Research Article

Solid-Liquid Phase Equilibria of the Quaternary System (LiCl + LiBO\(_2\) + Li\(_2\)B\(_4\)O\(_7\) + H\(_2\)O) at 308.15 K: Experimental and Theoretical Prediction

Hongya Shen, Qi Liu, Xiuxiu Yang, Yafei Guo, Dan Li, Lingzong Meng, and Tianlong Deng

1Key Laboratory of Marine Resource Chemistry and Food Technology (TUST), Ministry of Education, College of Chemical Engineering and Materials Science, Tianjin University of Science and Technology, Tianjin 300457, China
2School of Chemistry and Chemical Engineering, Linyi University, Linyi 276000, China

Correspondence should be addressed to Yafei Guo; guoyafei@tust.edu.cn and Tianlong Deng; tldeng@tust.edu.cn

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The isothermal dissolution equilibrium method was employed to obtain the solubilities and physicochemical properties of the quaternary system (LiCl + LiBO\(_2\) + Li\(_2\)B\(_4\)O\(_7\) + H\(_2\)O) at 308.15 K in this work. The dry-salt phase diagram, water-phase diagram, and physicochemical properties, including density, refractive index, and pH against composition in the quaternary system, were established for the first time. The dry-salt phase diagram includes two invariant points, five univariate solubility curves, and four single salt crystalline phase regions (LiCl·H\(_2\)O, LiBO\(_2\)·2H\(_2\)O, LiBO\(_2\)·8H\(_2\)O and Li\(_2\)B\(_4\)O\(_7\)·3H\(_2\)O), respectively. In addition, the physicochemical properties of density, refractive index, and pH in the system change regularly with the changing of the lithium metaborate concentration. Based on the Pitzer model, the mixing ion parameters of \(\theta\)\(_{\text{Cl,B4O5(OH)4}}\), \(\theta\)\(_{\text{B(OH)4,B4O5(OH)4}}\) and \(\Psi\)\(_{\text{Li,Cl,B4O5(OH)4}}\), \(\Psi\)\(_{\text{Li,B(OH)4,B4O5(OH)4}}\) and the predictive solubilities in the quaternary system were fitted. Although there is a slight deviation between the calculated and experimental values, the solubility of boron in the quaternary system agrees well, which provides data support for the study of the solubility of boron.

1. Introduction

Qinghai Salt Lake is rich in lithium and boron resources, which have high mining value [1]. After the brine evaporates, a large amount of NaCl and KCl are precipitated [2], and the composition of brine can be regarded as a complex brine system (Li\(^{+}\), Mg\(^{2+}\)/Cl\(^{-}\), SO\(_4^{2-}\), Borate–H\(_2\)O) [3]. The exploitation of lithium from brine resources has become a hot research spot [4, 5]. Since boron in brine is usually borate, it also changes correspondingly with the difference in pH value, coexisting ions, and solution concentration [6]. Therefore, studying the phase equilibria of brine systems with different forms of lithium boron components, especially the deep processing of lithium borate resources, has important strategic significance for the development and utilization of salt lake resources to create high-value-added products and realize the diversification of salt lake products [7–9].

In recent years, owing to the existence of various forms of borate in solution, extensive literature reports have been done on the phase equilibria of boron-containing complex brine systems at different temperatures, for example, (KBO\(_2\) + K\(_2\)SO\(_4\) + H\(_2\)O) system at 288.15 and 308.15 K [10], (Li\(_2\)SO\(_4\) + LiBO\(_2\) + Li\(_2\)B\(_4\)O\(_7\) + H\(_2\)O) system at 288.15 K [11], (Li\(_2\)B\(_4\)O\(_7\) + K\(_2\)B\(_4\)O\(_7\) + RbB\(_3\)O\(_8\) + H\(_2\)O) system at 323 K [12], (LiCl + LiB\(_2\)O\(_3\) + H\(_2\)O) and (Li\(_2\)SO\(_4\) + LiB\(_2\)O\(_3\) + H\(_2\)O) systems at 298.15 K [13]. The temperature in the Qinghai salt lake region can reach 308.15 K in summer [14]. Therefore, the phase equilibria study of this brine system has a certain theoretical reference value for the rational development of salt lake resources with solar ponds technology. Although some subsystems such as (LiCl + LiBO\(_2\) + H\(_2\)O) at 288.15,
298.15, 308.15 K and 323.15 K [15–17] and (LiBO2 + Li2B4O7 + H2O) at 288.15, 298.15 and 323.15 K [11, 18] have been reported, the phase equilibrium of the quaternary system (LiCl + LiBO2 + Li2B4O7 + H2O) has not been reported in the literature. On the other hand, the Pitzer model based on binary and ternary systems has been widely used to calculate the theoretical solubility of salt–water systems [18–20]. Unfortunately, the literature did not report several ion-interaction parameters for the system (LiCl + LiBO2 + Li2B4O7 + H2O). Therefore, this paper not only presents the solubility and physicochemical properties of the system (LiCl + LiBO2 + Li2B4O7 + H2O) at 308.15 K but also presents a predictive calculation of the solubility after obtaining the mixing ion-interaction parameters using the Pitzer model.

2. Experimental

2.1. Apparatus and Materials. It can be seen from Table 1 that the purity of the reagents used in this experiment was analytically pure. During this work, deionized distilled water (DDW) was used to prepare a series of artificially synthesized brines and chemical analyses, with conductivity (κ) less than or equal to 1.2 × 10⁻⁴ S·m⁻¹.

The solution reached solid-liquid equilibrium by the constant temperature magnetic stirring thermostat (HXC-500-6A, Beijing Fortune Joy Sci. Technology, Co., Ltd.) with a measurement accuracy of 0.1 K. The densities of solution and water were measured by a densitometer (DMA 4500, Anton Paar, Austria) accurately measured pH values with an error of ±0.001. X-ray powder diffraction with a scan rate of 400′·min⁻¹ and a test range of 10–80° (Smartlab, Rigaku, Japan) is used to identify the solid phases. In this work, all experimental data was measured in triplicate and the average was chosen.

2.2. Experimental Methods. After checking the solubility data of the common saturation point of the subsystem in this system, the third salt was mixed in a series of Teflon bottles with a volume of 250 cm³ from the common saturation point of the ternary system with a certain gradient by isothermal solution equilibrium method. LiCl with mass gradient and the quantitative water were added from the common saturation point of LiBO2-8H2O and Li2B4O7-3H2O to form a complex. It was put into a constant temperature water bath magnetic stirring tank. The water bath temperature was controlled at (308.15 ± 1) K. Set the stirring speed at 200 rpm to accelerate the formation of the equilibrium. After continuous stirring for about 50 days, when the liquid and solid phases were separated, an appropriate amount of sample was subsequently taken with a clean pipette for analysis. After the remaining samples were continuously stirred for about 60 days, an aliquot of the supernatant solution was taken for reanalysis. When the relative error of the analytical results for the sampling of different solutions (the concentrations of Li⁺, Cl⁻, BO₂⁻ and B₄O₇²⁻) was within 0.003 [21], it proved that the brine reached equilibrium. Subsequently, the physicochemical properties of the liquid phase were analyzed by refractive index, density, and pH, corresponding to those of the solid phase studied by X-ray powder diffraction, respectively.

2.3. Analytical Methods. For the quaternary system (LiCl + LiBO2 + Li2B4O7 + H2O), the mercury titration method was used to measure the concentration of chloride ions with diphenylazocarbazide and bromophenol blue as indicators, and the error of the measurement value was less than 0.003 in a mass fraction [22]. The content of boron was analyzed by a modified mannitol titration with a relative uncertainty of ±0.0005 and recorded as a mass fraction [22]. And the lithium-ion concentration in the solution was measured by ICP-OES (Prodigy, Teledyne Leeman Labs, USA) [11]. Due to the diverse existence of boron in aqueous solutions [6], only the total boron concentration can be measured. However, lithium metaborate and lithium tetraborate as the initial reagents are also the solid equilibrium phases in this experiment. Therefore, we assume that only B(OH)₄⁻ and B₄O₆(OH)₄²⁻ are present in the solution to measure solubility. Combining the concentrations of lithium and boron, the concentrations of two borates LiBO2 and Li2B4O7 are calculated with Eqs. (1) and (2).

\[ x + 2y = n_{Li} - n_{LiCl}, \]  
\[ x + 4y = n_B, \]

where \(x, y\) and \(n_{LiCl}\) are the molar concentrations of LiBO2, Li2B4O7 and LiCl, respectively, and \(n_{Li}\) is the total molar concentration of Li⁺ in the system. Similarly, \(n_B\) is boron (BO₂⁻, B₄O₇²⁻) ions of the total molar concentration. Considering the influence of reagent impurity, temperature fluctuation and concentration measurement errors, the standard uncertainty of LiCl impurity was less than 0.003. The uncertainty of LiBO2 and Li2B4O7 concentrations did not exceed 0.005.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>CAS reg. NO.</th>
<th>Grade</th>
<th>Initial mass fraction purity</th>
<th>Purification method</th>
<th>Final mass fraction purity</th>
<th>Analysis method</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl·H2O</td>
<td>10102-25-7</td>
<td>AR</td>
<td>0.99</td>
<td>Recrystallization</td>
<td>0.992</td>
<td>Titration for Cl</td>
</tr>
<tr>
<td>LiBO2·8H2O</td>
<td>63454-43-3</td>
<td>AR</td>
<td>0.99</td>
<td>Recrystallization</td>
<td>0.992</td>
<td>Titration for BO2</td>
</tr>
<tr>
<td>Li2B4O7</td>
<td>12007-60-2</td>
<td>AR</td>
<td>0.99</td>
<td>Recrystallization</td>
<td>0.992</td>
<td>Titration for B4O7</td>
</tr>
</tbody>
</table>

*AR from Shanghai Macklin Biochemical Technology Co., Ltd. **AR from Sinopharm Chemical Reagent Co., Ltd. ***AR from Sinopharm Chemical Reagent Co., Ltd.
3. Results and Discussion

3.1. Phase Diagram of the Quaternary System (LiCl + LiBO₂ + Li₂B₄O₇ + H₂O). Table 2 shows the solubility of the liquid equilibrium phase in the quaternary system (LiCl + LiBO₂ + Li₂B₄O₇ + H₂O) at 308.15 K, where the Jánecke dry-salt index (Z) is calculated from the mass fraction (w) using equations (3)–(6). Z (B) is calculated based on 100 g of total dry salt, and the specific calculation method is shown in the following formula [22].

\[
Z(\text{LiCl}) = \frac{w(\text{LiCl})}{w(\text{LiCl}) + w(\text{LiBO}_2) + w(\text{Li}_2\text{B}_4\text{O}_7)}
\]

\[
Z(\text{LiBO}_2) = \frac{w(\text{LiBO}_2)}{w(\text{LiCl}) + w(\text{LiBO}_2) + w(\text{Li}_2\text{B}_4\text{O}_7)}
\]

\[
Z(\text{Li}_2\text{B}_4\text{O}_7) = \frac{w(\text{Li}_2\text{B}_4\text{O}_7)}{w(\text{LiCl}) + w(\text{LiBO}_2) + w(\text{Li}_2\text{B}_4\text{O}_7)}
\]

\[
Z(\text{H}_2\text{O}) = \frac{w(\text{H}_2\text{O})}{w(\text{LiCl}) + w(\text{LiBO}_2) + w(\text{Li}_2\text{B}_4\text{O}_7)}
\]

The boundary points A, B, C and D on the dry basis diagram of the quaternary system are the saturation points of the three ternary subsystems (LiCl + LiBO₂ + H₂O), (LiCl + Li₂B₄O₇ + H₂O) and (LiBO₂ + Li₂B₄O₇ + H₂O) shown in Figure 1(a). The dry-salt phase diagram in Figure 1 includes two invariant points F₁ saturated with LiCl·H₂O, LiBO₂·2H₂O and Li₂B₄O₇·3H₂O and F₂ saturated with LiBO₂·8H₂O, LiBO₂·2H₂O and Li₂B₄O₇·3H₂O, five univariant solubility curves corresponding to F₁A (LiCl·H₂O + LiBO₂·2H₂O), CF₁ (LiCl·H₂O + Li₂B₄O₇·3H₂O), F₁F₂ (LiBO₂·2H₂O + Li₂B₄O₇·3H₂O), BF₂ (LiBO₂· 2H₂O + LiBO₂·8H₂O), F₂D (LiBO₂·8H₂O + Li₂B₄O₇·3H₂O), and four crystallization fields corresponding to single salts LiCl·H₂O, LiBO₂·2H₂O, LiBO₂·8H₂O, and Li₂B₄O₇·3H₂O. The size of the crystallization area decreases in the order Li₂B₄O₇·3H₂O, LiBO₂·2H₂O, LiBO₂·8H₂O, and LiCl·H₂O. The results show that Li₂B₄O₇·3H₂O has the smallest solubility and is easy to crystallize from brine. Figure 1(b) is a partial enlargement of the phase diagram in the quaternary system (LiCl + LiBO₂ + Li₂B₄O₇ + H₂O). Figure 2 shows the X-ray diffraction patterns of the invariant points F₁ and F₂. Comparing with the characteristic peaks of the standard PDF card, it shows that the salts LiCl·H₂O+ LiBO₂·2H₂O+ Li₂B₄O₇·3H₂O and LiBO₂·2H₂O+ LiBO₂·8H₂O+ Li₂B₄O₇·3H₂O coexist at the invariant points F₁ and F₂.

Figure 3 plots the water content diagram with LiBO₂·3H₂O and Z(H₂O) as the abscissa and ordinate. In the univariant solubility curve CA, Z(H₂O) has not significantly changed from 113.36 to 90.48. The Z(H₂O) in the univariant solubility curve F₁B decreases with the increase of Z(LiBO₂). The 100Z (H₂O) in the curves F₁F₂ and F₂D increases as 100Z (LiBO₂) increases, reaching the maximum value of 1471.67 at point D. The 100Z (H₂O) is 97.51 and 1235.11 at the invariant points F₁ and F₂. In general, the concentration of the solution can be judged by the changing trend of the univariant curves.

3.2. Physicochemical Properties. The relevant physicochemical properties of the electrolyte solution in the quaternary system (LiCl + LiBO₂ + Li₂B₄O₇ + H₂O), such as density, refractive index and pH value, are shown in Table 3. Figure 4 reflects the variation trend of the physicochemical properties of the electrolyte solution.
Figure 1: Dry-salt phase diagram of the quaternary system LiCl – LiBO₂ – Li₂B₄O₇ – H₂O at 308.15 K (a) phase diagram; (b) part-enlarge ment diagram.

Figure 2: Continued.
properties in this system with \(Z(\text{LiBO}_2)\). The change rule of densities in Figure 4(a) is roughly consistent with the refractive indices in Figure 4(b). As \(Z(\text{LiBO}_2)\) increases, the values also increase in the curves of CF1 and F1A, reaching their maximum (1.3846 g\(\cdot\)cm\(^{-3}\) and 1.4594) at point A. But values sharply decrease in the curves of F1F2, and there are minimums (1.0633 and 1.3454) at point F2. Moreover, the changing trend of the pH curve in Figure 4(c) is different from that of the former two. The pH value in the liquid phase gradually increases from point C (4.14) to point D (10.65). The specific trend of the pH value increases from C to F2 and decreases in the F1A and F2B curves with the increase of \(Z(\text{LiBO}_2)\). The densities, refractive indices, and pH values in the curve of F2D have almost the same trend.

Calculate density (\(\rho\)) and refractive index (\(n_D\)) from reported empirical equations [23].

\[
\ln \frac{n_D}{n_D^0} = \sum B_i w_i,
\]

\[
\ln \frac{\rho}{\rho_0} = \sum A_i w_i.
\]

In the above formula, \(\rho\) and \(n_D\) are the density values and the refractive indices in the solution. Correspondingly, \(\rho_0\) and \(n_{D0}\) represent pure water at 308.15 K, while \(\rho_0\) is 0.99484 g\(\cdot\)cm\(^{-3}\) and \(n_{D0}\) is 1.33131. \(w_i\) expressed the mass fraction of the \(i\)-th component in the solution. \(A_i\) and \(B_i\) denote constants for the \(i\)-th component of the density and refractive index in solution, which can be fitted with the experimental data. For LiCl, LiBO\(_2\) and Li\(_2\)B\(_4\)O\(_7\), \(A_i\) is 0.005466, 0.01083, and 0.008395, respectively. Except for a few complicated points, the difference between the calculated results and the measured densities and refractive index do not exceed 0.0080 and 0.0056, respectively, which proves the reliability of the data.

4. Solubility Prediction

4.1. Model Parameterization. Among many complex thermodynamic calculation models of water-salt systems, the Pitzer model is widely used in the calculation of solubility of water-salt systems [16, 24]. However, at present, there is no literature on thermodynamic calculations based on the
Pitzer ionic interaction model for quaternary systems (LiCl + LiBO\(_2\) + Li\(_2\)B\(_4\)O\(_7\) + H\(_2\)O). Therefore, we will use the Pitzer model to fit the solubility data of this system at 308.15 K. The primary expressions for calculating solubility in this model are equations (8) to (10) [24].

\[
\left(\frac{\Phi}{1}\right) = \left(\sum_i \frac{-A_i^{3/2}}{I + b_i^{1/2}}\right) + \sum_{c} \sum_{a} {m_c m_a} (B_{ca}^\Phi + Z C_{ca}) + \sum_{c} \sum_{c'} {m_c m_{c'}} (\Phi_{cc'}^\Phi + \sum_{a} {m_a \Psi_{cc'a}}) + \sum_{a} \sum_{a'} {m_a m_{a'}} (\Phi_{aa'}^\Phi + \sum_{c} {m_{c} \Psi_{ca' a'}}).
\]

\( (8) \)

\[
\ln y_M = Z_M^2 F + \sum_{a} {m_a (2B_{Ma} + Z C_{Ma})} + \sum_{c} {m_c (\Phi_{Mc} + \sum_{a} {m_a \Psi_{Mc'a}})} + \sum_{a} \sum_{a'} {m_a m_{a'} \Psi_{Ma'a'}}.
\]

\( (9) \)

\[
\ln y_X = Z_X^2 F + \sum_{c} {m_c (2B_{cX} + Z C_{cX})} + \sum_{a} {m_a (\Phi_{Xa} + \sum_{c} {m_c \Psi_{Xca}})} + \sum_{c} \sum_{c'} {m_c m_{c'} \Psi_{c' cX}}.
\]

\( (10) \)
where the subscripts $M$, $c$, and $c'$ are the cations in the solution, $X$, $a$ and $a'$ are the anions in the solution, $Z_i$ represents the valence of the ions, $m_i$ refers to the concentration of the substance in the solution (mol·kg$^{-1}$), $\Phi$ and $i$ are the permeability coefficient and activity coefficient. Other symbols in the equations, for instance, $F$, $C$, $Z$, $A$, $B$, are described in references [25, 26]. However, Debye–Hückel parameter $A\Phi$ at 308.15K is 0.398535 in the study.

At a specific temperature and pressure, the solubility equilibrium constant ($K_{sp}$) of the hydrated salt for the dissolution reaction can be obtained by the following formula [24].

$$M_{x_M}X_{x_X}$ \cdot nH_2O = v_M M^{x_M^+} + v_X X^{x_X^-} + nH_2O,$$

$$\ln K_{sp} = v_M \ln (m_M \gamma_M) + v_X \ln (m_X \gamma_X) + n \ln \alpha_W,$$

$$= v_M \ln m_M + v_M \ln \gamma_M + (v_X + v_X) \ln \gamma_x + n \ln \alpha_W,$$

(11)

where $\gamma_M$ and $\gamma_X$ are the activity coefficient, and the mean activity coefficient is denoted by $\gamma_x$.

---

**Figure 4:** Physicochemical properties versus composition diagram of the quaternary system $LiCl - LiBO_2 - Li_2B_4O_7 - H_2O$ at 308.15 K (a) density versus 100Z (LiBO$_2$); (b) refractive index versus 100Z (LiBO$_2$); (c) pH versus 100Z (LiBO$_2$).

**Table 4:** Pitzer single salt parameters of electrolyte in the quaternary system $LiCl - LiBO_2 - Li_2B_4O_7 - H_2O$ at 308.15 K.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\beta^{(0)}$</th>
<th>$\beta^{(1)}$</th>
<th>$\beta^{(2)}$</th>
<th>$\gamma^{(0)}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>2.0</td>
<td>0.0</td>
<td>0.2016</td>
<td>-0.1879</td>
<td>0.0</td>
<td>-0.004044</td>
<td>[12]</td>
</tr>
<tr>
<td>LiCl</td>
<td>1.4</td>
<td>1.5</td>
<td>-0.2706</td>
<td>41.8193</td>
<td>-44.3491</td>
<td>0.007996</td>
<td>[12]</td>
</tr>
<tr>
<td>LiB (OH)$_4$</td>
<td>2.0</td>
<td>0.0</td>
<td>-0.331042</td>
<td>-0.152813</td>
<td>0.0000</td>
<td>0.01012000</td>
<td>[27]</td>
</tr>
</tbody>
</table>

$C$ (a)
Boron exists in various forms in borate solution, in which B(OH)₄⁻ and B₄O₅(OH)₄²⁻ are on behalf of the metaborate and tetraborate ions [6, 27]. In addition, other existing forms of boron lack the relevant Pitzer binary and mixing parameters at 308.15 K, so thermodynamic properties cannot be fitted. Therefore, we only selected B(OH)₄⁻ and B₄O₅(OH)₄²⁻ two ions for solubility calculations. The single salt parameters of LiCl and LiB(OH)₄, and the solubility product constants (Ksp) of LiCl·H₂O, LiBO₂·H₂O and Li₂B₂O₇·8H₂O were obtained from the literature [16, 28]. The single salt parameters of Li₂B₂O₇(OH)₄ at 308.15 K were lacking in the literature, and the temperature is close to 298.15 K, so Deng's parameters at 308.15 K were chosen in the calculation [29]. The Pitzer mixing parameters θ_{LiBO2H4} and Ψ_{LiClBOH4} were cited from our previous work [16]. The missing Pitzer mixing parameters θ_{LiB4O5SOH4} and Ψ_{LiClB4O5SOH4} were fitted with the solubilities of the system LiCl–Li₂B₂O₇–H₂O at 308.15 K [30]. The parameters θ_{LiB4O5SOH4} and Ψ_{LiClB4O5SOH4} were reported in our previous [31]. However, the calculated solubility data with above parameters for points F₁ and F₂ show great deviation with the experimental results. The parameters θ_{LiB4O5SOH4} and Ψ_{LiClB4O5SOH4} were adjusted again. The single salt parameters and mixing ion parameters of the system used in the study are shown in Tables 4 and 5.

Pitzer mixing parameters θ_{LiB4O5SOH4} and Ψ_{LiClB4O5SOH4}, Ψ_{LiClB4O5SOH4} and Ψ_{LiClB4O5SOH4} mixing parameters in the quaternary system.

### Table 5: Pitzer mixing parameters in the quaternary system LiCl–LiBO₂–Li₂B₂O₇–H₂O at 308.15 K.

<table>
<thead>
<tr>
<th>Species</th>
<th>θ</th>
<th>ψ</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻·B(OH)₄⁻</td>
<td>−0.1781</td>
<td></td>
<td>[12]</td>
</tr>
<tr>
<td>Cl⁻·B₄O₅(OH)₄²⁻</td>
<td>−0.1500</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>B(OH)₄⁻·B₂O₅(OH)₄²⁻</td>
<td>0.0620</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>Li⁺·Cl⁻·B(OH)₄⁻</td>
<td>0.006856</td>
<td></td>
<td>[12]</td>
</tr>
<tr>
<td>Li⁺·Cl⁻·B₂O₅(OH)₄²⁻</td>
<td>0.0233</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>Li⁺·B(OH)₄⁻·B₂O₅(OH)₄²⁻</td>
<td>0.0000</td>
<td></td>
<td>This work</td>
</tr>
</tbody>
</table>

### Table 6: Comparison of experimental and calculated values of invariant points in the quaternary system LiCl–LiBO₂–Li₂B₂O₇–H₂O at 308.15 K.

<table>
<thead>
<tr>
<th>No.</th>
<th>Value</th>
<th>Composition of the liquid phase, 100uᵃ</th>
<th>Equilibrium solid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Experimental</td>
<td>LiCl 0.00 LiBO₂ 0.21 Li₂B₂O₇ 0.79</td>
<td>LiCl·H₂O + Li₂B₂O₇(OH)₄·H₂O</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
<td>LiCl 0.00 LiBO₂ 0.25 Li₂B₂O₇ 0.75</td>
<td>LiCl·H₂O + Li₂B₂O₇(OH)₄·H₂O</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>LiCl 0.45 LiBO₂ 0.55 Li₂B₂O₇ 0.00</td>
<td>LiCl(OH)₂·6H₂O + Li₂O₂(OH)₄·H₂O</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
<td>LiCl 0.55 LiBO₂ 0.45 Li₂B₂O₇ 0.00</td>
<td>LiCl(OH)₂·6H₂O + Li₂O₂(OH)₄·H₂O</td>
</tr>
<tr>
<td>D</td>
<td>Experimental</td>
<td>LiCl 0.30 LiBO₂ 0.70 Li₂B₂O₇ 0.00</td>
<td>LiCl·H₂O + LiCl(OH)₄ + Li₂B₂O₇(OH)₃·H₂O</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
<td>LiCl 0.30 LiBO₂ 0.70 Li₂B₂O₇ 0.00</td>
<td>LiCl·H₂O + LiCl(OH)₄ + Li₂B₂O₇(OH)₃·H₂O</td>
</tr>
<tr>
<td>F₁</td>
<td>Experimental</td>
<td>LiCl 0.26 LiBO₂ 0.74 Li₂B₂O₇ 0.00</td>
<td>LiCl(OH)₂·6H₂O + Li₂O₂(OH)₄·H₂O</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
<td>LiCl 0.32 LiBO₂ 0.68 Li₂B₂O₇ 0.00</td>
<td>LiCl(OH)₂·6H₂O + Li₂O₂(OH)₄·H₂O</td>
</tr>
</tbody>
</table>

ᵃStandard uncertainties u, u (T) = 0.02 K, u (p) = 0.005 MPa, u (LiCl) = 0.003, u (LiBO₂) = 0.005, and u (Li₂B₂O₇) = 0.005. The column no. Column corresponds to the no. Column in Table 2.

Borate exists in various forms in borate solution, in which B(OH)₄⁻ and B₂O₅(OH)₄²⁻ are on behalf of the metaborate and tetraborate ions [6, 27]. In addition, other existing forms of boron lack the relevant Pitzer binary and mixing parameters at 308.15 K, so thermodynamic properties cannot be fitted. Therefore, we only selected B(OH)₄⁻ and B₂O₅(OH)₄²⁻ two ions for solubility calculations. The single salt parameters of LiCl and LiB(OH)₄, and the solubility product constants (Ksp) of LiCl·H₂O, LiBO₂·H₂O and Li₂B₂O₇·8H₂O were obtained from the literature [16, 28]. The single salt parameters of Li₂B₂O₇(OH)₄ at 308.15 K were lacking in the literature, and the temperature is close to 298.15 K, so Deng’s parameters at 298.15 K were chosen in the calculation [29]. The Pitzer mixing parameters θ_{LiBO2H4} and Ψ_{LiClBOH4} were cited from our previous work [16]. The missing Pitzer mixing parameters θ_{LiB4O5SOH4} and Ψ_{LiClB4O5SOH4} were fitted with the solubilities of the system LiCl–Li₂B₂O₇–H₂O at 308.15 K [30]. The parameters θ_{LiB4O5SOH4} and Ψ_{LiClB4O5SOH4} were reported in our previous [31]. However, the calculated solubility data with above parameters for points F₁ and F₂ show great deviation with the experimental results. The parameters θ_{LiB4O5SOH4} and Ψ_{LiClB4O5SOH4} were adjusted again. The single salt parameters and mixing ion parameters of the system used in the study are shown in Tables 4 and 5.

Pitzer mixing parameters θ_{LiB4O5SOH4} and Ψ_{LiClB4O5SOH4}, Ψ_{LiClB4O5SOH4} and Ψ_{LiClB4O5SOH4} mixing parameters in the quaternary system.

**4.2. Solubility Calculation.** Before using the Pitzer model to calculate the solubility of the system (LiCl+LiBO₂+Li₂B₂O₇+H₂O) at 308.15 K, it is necessary to obtain the corresponding Pitzer parameters. It can be seen from the existing literature that when LiCl·H₂O, LiBO₂·H₂O, LiBO₂·8H₂O, and Li₂B₂O₇·3H₂O are in the dissolution equilibrium, the solubility product constants (lnKsp) are 12.0072, −1.0200, −0.5140, and −7.5511, respectively [31]. We calculated the solubility at 308.15 K by combining the above lnKsp values, Pitzer single parameters and the mixing parameters. Table 6 lists the solubilities for the boundary points and invariant points in the quaternary system (LiCl+LiBO₂+Li₂B₂O₇+H₂O) at 308.15 K, and the corresponding phase diagram is shown in Figure 5. The calculated phase diagram indicated by the red dotted line cannot completely coincide with the experimental data curve. There is an obvious deviation, especially in the solubility curves for LiBO₂·8H₂O and Li₂B₂O₇·3H₂O saturation. The calculated saturation solubility isotherms for LiBO₂·8H₂O and Li₂B₂O₇·3H₂O were still significantly inconsistent with the experimental data despite changing the mixing parameters several times. At point C, the experimental value is closest to the calculated value, and the relative error is the smallest. At the invariant points F₁ and F₂, the deviation of lithium borate content is larger, while the deviation of lithium chloride is smaller. Therefore, the solubility calculated by the Pitzer model cannot exactly match the experimental value. However, except for curve DF₂ in Figure 5, the fitted values on other solubility curves are consistent with the experimental data, indicating that the Pitzer model can explain the solubility changes very well. At the F₁ point, the maximum deviation between the mass fraction of w(LiCl), w(LiBO₂) and w(Li₂B₂O₇) and the theoretical value is 0.0, 0.0466, 0.0005, respectively, and the
Figure 5: Experimental and calculated phase diagram in quaternary system LiCl–LiBO2–Li3B4O7–H2O at 308.15 K; red dashed lines for the calculated data, solid black lines for the experimental data.

Figure 6: Boron species distribution in solution in the quaternary system LiCl–LiBO2–Li3B4O7–H2O at 308.15 K.

The deviation value at the F2 point is 0.0.028, 0.0006, respectively. However, the variation trend of the solubility curve calculated in Figure 5 is consistent with the experimental results, indicating that the Pitzer model can be used to describe solubility. The error between the experimental value and the calculated value is caused for various reasons. The parameters required in the calculations are derived from different kinds of literature and cannot be matched with each other. In addition, assumed only two boron species of B(OH)4− and B2O3(OH)22−, were used in this system for the calculation, but other boron species may be present in the brine, such as B(OH)3, B2O5(OH)32−, and B3O5(OH)42− [6, 27]. The results show that this assumption is not precise enough. The relative errors for the experimental solubility calculated using the concentration of lithium and boron are a little larger. It is worth noting that the errors between experimental solubility and computed results are unavoidable. Thus, a large number of thermodynamic models for boron-containing systems are necessary to fit the Pitzer model. The concentration of various boron species can be obtained similarly using the concentration between different boron species [6], pH value, reaction equilibrium constant, etc. [32, 33]. In the calculation of the boron ion, its activity coefficient is considered to be 1.0 [6]. The existing literature shows that the reaction equilibrium constants between different boron species have not been reported in the lithium borate system. For this work, we have chosen an approximation of the reaction equilibrium constant for calculation [6]. Figure 6 shows the boron species' calculated distribution in this quaternary system (LiCl+LiBO2+Li3B4O7+H2O), and the main boron species in the different curves vary greatly. In curves DF2 and BF2, the main boron species include B(OH)4− and B2O3(OH)22−. Other types of boron can be ignored. In curve F1F2, the B2O3(OH)4− can be ignored. In curve CF1, B(OH)3 is the main boron species, which may be caused by m(LiCl). LiCl solution is acidic, and as m(LiCl) increases, B(OH)3 is formed by combining B(OH)4− and H+. So, calculations assuming two boron species in solution may not be precise enough. The solubility of lithium borate is the main target of our study rather than the concentration of boron species in this study. Therefore, boron species other than B(OH)4− and B2O3(OH)22− were not considered in this solubility calculation due to the lack of parameters for various boron species at 308.15 K.

5. Conclusion

In this paper, the isothermal solution equilibrium method carried out the phase equilibrium study in the system (LiCl+LiBO2+Li3B4O7+H2O) at 308.15 K. According to each experimental data of the measured equilibrium solution, the corresponding phase diagrams were obtained. The dry-salt diagram of the quaternary system includes two invariant points, four single salt crystallization fields for LiCl+H2O, LiBO2+H2O, LiBO2·H2O and Li3B4O7·3H2O, and five univariant solubility curves. The densities, refractive indices, and pH values of this system show certain regularity with the increased concentration of lithium metaborate in the solution. In addition, the results calculated by the empirical equation are highly identical to the experimental data. The solubility of this system was calculated based on the Pitzer model combined with the corresponding Pitzer parameters and the solubility product constant of the solid equilibrium phase. There is a certain deviation in the calculated solubility compared with the experimental value in
this system. Although the assumption that there are only two boron species in the brine cannot be fully applied to solubility calculations, the results of such calculations are still able to explain the experimental values well. The phase diagrams and thermodynamic model results in the quaternary system \((\text{LiCl} + \text{LiBO}_2 + \text{Li}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O})\) can not only supplement the database of such boron resources but also provide a theoretical basis for their comprehensive utilization and provide a good theoretical reference value for the construction of general thermodynamic models.

**Data Availability**

The data used to support the findings of this study are available from the corresponding author upon request.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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