left( \tau_{w,i}m_i \right) / \sum_{i=1}^{n} (m_i)
\]

(5)
The relations between parameters $\tau_{w,i}$, $\tau_{i,w}$, and the temperature $T$ are as follows:

$$
\tau_{w,i} = \tau_{w,i}^{(0)} + \frac{\tau_{w,i}^{(1)}}{T}
$$

$$
\tau_{i,w} = \tau_{i,w}^{(0)} + \frac{\tau_{i,w}^{(1)}}{T}
$$

Based on the above descriptions, the final equation can be written as:

$$
\ln a_i = \left( \frac{\sum_{i=1}^{n} (\tau_{w,i} m_i) G_{w,x}}{\sum_{i=1}^{n} (m_i) + m_w G_{w,x}} + \frac{\sum_{i=1}^{n} (\tau_{w,i} m_i) G_{w,x}}{m_w + \sum_{i=1}^{n} (m_i) G_{w,x}} \right)
$$

$$
+ m_w \left( -\frac{\sum_{i=1}^{n} (\tau_{w,i} m_i) G_{w,x}^2}{(\sum_{i=1}^{n} (m_i) + m_w G_{w,x})^2} \right)
$$

$$
- \frac{\sum_{i=1}^{n} (\tau_{w,i} m_i) G_{w,x}}{(m_w + \sum_{i=1}^{n} (m_i) G_{w,x})}
$$

$$
+ \ln \frac{1000/M_i}{1000/M_x + \sum_{i=1}^{n} (m_i)}
$$

The reference state of activity coefficients in the excess Gibbs energy model is $\gamma_i \to 1$ as $x_i = (n_i/n) \to 1$. In the final equations, five parameters ($h$, $\tau_{w,i}^{(0)}$, $\tau_{w,i}^{(1)}$, $\tau_{i,w}^{(0)}$, and $\tau_{i,w}^{(1)}$) were fitted to the experimental data.

### 3. RESULTS AND DISCUSSION

The experimental data for LiCl + CaCl$_2$ + H$_2$O at different molality are listed in Tables 2−4. Meanwhile, experimental results were analyzed and summarized, as shown in Figures 2−6. Besides, the possible relationship between solubility of salt and saturated vapor pressure was obtained.
VLE behaviors of LiCl + CaCl2 + H2O were investigated.

### Table 2. Experimental VLE Data for Temperature T, Pressure P, and Molality m (m1: LiCl, m2: CaCl2) for the LiCl + CaCl2 + H2O System

| m1 = 20.08 mol·kg⁻¹, m2 = 0 mol·kg⁻¹ | m1 = 15.63 mol·kg⁻¹, m2 = 1.3 mol·kg⁻¹ | m1 = 10.4 mol·kg⁻¹, m2 = 3.14 mol·kg⁻¹ | m1 = 8.83 mol·kg⁻¹, m2 = 4.07 mol·kg⁻¹ |
|-------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| T (K)     | P (kPa) | T (K)     | P (kPa) | T (K)     | P (kPa) | T (K)     | P (kPa) |
| 329.25    | 6.46    | 322.55    | 6.005   | 325.35    | 5.935   | 327.45    | 6.065   |
| 341.15    | 11.69   | 337.95    | 11.425  | 336.65    | 10.425  | 339.15    | 11.22   |
| 348.05    | 13.9    | 346.35    | 16.135  | 347.65    | 16.86   | 347.45    | 15.875  |
| 355.05    | 21.025  | 353.85    | 21.7    | 353.15    | 20.71   | 354.05    | 20.83   |
| 360.95    | 26.94   | 359.05    | 26.75   | 359.25    | 26.41   | 359.55    | 25.76   |
| 363.85    | 30.275  | 362.75    | 30.965  | 363.45    | 31.13   | 365.25    | 32.275  |
| 369.45    | 36.82   | 367.45    | 36.83   | 367.95    | 37.05   | 368.85    | 37.275  |
| 372.15    | 40.755  | 370.25    | 40.01   | 370.85    | 41.06   | 371.95    | 41.6   |
| 376.45    | 47.275  | 373.15    | 45.645  | 373.35    | 46.72   | 375.05    | 46.74   |
| 378.35    | 50.335  | 376.35    | 51.035  | 376.95    | 51.26   | 378.45    | 52.29   |
| 381.55    | 55.795  | 379.25    | 56.395  | 379.45    | 56.045  | 380.25    | 55.655  |
| 384.55    | 61.82   | 381.05    | 60.29   | 382.55    | 61.96   | 382.65    | 60.855  |
| 386.55    | 66.375  | 383.45    | 65.38   | 384.35    | 65.77   | 385.85    | 67.385  |
| 388.55    | 71.07   | 386.35    | 71.995  | 386.75    | 71.65   | 387.65    | 72.395  |
| 390.75    | 76.355  | 388.25    | 76.15   | 388.95    | 77.325  | 389.45    | 75.935  |
| 393.05    | 81.74   | 390.35    | 81.79   | 390.75    | 82.03   | 391.45    | 81.91   |
| 394.85    | 86.21   | 392.05    | 86.77   | 392.25    | 86.485  | 393.55    | 87.5   |
| 396.45    | 91.295  | 393.65    | 90.945  | 393.95    | 91.5   | 394.75    | 92.16   |
| 398.25    | 96.385  | 395.55    | 97.045  | 395.45    | 96.43   | 395.95    | 95.84   |
| 400.05    | 101.205 | 397.05    | 101.205 | 397.05    | 101.205 | 397.85    | 101.195 |

Then, the thermodynamic model was studied, and Xu’s model was employed to correlate and predict VLE for the system. Xu’s model, ElecNRTL model,9,10 and Pitzer’s model9 were used to correlate VLE data in electrolyte systems, and VLE behaviors of LiCl + CaCl2 + H2O were investigated.

### 3.1. Discussion of Experimental Results

LiCl + H2O, CaCl2 + H2O, and LiCl + CaCl2 + H2O systems were chosen to study the VLE law, as shown in Tables 2–4 and Figures 4–6. From the tables and figures, we can see that the VLE law of LiCl + H2O, CaCl2 + H2O, and LiCl + CaCl2 + H2O is similar. For LiCl + H2O and CaCl2 + H2O systems, as the salt concentration increases, the saturated vapor pressure of water decreases regularly. From the results, we can see that as the temperature increases, the saturated vapor pressure also rises.
Table 4. Experimental VLE Data for Temperature $T$, Pressure $P$, and Molality $m$ ($m_a$: LiCl, $m_b$: CaCl$_2$) for the LiCl + CaCl$_2$ + H$_2$O System

| $T$ (K) | $P$ (kPa) | $m_a$ (mol/kg) | $m_b$ (mol/kg) |
|--------|-----------|----------------|----------------|
| 334.65 | 6.54      | 1.66           | 7.14           |
| 343.25 | 10.825    | 7.46           | 6.73           |
| 352.15 | 16.115    | 3.73           | 6.73           |
| 358.05 | 20.735    | 10.4           | 6.73           |
| 363.65 | 26.155    | 3.73           | 0             |
| 369.05 | 32.045    | 3.73           | 0             |
| 372.15 | 35.995    | 10.4           | 6.73           |
| 376.25 | 41.84     | 1.66           | 7.14           |
| 378.95 | 46.18     | 1.66           | 7.14           |
| 381.85 | 50.815    | 1.66           | 7.14           |
| 384.85 | 56.81     | 1.66           | 7.14           |
| 387.45 | 61.85     | 1.66           | 7.14           |
| 389.45 | 65.805    | 1.66           | 7.14           |
| 391.75 | 71.405    | 1.66           | 7.14           |
| 393.75 | 76.64     | 1.66           | 7.14           |
| 395.55 | 81.34     | 1.66           | 7.14           |
| 397.25 | 85.935    | 1.66           | 7.14           |
| 399.15 | 91.69     | 1.66           | 7.14           |
| 400.65 | 96.31     | 1.66           | 7.14           |
| 402.15 | 101.215   | 1.66           | 7.14           |

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

Figure 4. Experimental VLE data for the LiCl + CaCl$_2$ + H$_2$O system. Symbols (black box solid, $m_a = 20.08$ mol/kg, $m_b = 0$ mol/kg; red solid circle, $m_a = 15.63$ mol/kg, $m_b = 1.3$ mol/kg; blue triangle up solid, $m_a = 10.4$ mol/kg, $m_b = 3.14$ mol/kg; blue triangle up solid, $m_a = 7.46$ mol/kg, $m_b = 4.68$ mol/kg; pink triangle down solid, $m_a = 3.73$ mol/kg, $m_b = 6.73$ mol/kg; pickle green diamond solid, $m_a = 1.66$ mol/kg, $m_b = 7.14$ mol/kg) for experimental data (this work) and lines for correlation of the model.

Figure 5. Correlation of experimental VLE data for the LiCl + CaCl$_2$ + H$_2$O system. Symbols (black box solid, $m_a = 20.08$ mol/kg, $m_b = 0$ mol/kg; red solid circle, $m_a = 10.4$ mol/kg, $m_b = 3.14$ mol/kg; blue triangle up solid, $m_a = 7.46$ mol/kg, $m_b = 4.68$ mol/kg; pink triangle down solid, $m_a = 3.73$ mol/kg, $m_b = 6.73$ mol/kg; pickle green diamond solid, $m_a = 1.66$ mol/kg, $m_b = 7.14$ mol/kg) for experimental data (this work) and lines for correlation of the model.

Figure 6. Prediction of experimental VLE data for the LiCl + CaCl$_2$ + H$_2$O system. Symbols (black box solid, $m_a = 20.08$ mol/kg, $m_b = 0$ mol/kg; red solid circle, $m_a = 10.4$ mol/kg, $m_b = 3.14$ mol/kg; blue triangle up solid, $m_a = 7.46$ mol/kg, $m_b = 4.68$ mol/kg; pink triangle down solid, $m_a = 3.73$ mol/kg, $m_b = 6.73$ mol/kg; pickle green diamond solid, $m_a = 1.66$ mol/kg, $m_b = 7.14$ mol/kg) for experimental data (this work) and lines for prediction of the model.

Regularly. From Tables 2–4 and Figure 4, we can see that as the VLE pressure of $m_a$: LiCl = 2.43 mol/kg and $m_b$: CaCl$_2$ = 7.08 mol/kg in the LiCl + CaCl$_2$ + H$_2$O system is lowest, the activity at the same temperature is lowest, and as the VLE pressure of $m_a$: LiCl = 15.63 mol/kg and $m_b$: CaCl$_2$ = 1.30 mol/kg in LiCl + CaCl$_2$ + H$_2$O system is highest, the activity at the same temperature is highest. Simultaneously, the CaCl$_2$ + H$_2$O curve at saturated solubility and normal temperature is lower than LiCl + H$_2$O.

From the analysis of results, we can see that the hygroscopicity at some mixed concentration is also relatively strong, and we can calculate the strongest concentration of moisture absorption by modeling.

3.2. Results of the Modeling. 3.2.1. Correlation of the VLE. The model described above was used to correlate VLE data for the LiCl + CaCl$_2$ + H$_2$O system. The results of correlation for LiCl + H$_2$O, CaCl$_2$ + H$_2$O, and LiCl + CaCl$_2$ + H$_2$O systems are listed in Table 5 and Figure 5 in the form of mean deviation between literature and calculated values. Parameters $r_a, r_{b1}, r_{b2}, r_{b3}, r_{b4}, r_{b5}, r_{a1}, r_{b1}, r_{a2}, r_{b2}, r_{a3}, r_{b3}, r_{a4}, r_{b4}, r_{a5}, r_{b5}, h_1,$ and $h_2$ were obtained from the correlation of...
the prediction results are not better than the correlation results. However, the prediction result is worse of the LiCl + CaCl2 + H2O system used the modified parameters (LiCl-H2O and CaCl2-H2O) of Xu’s model were obtained. The calculations were compared to ElecNRTL model and Pitzer’s model. From comparisons, the result in this work is better than ElecNRTL model and Pitzer’s model. The model can be used to successfully predict VLE data for the LiCl + CaCl2 + H2O system with modified binary parameters.

### 4. CONCLUSIONS

In this paper, VLE data for LiCl + CaCl2 + H2O systems was measured and reported. The reliability of measurements was verified by comparing experimental data with literatures. Through the analysis of experimental data, it is shown that the solubility of salt is an important factor affecting saturated vapor pressure. As the VLE pressure of mLiCl = 2.43 mol/kg and mCaCl2 = 7.08 mol/kg is lowest, the activity at the same temperature is lowest, and the hygroscopicity at some mixed concentration is also relatively strong.

By the correlation of experimental data, modified parameters (LiCl-H2O and CaCl2-H2O) of Xu’s model were proposed in Xu’s model was used to describe the VLE law of the ternary electrolyte systems. However, the prediction result is worse than the correlation result.

For the LiCl + CaCl2 + H2O system, the prediction result is unsatisfactory. We have recalculated the parameters for LiCl + H2O and CaCl2 + H2O systems by using the experimental data in this work and modified the parameters for the binary electrolyte solutions, as listed in Table 7. Prediction results for the LiCl + CaCl2 + H2O system used the modified parameters are dY = 0.37 kPa and dP = 1.76%. The prediction with modified parameters is considered more accurate. However, the prediction results are not better than the correlation results (dY = 0.27 kPa and dP = 1.03%). If you want to calculate the VLE data more accurately, you can use the correlated model. The predicted model is relatively simple and convenient.

### 3.3. Comparison with Other Methods

The LiCl + CaCl2 + H2O system was selected for comparing ElecNRTL model, Pitzer’s model, and Xu’s model. Comparison results are shown in Table 8. Note that both ElecNRTL and Pitzer results were calculated by the software Aspen Plus 8.1.

For the LiCl + CaCl2 + H2O system, the dY value (0.27 kPa) of this work (correlation) used Xu’s model is smaller than that of ElecNRTL’s model (dY = 0.45 kPa) and Pitzer’s model (dY = 0.3 kPa). Besides, the dP value (1.03%) of this work (correlation) used Xu’s model is smaller than that of ElecNRTL’s model (dP = 2.3%) and Pitzer’s model (dP = 1.72%).

### 5. EXPERIMENTAL SECTION

#### 5.1. Materials

Anhydrous LiCl (purity ≥99.9%) and anhydrous CaCl2 (purity ≥99.99%) were purchased from Aladdin Industrial Corporation. Distilled water (18.2 Ω cm) was used for the preparation of solutions.

#### 5.2. 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.

During the experiments, the sample was placed into the glass ebulliometer, then heated by the heating mantle, and was controlled by the temperature controller. The operation pressure was controlled by the vacuum pump, the pressure sensor, and the control valve. The procedures were carried out with a pressure between 6.3 and 101.3 kPa. The vapor sample was condensed in a spherical condenser (length 40 cm) and then returned to the mixing chamber for recirculation.

The experimental steps are as follows: (1) First, we need to check the airtightness of the entire system by controlling the pressure. (2) We need to calibrate the temperature and pressure detectors. (3) The sample (40 mL) is placed into the glass ebulliometer. (4) The temperature heater is turned on, and the temperature is set by the temperature controller (110–180 V). (5) The vacuum pump is turned on, and the pressure is controlled by an electronic pressure relief valve. (6) The time was 0.5–1 h in the first equilibrium; then, the following

### Table 5. Correlation Results of VLE Data

| system        | data points | references |
|---------------|-------------|------------|
| CaCl2-H2O     | 5 to 101.3  | 322        |
| LiCl-H2O      | 5 to 101.3  | 47         |
| LiCl-CaCl2-H2O| 5 to 101.3  | 200        |

$dY = (1/N) \sum |P_{exp} - P_{cal}|$, where $N$ is the number of data points. $dP = (1/N) \sum |P_{exp} - P_{cal}|/P_{exp} \times 100\%$, where $N$ is the number of data points.

### Table 6. Model Parameters (Correlated) for Mixed Electrolyte Solutions

| system        | component | $a$  | $b$  | $\tau_{i,w}^{(0)}$ | $\tau_{w,i}^{(0)}$ | $\tau_{i,w}^{(1)}$ | $\tau_{w,i}^{(1)}$ |
|---------------|-----------|------|------|-------------------|-------------------|-------------------|-------------------|
| LiCl-CaCl2-H2O| LiCl      | 4.49 | 8.52 | -0.07             | 0.43              | -267.49           | 15.31             |
|               | CaCl2     | 2.47 | -0.47| 0.2               | -188.66           | -58.31            |                   |
equilibrium time was 10–20 min. (7) When the VLE state is reached, we recorded the temperature and pressure values.

The reliability of measurement was verified by comparing our experimental data (i.e., H₂O + CaCl₂, NaCl-KCl-H₂O) with those in literature (Figures 2 and 3). We have verified the accuracy and stability of the equipment by using the VLE data of the H₂O + CaCl₂ system in ref 5. The experimental data for LiCl + CaCl₂ + H₂O systems at different molality are listed in Tables 2–4.

Table 7. Model Parameters (Original and Modified) for Binary Electrolyte Solutions in Xu’s Model

| system             | model type | a     | h    | τ (0) | τ (0) | τ (1) | τ (1) |
|--------------------|------------|-------|------|-------|-------|-------|-------|
| CaCl₂·H₂O         | original   | 0.3   | 1.1  | −4.66 | 36.94 | −114.25 | −13200.53 |
| LiCl·H₂O          | original   | 2.15  | 0.957 | 2.06  | 822.12 | −93.41 |
| CaCl₂·H₂O         | modified   | 0.3   | 1.1  | 781.44 | −3771.77 | −98.47 | −6010.44 |
| LiCl·H₂O          | modified   | 2.15  | 4.99 | 13.17 | −4.29 | 16.17 |

Table 8. Comparison of Models for Electrolyte Solutions

| system            | P (kPa) | dY | dP | dY | dP | references |
|-------------------|---------|----|----|----|----|------------|
| LiCl·CaCl₂·H₂O    | 5 to 101.3 | 200 | 0.45 | 2.3 | 0.30 | 1.72 | 1, 2, and experimental data |
|                   |         |    |    | 0.27 | 1.03 | 0.37 | 1.76 |
|                   |         |    |    | 100% | 100% | 100% | 100% |

“dY = (1/N)Σ[P_{exp}−P_{calc}]”, where N is the number of data points. “dP = (1/N)Σ[P_{exp}−P_{calc}] × 100%, where N is the number of data points.

**NOMENCLATURE**

- a: activity
- G: excess Gibbs energy, J·mol⁻¹
- R: gas constant, J·mol⁻¹·K⁻¹
- m: molality, mol·kg⁻¹
- n: mole, mol
- mₜ: total molality of solute, mol·kg⁻¹
- mₙ: molar of free water, mol·kg⁻¹
- h: hydration numbers of the solute
- Z: solvation parameters
- T: temperature, K
- M: molecular weight of water
- γ: activity coefficients
- n: integral molar quantity, mol
- τ: parameter
- i: component i
- j: component j
- dY: mean absolute error, mol·kg⁻¹
- dP: mean relative error, %

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