Research Article

Phase Equilibria and Phase Diagrams for the Ternary Aqueous System Containing Lithium, Sodium, and Pentaborate Ions at 298.15 and 323.15 K and 101.325 kPa

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Phase equilibria and phase diagrams for the ternary aqueous system containing lithium, sodium, and pentaborate ions at 298.15 and 323.15 K and 101.325 kPa were investigated by the methods of isothermal dissolution equilibrium. From the experimental data, the phase diagrams and the diagrams of physicochemical properties versus composition of lithium pentaborate in the equilibrium systems were plotted, respectively. The phase diagrams of the ternary system LiB5O8 + NaB5O8 + H2O at two temperatures contain one invariant point, two univariant curves, and two crystallization regions corresponding to sodium pentaborate pentahydrate (NaB5O8·5H2O) and lithium pentaborate pentahydrate (LiB5O8·5H2O). Due to the different dissolution behaviors of pentaborate salts in the aqueous systems, the component of LiB5O8 has a relatively strong effect on the solubility of NaB5O8. It was found that this system belongs to a simple eutectic type at two temperatures, and neither double salts nor solid solutions were formed. The densities and refractive indices in the ternary system at 298.15 and 323.15 K are as similar as changing regularly with the increase of LiB5O8 concentration. On the basis of empirical equations of the density and refractive index in electrolytes, the calculated values of density and refractive index agreed well with the experimental values at both temperatures.

1. Introduction

Borates not only occupy an important role in the modern inorganic salt industry but also have been widely used in electronic manufacturing, new type of electrode materials, and nonlinear optical materials for their excellent characteristics, so the demand for borates is sharply increasing nowadays [1–3]. Due to the rapid depletion of solid boron mineral resources, the comprehensive exploitation for brine resources such as salt lake brines, underground brines, and geothermal waters has become the research hotspots around the world at present [4]. The phase diagram and phase equilibrium as well as the corresponding physicochemical properties are essential to give a theoretical guidance for exploiting the available brine resources and describing the thermodynamic behaviors for the salt minerals. It is well known that salt lake brine located in the Qaidam Basin of Qinghai-Tibet Plateau is famous for its high concentrations of lithium, sodium, potassium, and boron. Therefore, it is highly desirable to study the phase equilibria and phase diagram for the systems containing lithium, sodium, and boron [5, 6].

In recent years, lots of phase diagram containing borates including LiBO2 + CaB2O4 + H2O at 288.15 and 298.15 K [7], MgCl2 + MgSO4 + MgB2O4 + H2O at 323.15 K [8], MgB2O7 + Na2B4O7 + LiB4O7 + H2O at 288 K [9], K2B4O7 + Na2B4O7 + Li2B4O7 + H2O at 273 K [10], MgCl2 + MgB2O4 + H2O and MgSO4 + MgB2O4 + H2O at 323 K [11], and LiB4O7 + MgB2O7 + H2O and K2B4O7 + MgB4O7 + H2O at 273 K [12] have been reported. The existed forms of borates...
2. Experimental

2.1. Reagents and Apparatus. The chemicals used in this work are shown in Table 1. And, LiB₅O₈·5H₂O and NaB₅O₈·5H₂O were successfully synthesized in our laboratory based on the method described previously in detail [13]. In brief, to the molar ratio of LiOH·H₂O : H₃BO₃·H₂O = 1 : 5 : 10 and Na₂B₄O₇·H₂O : H₂O = 1 : 5 : 10, a certain amount of LiOH·H₂O or Na₂B₄O₇·10H₂O, H₃BO₃, and fresh CO₂-free deionized distilled water (DDW) were added in two beakers to synthesize LiB₅O₈·5H₂O and NaB₅O₈·5H₂O, respectively. Then, they were stirred for homogeneity at room temperature, and then transferred into two reactors to react for 7 days at 60°C under stirring with 200 rpm, respectively. Finally, LiB₅O₈·5H₂O and NaB₅O₈·5H₂O were produced after separation, filtration, washing and recrystallization, and drying at 35°C for use. And the synthetic samples were analyzed by chemical analysis and identified by the X-ray diffraction, and the results are shown in Table 1 and Figures 1 and 2, respectively. From the XRD patterns, it is shown that the peak positions and intensities of the synthesized chemicals LiB₅O₈·5H₂O and NaB₅O₈·5H₂O agree well with that of the standard samples. The DDW produced using a deionizer (ULUP-II-10T Sichuan Ulupure Co. Ltd., China) with conductivity less than 1×10⁻⁴ S·m⁻¹ and pH = 6.60 at 298.15 K was used during the whole experiment [14].

A magnetic stirring thermostatic water bath (HXC-500-6A, Beijing Fortune Joy Science Technology Co. Ltd, China) was employed for controlling the temperature with a precision of ±0.1 K for the phase equilibrium experiments. The refractive indices (n_D) were measured by an Abbe refractometer (Abbeimat 550, Anton Paar, Austria) with an uncertainty of ±0.0003. The densities (ρ) were measured using a digital U-tube densimeter (DMA 4500, Anton Paar, Austria) with an uncertainty of ±0.5 mg·cm⁻³. The standard uncertainties u(x) for pressure, temperature, and composition are u(ρ) = 5 kPa, u(T) = 0.1 K, u(LiB₅O₈) = 0.00063, and u(NaB₅O₈) = 0.00060. An X-ray diffractometer (MSAL XD-3, Beijing Purkinje Instrument Co. Ltd, China) was used to identify the solid phase [15].

2.2. Experimental Methods. The solid-liquid phase equilibrium of the ternary system LiB₅O₈ + NaB₅O₈ + H₂O at 298.15 and 323.15 K was studied by the isothermal dissolution equilibrium method as described previously [16]. On the basis of the binary solubility, a series of artificial synthetic complexes were prepared by mixing lithium pentaborate and sodium pentaborate with DDW. Then, complexes were put into the sealed polyethylene plastic bottles, which were placed in magnetic stirring thermostatic water baths with continuous stirring in order to accelerate the establishment of equilibrium states, and the temperatures were automatically controlled for T = 298.15 ± 0.1 and 323.15 ± 0.1 K using magnetic stirring thermostatic water baths, respectively. Then, the composition of the liquid phase in the bottle was determined by the mannitol gravimetric method with sodium hydroxide standard solution and the mixture indicator of methyl red and phenolphthalein with an uncertainty of 0.0005 in mass fraction. The concentration of Li⁺ and Na⁺ was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leman Corporation, America. Precision: ±0.01), and then evaluated using ion balance [18].

2.3. Analytical Methods. The borate ion concentration was determined by the mannitol gravimetric method with sodium hydroxide standard solution and the mixture indicator of methyl red and phenolphthalein with an uncertainty of 0.0005 in mass fraction. The concentration of Li⁺ and Na⁺ was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leman Corporation, America. Precision: ±0.01), and then evaluated using ion balance [18].

3. Results and Discussion

In order to evaluate and test the reliability of the experimental method in this work, a comparison of the solubilities in the boundary subsystems NaB₅O₈ + H₂O at 298.15 and 323.15 K in literature [19] is summarized in Table 2. The results show that the experimental results in this work agree well with previous reports, demonstrating that our experimental procedure and results are rational and reliable. The experimental solubilities and the relevant physicochemical properties including density and refractive index for the ternary systems LiB₅O₈ + NaB₅O₈ + H₂O at 298.15 and 323.15 K and 101.325 kPa are presented in Table 3, respectively. The composition of the liquid phase was expressed in mass fraction.

3.1. Solubilities of the Binary Systems LiB₅O₈ + H₂O and NaB₅O₈ + H₂O at 298.15 and 323.15 K. The solubilities of binary systems LiB₅O₈ + H₂O and NaB₅O₈ + H₂O at 298.15 and 323.15 K were firstly obtained by the isothermal dissolution equilibrium method in this work. As shown in Table 2, the solubilities of lithium pentaborate in the binary systems LiB₅O₈ + H₂O at 298.15 and 323.15 K in mass fraction of 100w were 14.00 and 22.19, respectively. Analogously, the solubilities of sodium pentaborate in the binary systems NaB₅O₈ + H₂O at 298.15 and 323.15 K in mass fraction of 100w were 12.23 and 20.73, respectively.
Table 1: Chemical samples used in this study.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Initial mass fraction</th>
<th>Purification method</th>
<th>Final mass fraction</th>
<th>Analytical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃BO₃</td>
<td>b A.R.</td>
<td>0.99</td>
<td>No further purification</td>
<td>—</td>
<td>Gravimetric method for B(OH)₃</td>
</tr>
<tr>
<td>LiOH·H₂O</td>
<td>a A.R.</td>
<td>0.99</td>
<td>No further purification</td>
<td>—</td>
<td>Titration method for OH⁻</td>
</tr>
<tr>
<td>Na₂B₄O₇·10H₂O</td>
<td>b A.R.</td>
<td>0.99</td>
<td>No further purification</td>
<td>—</td>
<td>Gravimetric method for B₄O₇²⁻</td>
</tr>
<tr>
<td>LiB₅O₈·5H₂O</td>
<td>a A.R.</td>
<td>0.99</td>
<td>Recrystallization</td>
<td>0.998</td>
<td>Gravimetric method for B₅O₈⁻</td>
</tr>
<tr>
<td>NaB₅O₈·5H₂O</td>
<td>a A.R.</td>
<td>0.99</td>
<td>Recrystallization</td>
<td>0.998</td>
<td>Gravimetric method for B₅O₈⁻</td>
</tr>
</tbody>
</table>

a A.R. from the Shanghai Macklin Biochemical Co. Ltd. b A.R. from the Simopharm Chemical Reagent Co. Ltd. c A.R. synthesized in our laboratory.

Figure 1: X-ray diffraction pattern of NaB₅O₈·5H₂O.

Figure 2: X-ray diffraction pattern of LiB₅O₈·5H₂O.

Table 2: Solubilities in the binary subsystems NaB₅O₈ + H₂O at 298.15 and 323.15 K and 0.1 MPa.a

<table>
<thead>
<tr>
<th>Binary system</th>
<th>T (K)</th>
<th>Solubility (100w⁻)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaB₅O₈ + H₂O</td>
<td>298.15</td>
<td>12.20</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>21.80</td>
<td></td>
</tr>
</tbody>
</table>

aStandard uncertainties u are u(T) = 0.1 K and u(p) = 5 kPa. u(w) for NaB₅O₈ is 0.00060 in mass fraction. w is the mass fraction.
Obviously, the solubilities of single salts of LiB$_5$O$_8$ or NaB$_5$O$_8$ increase with the increasing of temperature.

### 3.2. Phase Diagrams of the Ternary System LiB$_5$O$_8$ + NaB$_5$O$_8$ + H$_2$O at 298.15 and 323.15 K

From the experimental data in Table 2, the phase diagrams and part enlargement diagrams for the ternary system at 298.15 and 323.15 K are shown in Figures 3 and 4. In Figures 3 and 4, it can be clearly seen that they are all in one invariant point corresponding to $E_1$ at 298.15 K and $E_2$ at 323.15 K, i.e., cosaturated with LiB$_5$O$_8$:5H$_2$O and NaB$_5$O$_8$:5H$_2$O, two univariant solubility curves of $A_1E_1$ and $B_1E_1$ at 298.15 K, $A_1E_2$ and $B_2E_2$ at 323.15 K, and two crystallization regions corresponding to LiB$_5$O$_8$:5H$_2$O and NaB$_5$O$_8$:5H$_2$O respectively. In addition, due to the difference of the solubilities, the area of crystallization region for NaB$_5$O$_8$:5H$_2$O is relatively larger than that for LiB$_5$O$_8$:5H$_2$O at both temperatures. The composition for the two invariant points of LiB$_5$O$_8$ and NaB$_5$O$_8$ in the liquid phase in mass fraction of 100$\omega$ is 9.87 and 4.69 at 298.15 K and 14.80 and 7.60 at 323.15 K, respectively. The points $A_1$, $A_2$, and $B_1$, $B_2$ present the solubilities of the binary systems LiB$_5$O$_8$+H$_2$O and NaB$_5$O$_8$+H$_2$O at two temperatures, respectively. At both temperatures, the component of NaB$_5$O$_8$ in the ternary system is decreased sharply with the increase of LiB$_5$O$_8$ concentration in the solution, so it indicates that the component of lithium pentaborate existing in the solution has a strong salting-out effect of NaB$_5$O$_8$. The same coexisted equilibrium solid phases in the invariant points $E_1$ and $E_2$ identified by the powder X-ray diffraction are presented in Figure 5. A comparison for the ternary system LiB$_5$O$_8$ + NaB$_5$O$_8$ + H$_2$O at 298.15 and 323.15 K shows is shown in Figure 6. It can be clearly seen that the solubilities for the ternary system LiB$_5$O$_8$ + NaB$_5$O$_8$ + H$_2$O increased with the increase of temperature, but the crystallization regions for LiB$_5$O$_8$:5H$_2$O and NaB$_5$O$_8$:5H$_2$O did not change obviously with changing temperature. And, this ternary system at two temperatures belongs to a simple eutectic type, and neither double salts nor solid solutions were formed.

### 3.3. Refractive Index and Density Calculation

According to the semiempirical formulas of electrolyte aqueous solution with density and refractive index employed by Deng et al. [20], shown as equations (1) and (2), the density and refractive index of the experimental solution were calculated, and the results are listed in Table 3.

\[
\ln \frac{\rho}{\rho_0} = \sum A_i \times w_i, \quad (1)
\]

\[
\ln \frac{n_0}{n_i} = \sum B_i \times w_i, \quad (2)
\]

where $\rho$ and $\rho_0$ are the density of solution and pure water at the same temperature and $n_0$ and $n_i$ represent the refractive index of the solution and pure water at the same temperature, respectively. The $\rho_0$ values at 298.15 and 323.15 K are 0.997041 and 0.988038 g cm$^{-3}$, respectively; the $n_0$ values at 298.15 and 323.15 K are 1.33250 and 1.32904, respectively; and $w_i$ is the component same as Table 2. $A_i$ and $B_i$ represent the coefficients for the solid phase $i$ in this system. The $A_i$ and $B_i$ for LiB$_5$O$_8$ and NaB$_5$O$_8$ are shown in Table 4, and the maximal relative deviation of density

### Table 3: Solubilities, refractive indices, and densities for ternary system LiB$_5$O$_8$ + NaB$_5$O$_8$ + H$_2$O.

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition of liquid phase (100$\omega$)</th>
<th>Density, $\rho$ (g cm$^{-3}$)</th>
<th>Refractive index, $n_0$</th>
<th>Equilibrium solid phase$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiB$_5$O$_8$</td>
<td>NaB$_5$O$_8$</td>
<td>Exp. Value</td>
<td>Cal. Value</td>
</tr>
<tr>
<td>1,A</td>
<td>14.00</td>
<td>0.00</td>
<td>1.10136</td>
<td>1.096286</td>
</tr>
<tr>
<td>2</td>
<td>13.71</td>
<td>1.92</td>
<td>1.10231</td>
<td>1.08264</td>
</tr>
<tr>
<td>3</td>
<td>13.12</td>
<td>2.57</td>
<td>1.10473</td>
<td>1.08647</td>
</tr>
<tr>
<td>4</td>
<td>11.77</td>
<td>3.78</td>
<td>1.10618</td>
<td>1.107469</td>
</tr>
<tr>
<td>5,E</td>
<td>9.87</td>
<td>4.69</td>
<td>1.10757</td>
<td>1.099968</td>
</tr>
<tr>
<td>6</td>
<td>4.52</td>
<td>8.88</td>
<td>1.09087</td>
<td>1.090923</td>
</tr>
<tr>
<td>7</td>
<td>3.48</td>
<td>9.64</td>
<td>1.08973</td>
<td>1.088776</td>
</tr>
<tr>
<td>8</td>
<td>0.96</td>
<td>12.12</td>
<td>1.08658</td>
<td>1.088226</td>
</tr>
<tr>
<td>9,B</td>
<td>0.00</td>
<td>12.23</td>
<td>1.08213</td>
<td>1.081964</td>
</tr>
</tbody>
</table>

$^a$Standard uncertainties $u$ are $u(T) = 0.1$ K and $u(x) = 5$ kPa. $u(x)$ for LiB$_5$O$_8$ and NaB$_5$O$_8$ are 0.00063 and 0.00060 in mass fraction. $u(x)$ for $\rho$ and $n_0$ are 0.5 mg cm$^{-3}$ and 0.0003, respectively. $b$ $\omega$ is the mass fraction. $c$ NB5, NaB$_5$O$_8$:5H$_2$O; LB5, LiB$_5$O$_8$:5H$_2$O.
between experimental and calculated values was 0.0084, as for the refractive index, the deviation was less than 0.0013, which indicates that the physicochemical properties obtained are reliable. On the basis of the data of physicochemical property (including densities and refractive indices) in Table 2, the diagrams of physicochemical properties (density and refractive index) versus the composition of lithium pentaborate in the solution are plotted in Figures 7 and 8, respectively. It could be clearly seen that the density and refractive index changed regularly with the changing of lithium pentaborate concentration in the ternary system at two temperatures, which was increased, and then decreased as the increasing of the concentration of lithium pentaborate concentration, and show a similar changing tendency.

![Figure 3: Phase diagram and part enlargement of the compositions of the ternary system LiB₅O₈ + NaB₅O₈ + H₂O at 298.15 K; ○, experimental points at 298.15 K; —, solubility curve at 298.15 K.](image1)

![Figure 4: Phase diagram for the ternary system LiB₅O₈ + NaB₅O₈ + H₂O at 323.15 K; •, experimental points at 323.15 K; —, solubility curve at 323.15 K.](image2)
4. Conclusions

Phase equilibria and phase diagrams for the ternary systems of LiB$_5$O$_8$ + NaB$_5$O$_8$ + H$_2$O at 298.15 and 323.15 K were studied by the isothermal dissolution equilibrium method, and the solubilities and relevant physicochemical properties including density and refractive index were firstly obtained. For this system at two temperatures, the phase diagrams contain one invariant point, two univariant solubility curves, and two crystallization regions corresponding to LiB$_5$O$_8$·5H$_2$O and NaB$_5$O$_8$·5H$_2$O, and the area of crystallization region of NaB$_5$O$_8$·5H$_2$O at each temperature is relatively larger than that of LiB$_5$O$_8$·5H$_2$O. This ternary system at two temperatures belongs to simple eutectic type, and

\begin{table}
\centering
\begin{tabular}{cccc}
\hline
$T$ (K) & LiB$_5$O$_8$ & NaB$_5$O$_8$ & coefficient $A_i$
\hline
298.15 & 0.006777954 & 0.006683650 & 0.006777954
 & 0.001063948 & 0.000934748 & 0.001063948
323.15 & 0.006753151 & 0.006503464 & 0.006753151
 & 0.000967555 & 0.000922052 & 0.000967555
\hline
\end{tabular}
\caption{Coefficients of densities and refractive indices in the ternary system LiB$_5$O$_8$ + NaB$_5$O$_8$ + H$_2$O at 298.15 and 323.15 K and 0.1 MPa.}
\end{table}

*Standard uncertainties $u(x)$ are $u(T) = 0.1$ K and $u(p) = 5$ kPa.

4. Conclusions

Phase equilibria and phase diagrams for the ternary systems of LiB$_5$O$_8$ + NaB$_5$O$_8$ + H$_2$O at 298.15 and 323.15 K were studied by the isothermal dissolution equilibrium method, and the solubilities and relevant physicochemical properties including density and refractive index were firstly obtained. For this system at two temperatures, the phase diagrams contain one invariant point, two univariant solubility curves, and two crystallization regions corresponding to LiB$_5$O$_8$·5H$_2$O and NaB$_5$O$_8$·5H$_2$O, and the area of crystallization region of NaB$_5$O$_8$·5H$_2$O at each temperature is relatively larger than that of LiB$_5$O$_8$·5H$_2$O. This ternary system at two temperatures belongs to simple eutectic type, and
neither double salts nor solid solution was found. The density and refractive index in the two ternary systems at 298.15 and 323.15 K increased firstly and then decreased with increasing of LiB₅O₈ concentration. In addition, the density and refractive index for salt-water electrolytes were theoretically calculated by empirical equations, which agree well with the experimental values.

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.

Acknowledgments
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