Research Article

Density, pH, and Boron Species in the Ternary System $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ at 298.15 K and 323.15 K

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The densities and pH values in the system $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ at 298.15 K and 323.15 K were investigated. Combining the equilibrium constants for different boron species, the distributions of six boron species in the mixed solution were calculated with total boron concentration and pH values. The molar fractions of the six boron species are mainly affected by the total boron concentration and temperature, but rarely affected by the concentration of SO_4^{2-} . The dominant boron species in the mixed solution at the two temperatures is $\text{B}(\text{OH})_4^-$. The mole fraction of $\text{B}(\text{OH})_3$, $\text{B}_5\text{O}_6(\text{OH})_4^-$, and $\text{B}_3\text{O}_3(\text{OH})_4^-$ can be neglected. The polyborate ions are easier to form as the temperature increases. The results 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.

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 $\text{B}(\text{OH})_4^-$, $\text{B}_2\text{O}(\text{OH})_6^{2-}$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $\text{B}_5\text{O}_6(\text{OH})_4^-$, and $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ [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 $\text{NaCl--NaBO}_2\text{--Na}_2\text{B}_4\text{O}_7\text{--H}_2\text{O}$ 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 $\text{B}(\text{OH})_4^-$ and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$. The distributions of boron species in the system $\text{NaCl--NaSO}_4\text{--NaBO}_2\text{--H}_2\text{O}$ were also calculated in our previous work [9]. The preponderant boron species is $\text{B}(\text{OH})_4^-$, whose mole fraction is more than 0.95. The calculated results for distribution of boron species in the system $\text{KCl--K}_2\text{SO}_4\text{--K}_2\text{B}_4\text{O}_7\text{--H}_2\text{O}$ 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 $\text{NaBO}_2\text{--H}_2\text{O}$ and $\text{K}_2\text{B}_4\text{O}_7\text{--H}_2\text{O}$ [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. NaBO_2 is an important boron compound, especially in the industrial production of NaBH_4 [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 $\text{NaBO}_2\text{--H}_2\text{O}$ were presented [13], and the distributions for boron species in the mixed system $\text{Na}_2\text{SO}_4\text{--NaBO}_2\text{--H}_2\text{O}$ 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 $\text{Na}_2\text{SO}_4\text{--NaBO}_2\text{--H}_2\text{O}$ at 298.15 K and 323.15 K were presented, 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 double deionized water (DDW) with the conductivity less than $1.2 \cdot 10^{-4} \text{ S} \cdot \text{m}^{-1}$ and $\text{pH} = 6.60$ 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 Na_2SO_4 to the boron species distribution in the system $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$, the mix solution with different ratios of Na_2SO_4 and NaB(OH)_4 ($m(\text{Na}_2\text{SO}_4)/m(\text{NaB(OH)}_4)$) was prepared. First, the saturated solution in the systems $\text{NaBO}_2\text{--H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$ was prepared, respectively. Then, the mixed solution with different ratios of Na_2SO_4 and NaB(OH)_4 was prepared by mixing the two saturated solutions and DDW according to the solubility data of the $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ ternary system at 298.15 K and 323.15 K [19, 20]. The concentration of NaBO_2 and Na_2SO_4 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 $\pm 0.002 \text{ g} \cdot \text{cm}^{-3}$. The pH values were measured three times with the pH meter, and the uncertainty between the measurement results is 0.002. The concentration of SO_4^{2-} was determined by the barium sulfate gravimetric method, and the relative error is less than ± 0.0005 [21]. The concentration of BO_2^- 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 $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ 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 ($m(\text{B})$) as the abscissa were plotted, as shown in Figure 2. In the same ratio of Na_2SO_4 and NaB(OH)_4 , the densities increase as $m(\text{B})$ 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 Na_2SO_4 and NaB(OH)_4 in the ternary system.

3.2. pH Data and Boron Species Distribution. The experimental pH of the $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ 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 $m(\text{B})$ 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 $1.2 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{H}_2\text{O}$ growth rate showed a downward trend. On the same total boron concentration line, the pH value decreases with the increase of Na_2SO_4 mole fraction. The data show that the pH of the solution in the system $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ is mainly affected by $m(\text{B})$. The mole fraction of Na_2SO_4 for hydrolysis is lesser than that of NaBO_2 .

From the literature [12–15], B(OH)_3 was assumed as the reactants B(OH)_4^- , $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, and $\text{B}_5\text{O}_6(\text{OH})_4^-$ were formed with B(OH)_3 and H_2O . The reaction equation between boron species can be represented as

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
NaBO ₂ ·4H ₂ O	10555-76-7	Aladdin Industrial Corp., China	0.990	Analysis for BO ₂ ⁻
Na ₂ SO ₄	7757-82-6	Sinopharm Chemical Reagent Co., Ltd., China	0.990	Analysis for SO ₄ ²⁻

$$\begin{aligned}
 (\text{Total boron}) &= [\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-] + 3[\text{B}_3\text{O}_3(\text{OH})_4^-] \\
 &\quad + 3[\text{B}_3\text{O}_3(\text{OH})_5^{2-}] + 4[\text{B}_4\text{O}_5(\text{OH})_4^{2-}] + 5[\text{B}_5\text{O}_6(\text{OH})_4^-] \\
 &= [\text{B}(\text{OH})_3] + \frac{K_{11}[\text{B}(\text{OH})_3]}{[\text{H}^+]} + \frac{3K_{31}[\text{B}(\text{OH})_3]^3}{[\text{H}^+]} \\
 &\quad + \frac{3K_{32}[\text{B}(\text{OH})_3]^3}{[\text{H}^+]^2} + \frac{4K_{42}[\text{B}(\text{OH})_3]^4}{[\text{H}^+]^2} + \frac{5K_{51}[\text{B}(\text{OH})_3]^5}{[\text{H}^+]},
 \end{aligned} \tag{2}$$

$$x(\text{B}_p(\text{OH})_{3q}q(\text{H}_2\text{O})) = \frac{P \times [\text{B}_p(\text{OH})_{3q}q(\text{H}_2\text{O})_{n-q}^{q-}]}{[\text{Total boron}]} \tag{3}$$

In equation (2), K_{11} , K_{31} , K_{32} , K_{42} , and K_{51} represent the equilibrium constant equations for $\text{B}(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, 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 $\text{B}(\text{OH})_4^-$ 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 $x(\text{B}(\text{OH})_3)$ 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 $m(\text{B})$. $x(\text{B}(\text{OH})_3)$ will be no more than 0.001 if the $m(\text{B})$ is more than 1.3 mol·kg⁻¹. The x for $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, which was not considered in the calculation with Pitzer model [9], cannot be neglected in this calculation. $x(\text{B}_3\text{O}_3(\text{OH})_5^{2-})$ 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 $\text{B}_3\text{O}_3(\text{OH})_4^-$ is always below 0.0005 and can be neglected. The $x(\text{B}_5\text{O}_6(\text{OH})_4^-)$ is about 1.0×10^{-9} , which can be considered that $\text{B}_5\text{O}_6(\text{OH})_4^-$ does not exist in the mixed solution at 298.15 K. In Figure 3(b), the dominant boron species is also $\text{B}(\text{OH})_4^-$, but $x(\text{B}(\text{OH})_4^-)$ decreases as the concentration of total boron increases. $x(\text{B}(\text{OH})_4^-)$ is no less than 0.95 when $m(\text{B})$ is less than 1.2 mol·kg⁻¹. $x(\text{B}(\text{OH})_4^-)$ maintains no less than 0.85 when $m(\text{B})$ is more than 1.2 mol·kg⁻¹. $x(\text{B}_3\text{O}_3(\text{OH})_5^{2-})$ shows an uptrend and can occupy about 0.1 when $m(\text{B})$ is more than 2.4 mol·kg⁻¹. $x(\text{B}_4\text{O}_5(\text{OH})_4^{2-})$ also increase as $m(\text{B})$ increases and can reach the maximum data about 0.02. $x(\text{B}(\text{OH})_3)$ decreases as $m(\text{B})$ increases. If $m(\text{B})$ is greater than 0.5 mol·kg⁻¹, $x(\text{B}(\text{OH})_3)$ will not exceed 0.005. $x(\text{B}_3\text{O}_3(\text{OH})_4^-)$ 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.

In the diluted solution, $\text{B}(\text{OH})_3$ can be formed by hydrolysis of $\text{B}(\text{OH})_4^-$. As the concentration of $\text{B}(\text{OH})_4^-$ increases, $\text{B}_3\text{O}_3(\text{OH})_4^-$ forms with $\text{B}(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ with equation (5). The solution is alkaline because of hydrolysis of $\text{B}(\text{OH})_4^-$, so $\text{B}_3\text{O}_3(\text{OH})_4^-$ will combine OH^- to form $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$. As the increase of concentration of $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ forms with $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ and $\text{B}(\text{OH})_4^-$. Because of the OH^- formation and consumption, the concentration of OH^- first increases and then decreases as $m(\text{B})$ increases.

The dominant boron species in the system NaBO₂-Na₂SO₄-H₂O at the two temperatures is $\text{B}(\text{OH})_4^-$ with the mole fraction no less than 0.90. From the results of solubility calculation [9, 20], it can be considered that boron species mainly exists in the form of $\text{B}(\text{OH})_4^-$ in the mixed solution. The mole fractions for the six boron species in the mixed solution with different ratios show a slight difference at two temperatures. The results show that the mole fractions of the six boron species in the system NaBO₂-Na₂SO₄-H₂O are mainly affected by $m(\text{B})$ in the solution, but rarely effected by $m(\text{SO}_4^{2-})$. From 298.15 K to 323.15 K, the distribution of boron species in the mixed solution changed a lot. As temperature increases, the distribution of boron species becomes complicated. The polyborate ions are easily formed as the temperature increases in the NaBO₂-Na₂SO₄-H₂O system. The results show that the mole fraction of the six boron species in the system NaBO₂-Na₂SO₄-H₂O is mainly affected by the temperature.

FIGURE 1: The concentration in the system $\text{Na}_2\text{SO}_4\text{--NaBO}_2\text{--H}_2\text{O}$ at different temperatures. Black dotted line, 298.15 K [13]; brown dotted line, 323.15 K [14]. This work: black solid line, $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 1 : 8$; red solid line, $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 1 : 4$; blue solid line, $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 3 : 8$; green solid line, $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 1 : 2$.

TABLE 2: Density and pH values in the system $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ at 298.15 K.

$m(\text{B})$	$m/(\text{mol}\cdot\text{kg}^{-1}\cdot\text{H}_2\text{O})$	$m(\text{SO}_4^{2-})$	$\rho/\text{g}\cdot\text{cm}^{-3}$ 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.

$m(\text{B})$	$m/(\text{mol}\cdot\text{kg}^{-1}\cdot\text{H}_2\text{O})$	$m(\text{SO}_4^{2-})$	$\rho/\text{g}\cdot\text{cm}^{-3}$ 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 $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ at 323.15 K.

$m(\text{B})$	$m/(\text{mol}\cdot\text{kg}^{-1}\cdot\text{H}_2\text{O})$	$m(\text{SO}_4^{2-})$	$\rho/\text{g}\cdot\text{cm}^{-3}$	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

TABLE 3: Continued.

$m(\text{B})$	$m/(\text{mol}\cdot\text{kg}^{-1}\cdot\text{H}_2\text{O})$	$m(\text{SO}_4^{2-})$	$\rho/\text{g}\cdot\text{cm}^{-3}$	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

298.15 K
 —■— $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 1:8$
 —●— $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 1:4$
 —▲— $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 3:8$
 —▼— $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 1:2$

(a)

323.15 K
 —■— $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 1:8$
 —●— $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 1:4$
 —▲— $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 3:8$
 —▼— $m(\text{Na}_2\text{SO}_4) : m(\text{NaB}(\text{OH})_4) = 1:2$

(b)

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

The distribution of boron species in the system $\text{NaBO}_2\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ at 298.15 K was also calculated with the Pitzer model in our previous work [9]. In the

calculation [9], $x(\text{B}(\text{OH})_4^-)$ is more than 0.96 in the system $\text{NaBO}_2\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$, which shows that the boron species in the solution in the system can be considered as a single

FIGURE 3: The pH of mixed solution in the NaB(OH)_4 - Na_2SO_4 - H_2O 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 Na_2SO_4 and NaBO_2 at 298.15 K and 323.15 K. ■, B(OH)_3 ; ●, B(OH)_4^- ; ▲, $\text{B}_3\text{O}_3(\text{OH})_4^-$; ▼, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$; ◆, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$; ▼, $\text{B}_5\text{O}_6(\text{OH})_4^-$.

boron species B(OH)_4^- . The concentrations of 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 B(OH)_4^- in the system

NaBO_2 - Na_2SO_4 - H_2O 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

FIGURE 5: Reaction relationship between boron species.

FIGURE 6: Comparison of the mole fraction of $B(OH)_4^-$ in the system $NaBO_2-Na_2SO_4-H_2O$ at 298.15 K calculated in this work and with the Pitzer model [9]. Δ , this work; $\square$, ref. [9].

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 $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and $B_4O_5(OH)_4^{2-}$ 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, $B_3O_3(OH)_5^{2-}$ 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 $NaBO_2-Na_2SO_4-H_2O$ at 298.15 K and 323.15 K were investigated in this study. The densities and pH values change gradually with the changing of $m(B)$ and $m(SO_4^{2-})$. Combining the equilibrium constants for different boron species, the molar fractions of six boron species in the mixed solution were calculated with $m(B)$ 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 SO_4^{2-} . The polyborate ions are easier to form as the temperature increases. The dominant boron species in the system $NaBO_2-Na_2SO_4-H_2O$ at the two temperatures is $B(OH)_4^-$. The mole fraction of $B(OH)_3$ and $B_3O_3(OH)_4^-$ can be neglected. $B_5O_6(OH)_4^-$ 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 $\text{B}(\text{OH})_4^-$ 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 $\text{NaBO}_2\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$ 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.

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