Density, pH, and Boron Species in the Ternary System NaBO$_2$–Na$_2$SO$_4$–H$_2$O at 298.15 K and 323.15 K

Xiaohui Song, Shuaiqi Sun, Lingzong Meng, Rongjian Ying, Yafei Guo, and Tianlong Deng

1 School of Chemistry Engineering, Linyi University, Linyi 276000, China
2 Tianjin Key Laboratory of Marine Resources and Chemistry, Tianjin University of Science and Technology, Tianjin 300457, China

Correspondence should be addressed to Lingzong Meng; menglingzong@lyu.edu.cn, Rongjian Ying; yingrongjian@lyu.edu.cn, and Tianlong Deng; tldeng@tust.edu.cn

Received 28 September 2021; Revised 10 November 2021; Accepted 13 November 2021; Published 13 December 2021

1.Introduction

The Qaidam Basin in Qinghai Province is rich in boron resources. Boron is usually distributed in liquid brine boron deposits and solid borate deposits [1]. With the continuous development of social progress and high-tech, borates are widely used in glass production, agricultural and sideline products, and pharmaceuticals, and the application of boron-containing compounds is in aerospace and defense construction [2]. Borates are gaining more and more attention, and global demand for boron will continue to grow over time [3]. In chemical engineering, the formation conditions and transformation rules of borate and hydrated borate crystals were expounded, and borate minerals were comprehensively developed and utilized to select the optimal extraction process [4]. In the last century, high-quality solid boron deposits were almost depleted. Therefore, it is urgent to solve the problem of developing liquid boron resources in western China as soon as possible. Aqueous boron species can be found in natural waters, including seawater, salt lakes, oilfield brine, and hydrothermal fluids [5].

The behavior of borate solution extremely complicated, and it can exist in several different species in aqueous solution, such as metaborate B(OH)$_4^-$, B$_2$O$_6$(OH)$_2^{2-}$, B$_3$O$_6$(OH)$_4^{-}$, B$_5$O$_6$(OH)$_4^{-}$, and B$_6$O$_7$(OH)$_6^{2-}$ [6, 7]. The concentrations of various boron species in different aqueous borate solution can be calculated theoretically by the Pitzer model. In the quaternary system NaCl–NaBO$_2$–Na$_2$SO$_4$–H$_2$O at 298.15 K, the distributions of boron species in the liquid phase were calculated with the Pitzer model [8]. The main boron species in the mixed borate solution are B(OH)$_4^-$ and B$_4$O$_5$(OH)$_4^{2-}$. The concentrations of boron species in the system NaCl–NaSO$_4$–NaBO$_2$–H$_2$O were also calculated in our previous work [9]. The preponderant boron species is B(OH)$_4^-$, whose mole fraction is more than 0.95. The calculated results for distribution of boron species in the system KCl–K$_2$SO$_4$–K$_2$B$_2$O$_7$–H$_2$O at 298.15 K show that the mole fraction of the boron species is...
mainly affected by the concentration of boron but no other anions in the solution [10].

Boron form depends on boron concentration, pH, temperature, and ionic strength [11]. With the pH values in the solution and equilibrium constant between different boron species, the distribution of boron species was calculated [12–15]. The calculated results in these literatures [13, 14] are in agreement with those with the Pitzer model in the systems NaBO₂–H₂O and K₂B₂O₇–H₂O [9, 10]. The concentration of boron species was calculated in references [12–15], and it was considered that the activity coefficients of all boron ions were 1.0. Although the calculation may not be correct, the calculated results can also describe the distribution of boron species in the solution.

The total boron concentration, pH value, metal cations, and temperature in the medium all affect the existence form and equilibrium relationship of borate anions, among which the total boron concentration and pH value are particularly important. At present, there are relatively few studies on the distribution of chemical species in the solution of multiple systems. NaBO₂ is an important boron compound, especially in the industrial production of NaBH₄ [16, 17], and it is a promising hydrogen solid carrier due to its easy hydrolysis and adjustable hydrogen release [18]. The physicochemical properties and distribution in the system NaBO₂–H₂O were presented [13], and the distributions for boron species in the mixed system Na₂SO₄–NaBO₂–H₂O at 298.15 K were also calculated with the Pitzer model [9]. However, the physicochemical properties including pH and density in the system were not reported. The distribution balance of boron species in the solution changes with temperature. In this work, the pH values and density values of the system Na₂SO₄–NaBO₂–H₂O at 298.15 K and 323.15 K were measured, and the distribution of boron species was also calculated.

2. Experimental

2.1. Materials and Apparatus. The chemical reagents used in this experiment are given in Table 1. Experimental water was deionized water (DDW) with the conductivity less than 1.2·10⁻⁴ S·m⁻¹ and pH = 6.60 at 298.15 K. The values of pH were determined by an imported pH meter (Orion 310P-01A from US, the accuracy of ±0.001 for pH determination).

2.2. Experimental Method. To affirm the effect from Na₂SO₄ to the boron species distribution in the system NaBO₂–Na₂SO₄–H₂O, the mix solution with different ratios of Na₂SO₄ and NaB(OH)₃ (m(Na₂SO₄)/m(NaB(OH)₃)) was prepared. First, the saturated solution in the systems NaBO₂–H₂O and Na₂SO₄–H₂O was prepared, respectively. Then, the mixed solution with different ratios of Na₂SO₄ and NaB(OH)₃ was prepared by mixing the two saturated solutions and DDW according to the solubility data of the NaBO₂–Na₂SO₄–H₂O ternary system at 298.15 K and 323.15 K [19, 20]. The concentration of NaBO₂ and Na₂SO₄ was tabulated, as shown in Figure 1.

The mixed solution was then used for physicochemical property measurement. The densities (ρ) were measured using a density bottle with an uncertainty less than ±0.002 g·cm⁻³. The pH values were measured three times with the pH meter, and the uncertainty between the measurement results is 0.002. The concentration of SO₄²⁻ was determined by the barium sulfate gravimetric method, and the relative error is less than ±0.0005 [21]. The concentration of BO₃⁻ was obtained by the modified mannitol gravimetric method [21, 22] with the relative error less than 0.003.

3. Results and Discussion

3.1. Density. The density values of the NaBO₂–Na₂SO₄–H₂O ternary system at 298.15 K and 323.15 K are given in Tables 2 and 3, respectively. The density diagrams with the concentration of boron (m(B)) as the abscissa were plotted, as shown in Figure 2. In the same ratio of Na₂SO₄ and NaB(OH)₃, the densities increase as m(B) increases, as shown in Figure 2. The densities also increase at the same concentration of one salt as the concentration of the other salt increases. However, the densities decrease at the same concentration with the increase of temperature. With the changing trends in the density diagrams, shown in Figure 2, the densities can be used to roughly estimate the concentrations of Na₂SO₄ and NaB(OH)₃ in the ternary system.

3.2. pH Data and Boron Species Distribution. The experimental pH of the NaBO₂–Na₂SO₄–H₂O ternary system with different ratios is given in Tables 2 and 3. From the pH data, the pH diagrams are shown in Figure 3 to show the relationship between m(B) and pH at 298.15 K and 323.15 K. On the same scale, the pH value increases with the increase of the total boron concentration. But more than 1.2 mol·kg⁻¹·H₂O growth rate showed a downward trend. On the same total boron concentration line, the pH value decreases with the increase of Na₂SO₄ mole fraction. The data show that the pH of the solution in the system NaBO₂–Na₂SO₄–H₂O is mainly affected by m(B). The mole fraction of Na₂SO₄ for hydrolysis is lesser than that of NaBO₂.

From the literature [12–15], B(OH)₃ was assumed as the reactants B(OH)₅⁻, B₂O₅(OH)₆⁻, B₂O₅(OH)₆²⁻, B₄O₉(OH)₆⁻, and B₂O₆(OH)₄⁻ were formed with B(OH)₃ and H₂O. The reaction equation between boron species can be represented as

$$pB(OH)_3 + nH_2O = B_p(OH)_{n-p}^- + qH^+$$

(1)

The ion equilibrium constants among different boron species were reported under different ionic strengths in different media by potentiometric titration of hydrogen electrode. According to the calculation method in the literature [12–15], the total boron concentration, the measured pH value, and the equilibrium constant are mentioned in the literature [23, 24], as shown in equation (2). The mole fractions of different boron species were calculated using equation (3).
Table 1: Chemical reagents in this work.

| Chemical   | CAS reg. no. | Source                                      | Mass fraction purity | Analysis method |
|------------|--------------|---------------------------------------------|----------------------|-----------------|
| NaBO₂·4H₂O | 10555-76-7   | Aladdin Industrial Corp., China             | 0.990                | Analysis for BO₂⁻ |
| Na₂SO₄     | 7757-82-6    | Sinopharm Chemical Reagent Co., Ltd., China | 0.990                | Analysis for SO₄²⁻ |

In equation (2), \( K_{11}, K_{31}, K_{132}, K_{322}, \) and \( K_{31} \) represent the equilibrium constant equations for \( \text{B(OH)}_4^- \), \( \text{B}_2\text{O}_3(\text{OH})_4^- \), \( \text{B}_3\text{O}_3(\text{OH})_5^{2-} \), \( \text{B}_4\text{O}_5(\text{OH})_4^{2-} \), and \( \text{B}_5\text{O}_6(\text{OH})_4^- \). The relationship between molar fraction of different boron species and total boron concentration is shown in Figure 4.

The mole fraction \( x \) of \( \text{B(OH)}_4^- \) in the mixed solution at 298.15 K is no less than 0.98 in the concentration range (0.1349–3.3448 mol·kg⁻¹). The \( x(\text{B(OH)}_4^-) \) can reach about 0.01 when \( m(\text{B}) \) is less than 0.14 mol·kg⁻¹, but decreases to a very small value with the increase of \( m(\text{B}) \). \( x(\text{B(OH)}_4^-) \) will be no more than 0.001 if the \( m(\text{B}) \) is more than 1.3 mol·kg⁻¹. The \( x \) for \( \text{B}_2\text{O}_3(\text{OH})_4^{2-} \) increases as \( m(\text{B}) \) increases and reach about 0.11 when \( m(\text{B}) \) is about 4.0 mol·kg⁻¹. The mole fraction for \( \text{B}_2\text{O}_3(\text{OH})_4^- \) is always below 0.0005 and can be neglected. The \( x(\text{B}_2\text{O}_3(\text{OH})_4^-) \) is about 1.0 × 10⁻³, which can be considered that \( \text{B}_2\text{O}_3(\text{OH})_4^- \) does not exist in the mixed solution at 298.15 K. In Figure 3(b), the dominant boron species is also \( \text{B(OH)}_4^- \), but \( x(\text{B(OH)}_4^-) \) decreases as the concentration of total boron increases. \( x(\text{B(OH)}_4^-) \) is no less than 0.95 when \( m(\text{B}) \) is less than 1.2 mol·kg⁻¹. \( x(\text{B}_2\text{O}_3(\text{OH})_4^-) \) maintains no less than 0.85 when the \( m(\text{B}) \) is more than 1.2 mol·kg⁻¹. \( x(\text{B}_2\text{O}_3(\text{OH})_5^{2-}) \) shows an up trend and can occupy about 0.1 when \( m(\text{B}) \) is more than 2.4 mol·kg⁻¹. \( x(\text{B}_2\text{O}_3(\text{OH})_5^{2-}) \) also increase as \( m(\text{B}) \) increases and can reach the maximum data about 0.02. \( x(\text{B}_3\text{O}_3(\text{OH})_5^-) \) decreases as \( m(\text{B}) \) increases. If \( m(\text{B}) \) is greater than 0.5 mol·kg⁻¹, \( x(\text{B}_3\text{O}_3(\text{OH})_5^-) \) will not exceed 0.005. \( x(\text{B}_3\text{O}_3(\text{OH})_5^-) \) is always lower than 0.0015 and can be ignored in the solution. \( \text{B}_5\text{O}_6(\text{OH})_4^- \) in the solution can also be considered to be nonexistent at 323.15 K.

From the changing trend for the six boron species in the mixed solution in the system NaBO₂–Na₂SO₄–H₂O at 298.15 K and 323.15 K, the boron species may react with the equations (4)–(7). The reaction is shown in Figure 5.
Figure 1: The concentration in the system Na$_2$SO$_4$–NaBO$_2$–H$_2$O at different temperatures. Black dotted line, 298.15 K [13]; brown dotted line, 323.15 K [14]. This work: black solid line, $m$(Na$_2$SO$_4$): $m$(NaB(OH)$_4$) = 1:8; red solid line, $m$(Na$_2$SO$_4$): $m$(NaB(OH)$_4$) = 1:4; blue solid line, $m$(Na$_2$SO$_4$): $m$(NaB(OH)$_4$) = 3:8; green solid line, $m$(Na$_2$SO$_4$): $m$(NaB(OH)$_4$) = 1:2.

Table 2: Density and pH values in the system NaBO$_2$–Na$_2$SO$_4$–H$_2$O at 298.15 K.

| $m$(B) (mol·kg$^{-1}$·H$_2$O) | $m$(SO$_4$²⁻) | $\rho$/g·cm$^{-3}$ | experimental | pH      |
|---------------------------|---------------|-------------------|--------------|---------|
| 3.3448                    | 0.4633        | 1.2662            |              | 12.599  |
| 3.0581                    | 0.4446        | 1.2315            |              | 12.483  |
| 2.5537                    | 0.6161        | 1.1989            |              | 12.375  |
| 2.2157                    | 0.5467        | 1.1748            |              | 12.295  |
| 1.7677                    | 0.2139        | 1.1511            |              | 12.174  |
| 1.3498                    | 0.2473        | 1.1405            |              | 12.101  |
| 1.2175                    | 0.0580        | 1.1260            |              | 12.085  |
| 1.0604                    | 0.0873        | 1.1189            |              | 12.044  |
| 0.8267                    | 0.1203        | 1.1012            |              | 11.890  |
| 0.5299                    | 0.1195        | 1.0836            |              | 11.675  |
| 0.3675                    | 0.0963        | 1.0585            |              | 11.470  |
| 0.2419                    | 0.0498        | 1.0300            |              | 11.280  |
| 0.1349                    | 0.0219        | 1.0125            |              | 11.080  |
| 2.8124                    | 0.6591        | 1.2648            |              | 12.408  |
| 2.1781                    | 0.5638        | 1.2117            |              | 12.258  |
| 1.8646                    | 0.4336        | 1.1955            |              | 12.164  |
| 1.6635                    | 0.4156        | 1.1798            |              | 12.085  |
| 1.3954                    | 0.4710        | 1.1547            |              | 12.043  |
| 1.2528                    | 0.0745        | 1.1536            |              | 11.951  |
| 1.0949                    | 0.1603        | 1.1415            |              | 11.910  |
| 0.9543                    | 0.1652        | 1.1265            |              | 11.846  |
| 0.7217                    | 0.1868        | 1.1098            |              | 11.620  |
| 0.5193                    | 0.1836        | 1.0927            |              | 11.536  |
| 0.3362                    | 0.0883        | 1.0724            |              | 11.350  |
| 0.2375                    | 0.0643        | 1.0568            |              | 11.204  |
| 0.1368                    | 0.0513        | 1.0451            |              | 11.040  |
| 2.4851                    | 0.8987        | 1.2722            |              | 12.252  |
| 2.2952                    | 0.8514        | 1.2447            |              | 12.185  |
| 1.9784                    | 0.8157        | 1.2185            |              | 12.042  |
| 1.5674                    | 0.6249        | 1.1918            |              | 11.887  |
Table 2: Continued.

| m(B) | m(SO$_4^{2-}$) | ρ/g·cm$^{-3}$ experimental | pH   |
|------|---------------|--------------------------|------|
|      |               |                          |      |
| 1.3967 | 0.7111       | 1.1775                   | 11.828 |
| 1.2624 | 0.1465       | 1.1688                   | 11.788 |
| 1.0448 | 0.2950       | 1.1581                   | 11.689 |
| 0.7611 | 0.3327       | 1.1380                   | 11.523 |
| 0.5837 | 0.2786       | 1.1156                   | 11.368 |
| 0.4402 | 0.2037       | 1.1017                   | 11.230 |
| 0.2303 | 0.0967       | 1.0654                   | 11.036 |
| 0.1376 | 0.0645       | 1.0559                   | 10.940 |
| 2.2852 | 1.2224       | 1.3033                   | 12.248 |
| 1.9585 | 1.0544       | 1.2489                   | 12.108 |
| 1.7230 | 1.0046       | 1.2245                   | 12.034 |
| 1.4765 | 0.8662       | 1.2044                   | 11.901 |
| 1.3592 | 0.9317       | 1.1885                   | 11.893 |
| 1.2443 | 0.1184       | 1.1823                   | 11.843 |
| 1.1513 | 0.2679       | 1.1736                   | 11.781 |
| 0.9507 | 0.3188       | 1.1605                   | 11.690 |
| 0.8249 | 0.3885       | 1.1481                   | 11.605 |
| 0.6131 | 0.4012       | 1.1382                   | 11.480 |
| 0.3738 | 0.2326       | 1.1231                   | 11.259 |
| 0.2341 | 0.1564       | 1.0912                   | 11.080 |

Table 3: Density and pH values in the system NaBO$_2$–Na$_2$SO$_4$–H$_2$O at 323.15 K.

| m/(mol·kg$^{-1}$·H$_2$O) | m(SO$_4^{2-}$) | ρ/g·cm$^{-3}$ | pH   |
|--------------------------|---------------|--------------|------|
|                          |               |              |      |
| 3.7975                   | 0.4724        | 1.2210       | 11.821 |
| 3.3448                   | 0.4633        | 1.1949       | 11.803 |
| 3.0581                   | 0.4446        | 1.1519       | 11.763 |
| 2.5537                   | 0.6161        | 1.1385       | 11.742 |
| 2.2157                   | 0.5490        | 1.1274       | 11.723 |
| 1.7872                   | 0.2139        | 1.1001       | 11.708 |
| 1.3639                   | 0.2477        | 1.0774       | 11.618 |
| 1.2307                   | 0.0502        | 1.0657       | 11.588 |
| 1.0533                   | 0.0879        | 1.0523       | 11.501 |
| 0.8355                   | 0.1040        | 1.0466       | 11.354 |
| 0.5765                   | 0.1002        | 1.0312       | 11.142 |
| 2.8124                   | 0.6591        | 1.2448       | 11.593 |
| 2.1781                   | 0.5638        | 1.2020       | 11.584 |
| 0.3748                   | 0.1127        | 1.0185       | 10.976 |
| 0.2448                   | 0.0580        | 1.0124       | 10.839 |
| 0.1470                   | 0.0258        | 0.9991       | 10.674 |
| 3.3084                   | 0.7658        | 1.2852       | 11.685 |
| 1.8646                   | 0.4336        | 1.1652       | 11.554 |
| 1.6544                   | 0.4229        | 1.1452       | 11.501 |
| 1.4697                   | 0.4710        | 1.1324       | 11.201 |
| 1.2558                   | 0.1484        | 1.1256       | 11.457 |
| 1.0043                   | 0.2114        | 1.1056       | 11.358 |
| 0.7211                   | 0.1898        | 1.0826       | 11.141 |
| 0.5121                   | 0.1360        | 1.0654       | 10.941 |
| 0.3350                   | 0.0894        | 1.0431       | 10.754 |
| 0.2496                   | 0.0577        | 1.0350       | 10.654 |
| 0.1605                   | 0.0432        | 1.0212       | 10.498 |
| 2.9023                   | 0.9895        | 1.2909       | 11.589 |
| 2.6913                   | 0.9667        | 1.2716       | 11.474 |
| 2.4582                   | 0.9062        | 1.2385       | 11.452 |
| 1.9784                   | 0.8157        | 1.2077       | 11.408 |
| 1.5846                   | 0.6249        | 1.1781       | 11.368 |
| 1.4568                   | 0.6578        | 1.1669       | 11.387 |
The distribution of boron species in the system NaBO₂–Na₂SO₄–H₂O at 298.15K was also calculated with the Pitzer model in our previous work [9]. In the calculation [9], x(B(OH)₄⁻) is more than 0.96 in the system NaBO₂–Na₂SO₄–H₂O, which shows that the boron species in the solution in the system can be considered as a single

### Table 3: Continued.

| m (mol·kg⁻¹·H₂O) | m(SO₄²⁻) | ρ (g·cm⁻³) | pH |
|------------------|----------|------------|----|
| 1.2760           | 0.1465   | 1.1562     | 11.327 |
| 1.0560           | 0.2516   | 1.1399     | 11.234 |
| 0.7693           | 0.3327   | 1.1187     | 11.085 |
| 0.5899           | 0.2449   | 1.0982     | 10.833 |
| 0.4972           | 0.2659   | 1.0845     | 10.760 |
| 0.3913           | 0.1306   | 1.0712     | 10.550 |
| 0.2327           | 0.0227   | 1.0513     | 10.550 |
| 0.1526           | 0.0151   | 1.0365     | 10.380 |
| 2.2852           | 1.2224   | 1.2847     | 11.413 |
| 2.1438           | 1.1945   | 1.2696     | 11.387 |
| 2.1061           | 0.9819   | 1.2472     | 11.326 |
| 1.8726           | 0.8800   | 1.2256     | 11.298 |
| 1.4764           | 0.8663   | 1.1905     | 11.253 |
| 1.3634           | 0.9253   | 1.1875     | 11.233 |
| 1.3153           | 0.9486   | 1.1821     | 11.223 |
| 1.1513           | 0.2827   | 1.1727     | 11.204 |
| 0.9609           | 0.3702   | 1.1568     | 11.153 |
| 0.8337           | 0.4002   | 1.1455     | 10.931 |
| 0.5791           | 0.4659   | 1.1174     | 10.754 |
| 0.4363           | 0.3071   | 1.1017     | 10.621 |
| 0.3033           | 0.1717   | 1.0793     | 10.518 |
| 0.1378           | 0.0902   | 1.0641     | 10.331 |

**Figure 2:** The density of mixed solution of the NaBO₂–Na₂SO₄–H₂O system. (a) 298.15K. (b) 323.15K. Black line, m(Na₂SO₄): m(NaB(OH)₄) = 1:8; red line, m(Na₂SO₄): m(NaB(OH)₄) = 1:4; blue line, m(Na₂SO₄): m(NaB(OH)₄) = 3:8; green line, m(Na₂SO₄): m(NaB(OH)₄) = 1:2.

The distribution of boron species in the system NaBO₂–Na₂SO₄–H₂O at 298.15 K was also calculated with the Pitzer model in our previous work [9]. In the...
The concentration of boron species $\text{B(OH)}_3^-$ and $\text{B}_3\text{O}_3\text{(OH)}_4^{-}$ in the solution can be neglected. The comparison of the mole fraction of $\text{B(OH)}_4^{-}$ in the system $\text{NaBO}_2–\text{Na}_2\text{SO}_4–\text{H}_2\text{O}$ at 298.15 K calculated in this work and with the Pitzer model [9] is shown in Figure 6. The results in this work are nearly the same as those calculated by Pitzer.

**Figure 3:** The pH of mixed solution in the $\text{NaB(OH)}_4–\text{Na}_2\text{SO}_4–\text{H}_2\text{O}$ system. (a) 298.15 K. (b) 323.15 K. Black line, $m(\text{Na}_2\text{SO}_4): m(\text{NaB(OH)}_4) = 1:8$; red line, $m(\text{Na}_2\text{SO}_4): m(\text{NaB(OH)}_4) = 1:4$; blue line, $m(\text{Na}_2\text{SO}_4): m(\text{NaB(OH)}_4) = 3:8$; green line, $m(\text{Na}_2\text{SO}_4): m(\text{NaB(OH)}_4) = 1:2$.}

**Figure 4:** Boron species distribution in mixed aqueous solution of $\text{Na}_2\text{SO}_4$ and $\text{NaBO}_2$ at 298.15 K and 323.15 K. $\square$, $\text{B(OH)}_3^-$; $\blacklozenge$, $\text{B}_2\text{O}_3\text{(OH)}_4^{2-}$; $\blacktriangleleft$, $\text{B}_2\text{O}_3\text{(OH)}_5^{2-}$; $\blacksquare$, $\text{B}_2\text{O}_5\text{(OH)}_4^{2-}$; $\blacktriangle$, $\text{B}_2\text{O}_6\text{(OH)}_4^{2-}$.

The concentration of boron species $\text{B(OH)}_3^-$ and $\text{B}_2\text{O}_3\text{(OH)}_4^{2-}$ in the solution can be neglected. The comparison of the mole fraction of $\text{B(OH)}_4^{-}$ in the system $\text{NaBO}_2–\text{Na}_2\text{SO}_4–\text{H}_2\text{O}$ at 298.15 K calculated in this work and with the Pitzer model [9] is shown in Figure 6. The results in this work are nearly the same as those calculated by Pitzer.
with the Pitzer model [9], as shown in Figure 6, which shows that the two methods are reliable for the distribution of boron species calculation. However, there are still some differences for the calculation with the two methods. Only four boron species $\text{B(OH)}_3$, $\text{B(OH)}_4^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ were considered in the Pitzer model because of not enough parameters in the literature [9], but six boron species exist in this work. From the calculated results in this work, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ cannot be neglected in the mixed solution. The activity coefficients for boron species were not considered in this work, but the activity coefficients were calculated with the Pitzer model. The pH values can be calculated with the Pitzer model. However, the calculation cannot be obtained in this work if the pH values were not known. The results from the two methods show a slight difference, but the two methods can both be used to describe the distribution of boron species in the mixed solution.

4. Conclusions

The densities and pH values in the system NaBO$_2$–Na$_2$SO$_4$–H$_2$O at 298.15 K and 323.15 K were investigated in this study. The densities and pH values change gradually with the changing of $m(\text{B})$ and $m(\text{SO}_4^{2-})$. Combining the equilibrium constants for different boron species, the molar fractions of six boron species in the mixed solution were calculated with $m(\text{B})$ and pH values. The distribution of six boron species in mixed solutions was obtained. The mole fractions of boron species are mainly affected by the concentration of total boron and temperature, but rarely affected by the concentration of $\text{SO}_4^{2-}$. The polyborate ions are easier to form as the temperature increases. The dominant boron species in the system NaBO$_2$–Na$_2$SO$_4$–H$_2$O at the two temperatures is $\text{B(OH)}_4^-$. The mole fraction of $\text{B(OH)}_3$ and $\text{B}_3\text{O}_3(\text{OH})_4^-$ can be neglected. $\text{B}_5\text{O}_6(\text{OH})_4^{2-}$ in the
solution in the ternary system can be considered to be nonexistent. In the solubility calculation, it can be considered that there is only one boron species B(OH)_4^- in the system. The calculation of distribution for boron species in this study and those with the Pitzer model can both be used to describe the distribution of boron species in the mixed solution. The results on physicochemical properties and boron species distribution calculation in the system NaBO_2–Na_2SO_4–H_2O can supply theoretical reference for separating sodium metaborate salts from brine and development of universal thermodynamic models of brine systems with various boron species.

**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**

This work was jointly funded by the Natural Science Foundation of Shandong Province, China (ZR2020MB051), National Natural Science Foundation of China (22073068 and U1507112), and Yangtze Scholars and Innovative Research Team of the Chinese University (IRT-17R81).

**References**

[1] C. L. Gao, J. Q. Yu, D. P. Zhan, L. S. Zhang, and A. Y. Chen, "Formation and distribution characteristics of boron resource in salt lakes of Qaidam basin," *Journal of Salt Lake Research*, vol. 17, no. 4, pp. 6–13, 2009.

[2] J. Y. Zhang and Y. J. Wang, "The chemical synthesis, application and prospect of metal borate," *Chemistry and Adhesion*, vol. 43, no. 1, pp. 63–67, 2021.

[3] L. W. Wang, Q. S. Wang, and L. Wu, "Analysis of global exploration situation and potential of boron resources," *China Mining Magazine*, vol. 28, no. 4, pp. 74–78, 2019.

[4] Y. Q. Zhou, Y. Fang, and C. H. Fang, "Structure and research methods of aqueous borate solution," *Journal of Salt Lake Research*, vol. 18, no. 2, pp. 65–72, 2010.

[5] L. J. Gao, S. Y. Xia, S. P. Li, B. Hu, and Z. Hu, "Thermochromy of hydrated magnesium borates," *Journal of Chemical Thermodynamics*, vol. 29, no. 4, pp. 491–497, 1997.

[6] P. Wang, J. J. Kosinski, M. M. Lencika, A. Anderko, and R. D. Springer, "Thermodynamic modeling of boric acid and selected metal borate systems," *Pure and Applied Chemistry*, vol. 85, no. 11, pp. 2117–2144, 2013.

[7] S. Wang, X. Du, Y. Jing, Y. Guo, and T. Deng, "Solid-liquid phase equilibrium in the ternary systems (Li_2B_4O_7 + MgB_2O_4 + H_2O) and (Na_2B_4O_7 + MgB_2O_4 + H_2O) at 298.15 K," *Journal of Chemical & Engineering Data*, vol. 62, no. 1, pp. 253–258, 2017.

[8] L. Chen, X. Yang, Y. Guo, T. Deng, D. Li, and L. Meng, "Solubility determination and thermodynamic modelling of solid-liquid equilibria in the (NaCl + NaBO_2 + Na_2B_4O_7 + H_2O) system at 298.15 K," *The Journal of Chemical Thermodynamics*, vol. 152, Article ID 106283, 2021.

[9] D. Li, Q. Fu, T. Zhang et al., "Thermodynamic modeling of boron species in brine systems containing metaborate and its application in evaporation simulation," *Journal of Materials Research and Technology*, vol. 9, no. 6, pp. 13067–13075, 2020.

[10] D. Li, G. L. Zhou, S. S. Gu et al., "Thermodynamic and dynamic modeling of the boron species in aqueous potassium borate solution," *American Chemical Society Omega*, vol. 5, no. 26, pp. 15895–15842, 2020.

[11] C. H. Fang, Y. Fang, Y. Q. Zhou, F. Y. Zhu, H. Y. Liu, and W. Q. Zhang, "Recent progress on structure of aqueous polyborate solutions," *Journal of Salt Lake Research*, vol. 27, no. 2, pp. 11–40, 2019.

[12] H. Ge, Y. Fang, C. Fang et al., "Density, electrical conductivity, pH, and polyborate distribution of LiB(OH)_4, Li_2B_4O_7(OH)_4, and LiB_2O_4(OH)_4 solutions," *Journal of Chemical & Engineering Data*, vol. 59, no. 12, pp. 4039–4048, 2014.

[13] Y. Zhou, C. Fang, Y. Fang, and F. Zhu, "Volumetric and transport properties of aqueous NaB(OH)_4 solutions," *Chinese Journal of Chemical Engineering*, vol. 21, no. 9, pp. 1048–1056, 2013.

[14] F. Y. Zhu, C. H. Fang, Y. Q. Zhou, H. W. Ge, and H. Y. Liu, "Borate species, densities and conductivities for aqueous KB_2O_8, KBO_2 and KB_2O_4 solutions," *Journal of Salt Lake Research*, vol. 23, pp. 51–61, 2015.

[15] T. Zhang, L. Yang, D. Li, L. Meng, Y. Guo, and T. Deng, "Thermodynamic properties and thermodynamic modelling for aqueous mixed system containing lithium metaborate and sodium metaborate," *The Journal of Chemical Thermodynamics*, vol. 158, Article ID 106446, 2021.

[16] K. Y. Mustafa, A. A. Ceyhan, and Ö. Şahin, "Effects of different temperatures and additives on the metastable zone width precipitation kinetics of NaBO_2," *Russian Journal of Physical Chemistry A*, vol. 88, no. 3, pp. 402–408, 2014.

[17] M. B. Piskin, A. K. Figen, and H. Erguvan, "Investigation of the reaction mechanism and kinetics of production of anhydrous sodium metaborate (NaBO_2) by a solid–state reaction," *Research on Chemical Intermediates*, vol. 39, no. 2, pp. 569–583, 2013.

[18] P. Brack, S. E. Dann, and K. G. U. Wijayantha, "Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride (NaBH_4) solutions," *Energy Science & Engineering*, vol. 3, no. 3, pp. 174–188, 2015.

[19] S. Q. Chen, M. Wang, J. Hu, Y. F. Guo, and T. L. Deng, "Phase equilibria in the aqueous ternary systems (NaCl+NaBO_2+H_2O) and (Na_2SO_4+NaBO_2+H_2O) at 298.15 K and 0.1 MPa," *Journal of Chemical and Engineering Data*, vol. 63, no. 12, pp. 4662–4668, 2018.

[20] L. Yang, X. Yang, D. Li et al., "Solubility measurement and thermodynamic modeling of solid-liquid equilibria in quaternary system NaCl-NaBO_2-BO_2-H_2O at 323.15 K," *The Journal of Chemical Thermodynamics*, vol. 159, Article ID 106472, 2021.

[21] Qinghai institute of salt lakes of CAS, *Analytical Methods of Brines and Salts*, Chinese Science Press, Beijing, China, 2 edition, 1988.

[22] H. W. Ge, Y. Yao, and T. L. Deng, "Study of improvement on mass titration of borate in brine (in Chinese)," *Accounts of Chemical Research*, vol. 29, pp. 112–117, 2017.

[23] J. E. Spessard, "Investigations of borate equilibria in neutral salt solutions," *Journal of Inorganic and Nuclear Chemistry*, vol. 39, no. 2, pp. 569–583, 2013.

[24] R. E. Mesmer, C. F. Baes, and F. H. Sweeton, "Acidity and homogenous catalysts for hydrogengenerationbyhydrolysis of aqueous potassium metaborate (KBO_2) by a solid–state reaction," *Research on Chemical Intermediates*, vol. 39, no. 2, pp. 569–583, 2013.