Stable Phase Equilibrium of the Aqueous Quaternary System Li⁺, K⁺, Mg²⁺ // Borate - H₂O at 323 K
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ABSTRACT
The stable phase equilibrium of the aqueous quaternary system Li⁺, K⁺, Mg²⁺ // borate-H₂O at 323 K was investigated using an isothermal dissolution method. The compositions, densities and refractive indices of the solution at equilibrium were measured. The phase diagram, water content diagram and the diagrams of the physicochemical properties (density and refractive index) versus composition were obtained using the measured data. The phase diagram of this quaternary system contains one invariant point E, three univariant curves (AE, BE and CE) and three crystalline phase areas. The invariant point is co-saturated with three salts, i.e. Li₂B₄O₇⋅3H₂O, K₂B₄O₇⋅4H₂O and MgB₄O₇⋅9H₂O. This quaternary system was simple and formed little double salt or solid solution. The sizes of salt crystallization areas were in the order of MgB₄O₇⋅9H₂O > Li₂B₄O₇⋅3H₂O > K₂B₄O₇⋅4H₂O, which demonstrates the salt MgB₄O₇⋅9H₂O can be more easily separated from the solution than the other two coexisting salts at 323 K. Comparisons between the stable phase diagrams at 323 K and 348 K show that both of K₂B₄O₇⋅4H₂O and Li₂B₄O₇⋅3H₂O crystallization zones were enlarged at 323 K, while the crystallization zones of MgB₄O₇⋅9H₂O was shrinked at 323 K.

Keywords: stable phase equilibrium, aqueous quaternary system, solubility, borate

1. INTRODUCTION
There are abundant underground brine resources in the west of Sichuan Basin which is well known for its plenty of sodium potassium, borate, magnesium and lithium [1-3]. Pingluo underground brine, one of the most important liquid mineral resources located in Sichuan Basin, belongs to borate type brine [4]. The concentration of potassium ion is up to 53.267 g/L, lithium ion is 89.9 mg/L, magnesium ion is 3.166 g/L and boron ion is 4994.36 mg/L [5]. The content of boron ion is higher in the brine than that found in comprehensive utilization and separate mining. To develop the brine reasonably, it is necessary to complete the study of phase equilibrium with boron ion in
Pingluo brine [6]. The content of these elementary compositions, far exceeded industrial exploitation indexes, is constituted the advantage of the liquid mineral resources. The development of modern science and technology has made the economic value of Sichuan Basin underground brine increasingly noticeable [7].

In recent years, the dissolvability data of inorganic salts and the phase diagram have been playing a significant role in exploiting underground brine and salt-lake brine resources. Great effort has been made to study a variety of phase equilibriums in water-salt system. For example, Ying Zeng studied the phase equilibrium in the quaternary system Li⁺ // Cl⁻, SO₄²⁻, borate - H₂O at 273 K [8], the ternary system NH₄⁺, Mg²⁺ // Cl⁻ - H₂O at 323 K [9] and Li⁺, K⁺ // Cl⁻ - H₂O at 298 K [10]; Xudong Yu studied the phase equilibrium in the ternary systems K⁺, Mg²⁺ // Cl⁻ - H₂O at 298 K, 323 K and 348 K [11-13]; Dewen Zeng investigated calculation of phase diagram of the system K⁺, Li⁺, Mg²⁺ // NO₃⁻ - H₂O from 273 to 333 K [14]; Sanjoy K. investigated thermodynamic modeling of aqueous Na⁺, K⁺, Mg²⁺ // SO₄²⁻ quaternary system [15]; Lightfoot W. J. investigated ternary systems K⁺, Mg²⁺ // Cl⁻ - H₂O at and 348 K [16]. These studies contribute a lot to the exploitation of various brine resources.

The crystallization zones of the salts were believed to be highly dependent on temperature [17]. During the extraction process of brine, 323 K and 348 K [18] are two important transformation temperature points. Since the phase equilibria of the quaternary system Li⁺, K⁺, Mg²⁺ // borate - H₂O has been studied only at 348 K [18], and the research at 323 K has not been conducted. In this manuscript, the stable phase equilibrium of the aqueous quaternary system Li⁺, K⁺, Mg²⁺ // borate - H₂O at 323 K were systematically studied with the presence of detailed corresponding data.

The research on quaternary system Li⁺, K⁺, Mg²⁺ // borate - H₂O was based on our previously studied ternary systems (, i.e, Li⁺, K⁺ // borate - H₂O, Li⁺, Mg²⁺ // borate - H₂O and Mg²⁺, K⁺ // borate - H₂O) at 323 K. All the three ternary systems at 323 K were simple, and more importantly, no double salt or solid solution was formed. Hence, further investigation has been done at 323 K on the quaternary system Li⁺, K⁺, Mg²⁺ // borate - H₂O by using the solubility data of the invariant point in ternary system. The compositions, densities and refractive indices of the solution at equilibrium were measured; the phase diagram, water content diagram and the diagrams of the physicochemical properties versus composition were constructed with the measured data. Also, comparisons between the stable phase diagrams at 323 K and 348 K [18] have been made.

2. MATERIALS AND METHODS

2.1 Reagents and Apparatus

The chemicals used in this work were of analytical purity grade and tabulated in Table 1. A deionized water, with an electrical conductivity less than 1×10⁻⁴ S m⁻¹ and pH ≈ 6.60, was obtained from ultra-pure water system (UPT-II-20T type, Sichuan ultrapure eurotronic technology co., Ltd, China).

The powder X-ray diffraction (XRD) measurements used to analyze the phase composition of solid salt were noted on a DX-2700 diffractometer with monochromatized Cu Kα radiation, under the operation conditions 30 mA and 40 kV [18]. A TH-Z82 type thermostatic water bath oscillator was used for the solubility experiments, with temperature controlling precision ± 0.2 K. A standard analytical
balance (FA1204B type, Mettler Toledo Instruments Co., Ltd), with 110 g capacity and ±0.0002 g resolution, was used to determine the density of solution [19]. A 2WAJ Abbe refractometer was used for measuring the refractive index of the equilibrated solution, the precision is ±0.0001. A 5300 V-type ICP-OES made by Perkin-Elmer Corp, United States, was employed to measure Li⁺ concentration in solution.

Table 1. Solubility and Analytical Experimental Reagents.

<table>
<thead>
<tr>
<th>chemical name</th>
<th>purity</th>
<th>source</th>
<th>analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>lithium tetraboratetrihydrate (Li₂B₄O₇⋅3H₂O)</td>
<td>0.995</td>
<td>Chengdu Kelong Chemical Reagent Plant</td>
<td>alkalimetry in the presence of mannitol for tetraborate</td>
</tr>
<tr>
<td>potassium tetraboratetrihydrate (K₂B₄O₇⋅4H₂O)</td>
<td>0.995</td>
<td>Chengdu Kelong Chemical Reagent Plant</td>
<td>alkalimetry in the presence of mannitol for tetraborate</td>
</tr>
<tr>
<td>magnesium tetraboratetrihydrate (MgB₄O₇⋅9H₂O)</td>
<td>0.985</td>
<td>Synthesized in laboratory [17]</td>
<td>titration with EDTA stand solution formagnesium</td>
</tr>
<tr>
<td>Ethylenediaminetetraacetic acid disodium salt (EDTA)</td>
<td>0.990</td>
<td>Chengdu Kelong Chemical Reagent Plant</td>
<td></td>
</tr>
</tbody>
</table>

2.2 Experimental Procedures

The stable phase equilibrium of aqueous quaternary system at 323 K was studied by means of an isothermal dissolution method. The component of the ternary subsystems invariant points was taken as the composition of primal samples. The primal samples were mixed by putting a third component at 323 K [20]. For example, from the invariant point cosaturated with lithium tetraborate trihydrate and magnesium tetraborate nonahydrate, a certain amount of potassium tetraborate tetrahydrate was gradually added to the solution to acquire experimental sample. A series of experimental samples were added to the sealed transparent glass bottles and the bottles were put into a TH-Z82 type thermostatic water bath kettle with an invariable oscillation frequency (110 rpm) to accelerate equilibration and keep the temperature (323 ± 0.2 K). Supernatant fluid was regularly taken for chemical analysis; the dissolution equilibrium was reached when the chemical composition of the solution kept constant. The equilibration time for the system was about 30 days, then the liquid phase and wet slag samples were separated to determine composition. The liquid phase was determined with chemical analysis methods, and the solid samples were determined with the powder X-ray diffraction method [21]. The density was determined using the weighing bottle method.

2.3 Analytical Methods

The concentration of Li⁺ was measured by ICP - OES (precision less than 0.5 %). The composition of borate was determined by neutralization titration in the presence of mannitol (precision: ± 0.5 %). The concentrations of Mg²⁺ were determined by ethylene diaminetetraacetic acid (EDTA) titration in the presence of mixed K - B (Acid chrome blue K- Naphthol green B), with a precision of ± 0.5 %. The composition of K⁺ was determined by a sodium tetrphenylborate (STPB) - cetyltrimethyl ammonium (CTAB) bromide titration with a precision of ± 0.5 % [22].
All samples were measured for 3 - 4 times in parallel.

3. RESULTS AND DISCUSSION

The compositions and physicochemical properties (refractive indices and densities) of the equilibrium solution and its corresponding solid phase of the quaternary system Li⁺, K⁺, Mg²⁺ // borate - H₂O at 323 K are shown in Table 2. In Table 2, $\alpha(X)$ is the mass fraction of component X, and $J(X)$ is the Jaécke index value of component X, calculated with 100 mol of dry salt as the benchmark; X can be Li₂B₄O₇, K₂B₄O₇,

\[
\alpha(Li_2B_4O_7) + \alpha(K_2B_4O_7) + \alpha(MgB_4O_7) + \alpha(H_2O) = 100%
\]

\[
[M] = \frac{\alpha(Li_2B_4O_7)}{169.12} + \frac{\alpha(K_2B_4O_7)}{233.44} + \frac{\alpha(MgB_4O_7)}{179.55}
\]

\[
J(Li_2B_4O_7) = \frac{\alpha(Li_2B_4O_7)}{169.12} \times 100
\]

\[
J(Li_2B_4O_7) + J(K_2B_4O_7) + J(MgB_4O_7) = 100
\]

Table 2. Experimental values of densities, refractive indices and solubility of the equilibrium solution in the quaternary system Li⁺, K⁺, Mg²⁺ / / B₄O₇²⁻ - H₂O at 323 K and Pressure $\rho = 0.1$ MPa.

<table>
<thead>
<tr>
<th>No</th>
<th>Density ρ/g·cm⁻³</th>
<th>Refractive Index/n₀</th>
<th>Composition of solution w(b)/x100</th>
<th>Jaécke index of dry salt $J(Li_2B_4O_7)+J(K_2B_4O_7)+J(MgB_4O_7)=100$</th>
<th>Solid phase</th>
</tr>
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<tbody>
<tr>
<td>1A</td>
<td>1.3839</td>
<td>1.3823</td>
<td>3.75 25.39 0.00 70.86 16.95 83.05 0.00 3005</td>
<td>LB+KB</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.4091</td>
<td>1.3846</td>
<td>3.90 26.47 1.09 68.54 16.77 79.56 4.27 2672</td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>1.4297</td>
<td>1.3885</td>
<td>3.80 26.51 2.59 67.10 14.98 75.21 9.81 2478</td>
<td>LB+KB</td>
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<tr>
<td>4</td>
<td>1.4503</td>
<td>1.3932</td>
<td>3.81 26.99 4.50 64.71 13.79 78.06 15.35 2204</td>
<td>LB+KB</td>
<td></td>
</tr>
<tr>
<td>5E</td>
<td>1.461</td>
<td>1.3961</td>
<td>2.29 15.68 4.00 78.03 13.13 65.24 21.63 4210</td>
<td>LB+KB+MB+MB</td>
<td></td>
</tr>
<tr>
<td>6B</td>
<td>1.3581</td>
<td>1.3850</td>
<td>0.00 25.57 7.43 67.01 0.00 72.58 27.42 2467</td>
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<td></td>
</tr>
<tr>
<td>7</td>
<td>1.3641</td>
<td>1.3861</td>
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<td>8</td>
<td>1.3767</td>
<td>1.3892</td>
<td>2.47 19.2 5.26 73.07 11.39 65.18 23.23 3217</td>
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<tr>
<td>9E</td>
<td>1.4610</td>
<td>1.3961</td>
<td>2.29 15.68 4.00 78.03 13.13 65.24 21.63 4210</td>
<td>LB+KB+MB+MB</td>
<td></td>
</tr>
<tr>
<td>10C</td>
<td>1.1400</td>
<td>1.3395</td>
<td>4.24 0.00 0.10 95.65 97.89 0.00 2.11 20751</td>
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<tr>
<td>11</td>
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<td>1.3406</td>
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<tr>
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<td></td>
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<tr>
<td>14</td>
<td>1.0922</td>
<td>1.3455</td>
<td>1.64 3.41 0.35 94.60 66.05 31.74 7.60 20041</td>
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<td>15</td>
<td>1.0932</td>
<td>1.3475</td>
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<td>16</td>
<td>1.1001</td>
<td>1.3517</td>
<td>2.17 5.17 0.85 91.81 41.15 46.65 12.20 12854</td>
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<td>17</td>
<td>1.1071</td>
<td>1.3531</td>
<td>2.83 6.58 1.34 89.25 31.95 53.80 14.25 9465</td>
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<tr>
<td>18</td>
<td>1.136</td>
<td>1.3563</td>
<td>3.34 10.29 2.27 84.10 25.82 57.61 16.56 6109</td>
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<tr>
<td>19</td>
<td>1.2166</td>
<td>1.3667</td>
<td>2.75 8.67 1.99 86.59 25.24 57.55 17.20 7456</td>
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</tr>
<tr>
<td>20</td>
<td>1.3549</td>
<td>1.3785</td>
<td>2.62 12.01 2.81 82.56 18.78 62.30 18.92 5554</td>
<td>LB+MB</td>
<td></td>
</tr>
<tr>
<td>21E</td>
<td>1.4610</td>
<td>1.3961</td>
<td>2.29 15.68 4.00 78.03 13.13 65.24 21.63 4210</td>
<td>LB+KB+MB</td>
<td></td>
</tr>
</tbody>
</table>

*Standard uncertainties $\alpha$ are $\alpha(T) = 0.50$ K; $\rho(\rho) = 0.05$; $\rho(\rho) = 2.0 \times 10^{-3}$ g/cm³; $\rho(\rho) = 1.0 -1.10$; $\rho(Li_2B_4O_7) = 0.0050; \rho(K_2B_4O_7) = 0.0050; \rho(MgB_4O_7) = 0.0050; \rho(B_4O_7)$, mass fraction of $B_4$, $J(X)$ is the Jaécke index value of component X, $\rho(Li_2B_4O_7); \rho(K_2B_4O_7); \rho(MgB_4O_7); \rho(H_2O)$, with $J(Li_2B_4O_7) + J(K_2B_4O_7) + J(MgB_4O_7) + J(H_2O) = 100$. The data of mass fraction and Jaécke index can comply with the formulas listed below:
With the Jémez index value, the stable phase diagram at 323 K was plotted, as shown in Figure 1. In Figure 1, the black points present the experimental points and the solid lines through the points express the isothermal dissolution curves. Points A, B, C are the invariant points of three ternary subsystems, and point E is the invariant point of the quaternary system. As shown in Table 2 and Figure 1, this quaternary system is of a simple type, no double salt or solid solution formed at 323 K. The phase diagram (Figure 1) contains one invariant point (E), three univariant curves (AE, BE and CE) and three crystalline phase areas. The composition of the equilibrium solution corresponding invariant point E is \(w(K_2B_4O_7) = 15.68\%\), \(w(Li_2B_4O_7) = 2.29\%\), \(w(MgB_4O_7) = 4.00\%\), \(w(H_2O) = 78.03\%\).

The size of the salts crystallization areas is in the order \(MgB_4O_7 \cdot 9H_2O > Li_2B_4O_7 \cdot 3H_2O > K_2B_4O_7 \cdot 4H_2O\), which demonstrates salt \(MgB_4O_7 \cdot 9H_2O\) can be more easily separated from the solution than the other coexisting salts in this quaternary system at 323 K.

Figure 2 shows the X-ray diffraction patterns of invariant point E. As shown in Figure 2, the abscissa ordinate is \(2\theta\) from 3° to 80°; the vertical ordinate is intensity. The crystallographic form of lithium, potassium and magnesium borates at 323 K in the quaternary system are \(Li_2B_4O_7 \cdot 3H_2O\), \(K_2B_4O_7 \cdot 4H_2O\) and \(MgB_4O_7 \cdot 9H_2O\) respectively. Comparing with the standard cards, it is found that salts \(Li_2B_4O_7 \cdot 3H_2O\), \(K_2B_4O_7 \cdot 4H_2O\) and \(MgB_4O_7 \cdot 9H_2O\) coexist at the invariant point E.

Figure 3 is the water content diagram of the system at 323 K, with \(J(K_2B_4O_7)\) as abscissa, and \(J(H_2O)\) as ordinate. On the univariant curve CE, the water content changes obviously with the increase of \(J(K_2B_4O_7)\) and reaches the minimum at the point E, whereas the changes of water content become slight on the other univariant curves AE and BE.

Figure 4 is the refractive index versus composition of the solution at equilibrium. As the change of \(J(K_2B_4O_7)\), the refractive index of the solution regularly changes. On the univariant curve CE, the refractive index increase obviously until it reaches the maximum at the invariant point E. Figure 5 is the density versus composition diagram of the equilibrated solution. On the univariant curve CE, the density decrease first and then increase with the increase of \(J(K_2B_4O_7)\).
Figure 6 shows the comparisons between the stable phase diagrams at 348 K \[18\] and 323 K. The crystallization forms of the salts are not changed with the increase of temperature, however, the crystallization zones of salts have changed. The crystallization zone of MgB\(_4\)O\(_7\)\(\cdot\)9H\(_2\)O is slightly enlarged at 348 K \[18\], and the crystallization zones of K\(_2\)B\(_4\)O\(_7\)\(\cdot\)4H\(_2\)O, Li\(_2\)B\(_4\)O\(_7\)\(\cdot\)3H\(_2\)O are both decreased in a way, which shows that K\(_2\)B\(_4\)O\(_7\)\(\cdot\)4H\(_2\)O and Li\(_2\)B\(_4\)O\(_7\)\(\cdot\)3H\(_2\)O are more easily extracted from brine at 323 K.

Figure 3. Water content diagram of the quaternary system Li\(^+\), K\(^+\), Mg\(^{2+}\) // borate - H\(_2\)O at 323 K.

Figure 4. Refractive indices vs composition diagram of the quaternary system Li\(^+\), K\(^+\), Mg\(^{2+}\) // borate - H\(_2\)O at 323 K.

Figure 5. Densities vs composition diagram of the quaternary system Li\(^+\), K\(^+\), Mg\(^{2+}\) // borate - H\(_2\)O at 323 K.

4. CONCLUSIONS
The stable phase equilibrium of the aqueous quaternary system Li\(^+\), K\(^+\), Mg\(^{2+}\) // borate - H\(_2\)O at 323 K were investigated using an isothermal dissolution method. The solubilities, densities and refractive indices of the solution were determined experimentally. The quaternary system is of a simple type, and neither solid solution nor double salt was formed at 323 K. The stable phase diagram is composed of one invariant point, three univariant curves and three crystalline regions. Comparisons between the stable phase diagrams at 323 K and 348 K \[18\] show that
the crystallization form of the salts are not changed with the increase of temperature, whereas the scopes of the crystallization regions are distinctly changed. At 348 K, the crystallization region of MgB$_4$O$_7$·9H$_2$O becomes obviously larger, and K$_2$B$_4$O$_7$·4H$_2$O becomes smaller. MgB$_4$O$_7$·9H$_2$O can be more easily separated at high temperature. On the univariant curve CE, the water content changes obviously with the increase of $J$ (K$_2$B$_4$O$_7$) from 20750 to 4210, and the refractive index increase obviously until it reaches the maximum at the invariant point E from 1.3395 to 1.3961, and the density decrease first and then increase with the increase of $J$ (K$_2$B$_4$O$_7$).

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