

Research Article

Thermodynamic Modeling of Boron Species in the Ternary System $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K

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The solubilities; concentration of four boron species $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$; and H^+ (OH^-) in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ were calculated with the Pitzer model. The boron species $\text{B}_5\text{O}_6(\text{OH})_4^-$ was not considered in the model calculation. The calculated solubility and pH data are in accordance with the experimental results. The Pitzer model can be used to describe the experimental values. The distributions of the four boron species in the solution were obtained. The mole fractions of the four boron species are mainly affected by the ratio of B_2O_3 and Na_2O in the solution. The dominant boron species in the solution saturated with different salts vary greatly. The results can supply a theoretical reference for sodium borate separation from brine.

1. Introduction

The Qaidam Basin in Qinghai is the gathering place of salt lake resources in China [1]. In addition to the rich mineral resources such as potassium, sodium, magnesium, and lithium, the salt lake brine also has a large amount of borates [2–5]. These resources have important application value for the development of industry, agriculture, and economic construction [6]. There are many boron species in the borate solution. The boron species have complex structure and are mainly affected by the boron concentration, pH, and coexisting ions in solution [7–9]. The phase equilibria of water-salt systems can supply theoretical basis for the development of salt lake brine resources [10]. Therefore, the research on the phase equilibrium of the brine systems containing boron is meaningful to the comprehensive utilization and development of boron resources from brines [11].

The system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ is the simple subsystem of the complicated brine system. The phase equilibria in the

system in a wide temperature range (273.15~373.15 K) were reported [12–15]. The salts H_3BO_3 , $\text{NaB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, and $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ were found in the system at 298.15 K [12–14]. The different salt forms with different ratios of Na_2O and B_2O_3 in the solution. The change trends for concentration of total boron in the solution can be obtained with the phase equilibrium results, but the exact concentration of various boron species in the solution cannot be obtained with the phase equilibrium results.

The thermodynamic model is the effective method to calculate the concentration of boron species [16]. The MSE model was applied to calculate the solubilities in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 303.15 K, 333.15 K, 348.15 K, and 367.15 K [17]. However, the concentrations of different boron species and H^+ (OH^-) in the system were not presented [17]. The Pitzer model was widely applied in the solubility calculation in the brine systems [18, 19]. The Pitzer model in the system $\text{Na}^+-\text{K}^+-\text{Ca}^{2+}-\text{Mg}^{2+}-\text{H}^+-\text{Cl}^- - \text{SO}_4^{2-} - \text{CO}_2-\text{B}(\text{OH})_4^- - \text{H}_2\text{O}$ was reported by Felmy and Weare [20].

The solubilities in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 293.15 K were reported with the Pitzer model. The concentration of H^+ (OH^-) in the system containing boric acid or borate cannot be neglected [21, 22]. However, H^+ (OH^-) was not considered in the Pitzer model for the system. The concentrations of different boron species in the ternary system were not yet calculated [20]. The solubilities in the systems $\text{NaCl}-\text{NaBO}_2-\text{Na}_2\text{B}_4\text{O}_7-\text{H}_2\text{O}$ and $\text{NaCl}-\text{Na}_2\text{SO}_4-\text{NaBO}_2-\text{H}_2\text{O}$ at 298.15 K were calculated with Pitzer model in our previous work [21, 22]. The concentrations of various boron species and H^+ in the mixed borate solution were also calculated. However, the Pitzer model containing H^+ (OH^-) in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K, which is

necessary for synthesis of sodium borate, is lacking. In this paper, the Pitzer model in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K was constructed, and the concentrations of various boron species and H^+ (OH^-) in the system were also calculated with the model.

2. Model Approach

The Pitzer thermodynamic model was widely used to calculate solubility, osmotic coefficient ϕ , ionic activity coefficients γ , and other thermodynamic properties [23–26]. These main equations for thermodynamic property calculation are as follows:

$$(\phi - 1) = \left(\frac{2}{\sum_i m_i} \right) \left[\frac{-A^\phi I^{3/2}}{1 + bI^{(1/2)}} + \sum_i \sum_i m_c m_a (B_{ca}^\phi + ZC_{ca}) \right. \\ \left. + \sum_c \sum_{c'} m_c m_{c'} \left(\Phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a} \right) + \sum_a \sum_{a'} m_a m_{a'} \left(\Phi_{aa'}^\phi + \sum_c m_c \psi_{cac'} \right) \right] \quad (1)$$

$$+ \sum_n \sum_c m_n m_c \lambda_{nc} + \sum_n \sum_a m_n m_a \lambda_{na} + \sum_n \sum_c \sum_a m_n m_c m_a \zeta_{nc} a, \\ \ln \gamma_M = z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c \left(2\Phi_{Mc} + \sum_a m_a \Psi_{Mca} \right) \\ + \sum_a \sum_{a'} m_a m_{a'} \Psi_{Maa'} + z_M \sum_c \sum_a m_c m_a C_{ca} + \sum_n (2\lambda_{nM}) + \sum_n \sum_a m_n m_a \zeta_{naM}, \quad (2)$$

$$\ln \gamma_X = z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_c m_c \left(2\Phi_{Xc} + \sum_a m_a \Psi_{cXa} \right) \\ + \sum_c \sum_{c'} m_c m_{c'} \Psi_{cc'X} + |Z_X| \sum_c \sum_a m_c m_a C_{ca} + \sum_n (2\lambda_{nX}) + \sum_n \sum_a m_n m_c \zeta_{ncX}, \quad (3)$$

$$\ln \gamma_N = \sum_c m_c (2\lambda_{Nc}) + \sum_a m_a (2\lambda_{Na}) + \sum_n \sum_a m_c m_a \zeta_{Nca}, \quad (4)$$

$$\ln \alpha_w = -\phi \left(\frac{M_W}{1000} \right) \sum m_i. \quad (5)$$

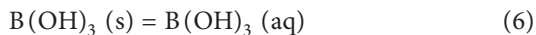
In the above equations, A^ϕ represent Debye–Hückel parameters. The subscripts M , c , c' , X , a , a' , and N express the different cations and anions, respectively. The symbols m_c and Z_c are the mass molality and the charge of cation c . λ_{Nc} , λ_{Na} , and ζ_{Nca} represent the interaction between the cations, anions, ionic species, and the neutral species. The other terms F , C , Z , B , and Φ in the above equations are defined in references [23–26]. In equation (5), α_w and M_W represent the water activity and molar mass of water ($\text{mol} \cdot \text{kg}^{-1}$), and the sum contains all solute species.

The solubilities of brine systems can be calculated with the Pitzer parameters and solubility products of the equilibrium solid phases (K_{sp}). In this study, the

solubilities of the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K were calculated with the model based on the Pitzer model. The pH for the solution in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K is in the range from 2.50 to 14.46 [12,27], which shows the concentration of H^+ or OH^- cannot be neglected in the solution. Therefore, the ions Na^+ , H^+ (OH^-), $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ in the solution were considered in the model calculation. The boron ion $\text{B}_5\text{O}_6(\text{OH})_4^-$ was not mentioned in the calculation because of the lack of parameters for $\text{B}_5\text{O}_6(\text{OH})_4^-$. The Pitzer parameters and μ^\ominus/RT of different boron species in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K were obtained from Felmy and Weare [20]. The lacking Pitzer

mixing ion-interaction parameters for boron ions are considered as zero.

Taking the solution saturated with H_3BO_3 in the ternary system for example, the dissolution equilibrium equations are as follows, and the relationship between boron ions can be expressed in equations (6)–(9).



The equilibrium constants for equations (6)–(9), which can be calculated with the standard chemical potentials by Felmy and Weare [20, 26], are shown in equations (10)–(13).

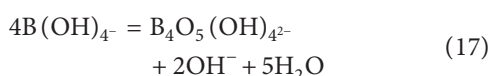
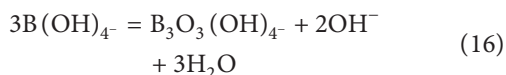
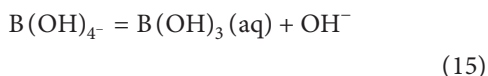
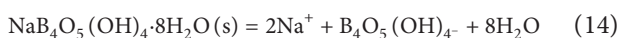
$$K_1 = m(B(OH)_3(aq)) \times \gamma(B(OH)_3(aq)), \quad (10)$$

$$K_2 = \frac{(m_{B(OH)_4^-} \times \gamma_{B(OH)_4^-}) \times (m_{H^+} \times \gamma_{H^+})}{(m_{B(OH)_3(aq)} \times \gamma_{B(OH)_3(aq)}) \times a_w}, \quad (11)$$

$$K_3 = \frac{(m_{B_3O_3(OH)_4^-} \times \gamma_{B_3O_3(OH)_4^-}) \times (m_{H^+} \times \gamma_{H^+}) \times a_w^2}{(m_{B(OH)_3(aq)} \times \gamma_{B(OH)_3(aq)})^3}, \quad (12)$$

$$K_4 = \frac{(m_{B_4O_5(OH)_4^{2-}} \times \gamma_{B_4O_5(OH)_4^{2-}}) \times (m_{H^+} \times \gamma_{H^+})^2 \times a_w^3}{(m_{B(OH)_3(aq)} \times \gamma_{B(OH)_3(aq)})^4}. \quad (13)$$

In equations (10)–(13), K_1 , K_2 , K_3 , and K_4 represent the equilibrium constant equations for equations (6)–(9). The solution is saturated with sodium borate when $B(OH)_3$ is unsaturated, and the solution is alkaline, taking $NaB_4O_5(OH)_4 \cdot 8H_2O$ for example. The dissolution equilibrium equations are as follows. The relationship between boron species can be represented in equations (15)–(17).



The solubility product constant of $NaB_4O_5(OH)_4 \cdot 8H_2O$ (K_5) at a certain temperature and pressure is shown in

equation (18). The equilibrium constants for equations (15)–(17) are shown in equations (19)–(21):

$$K_5 = (m_{Na^+} \times \gamma_{Na^+})^2 \times (m_{B_4O_5(OH)_4^{2-}} \times \gamma_{B_4O_5(OH)_4^{2-}}) \times a_w^8, \quad (18)$$

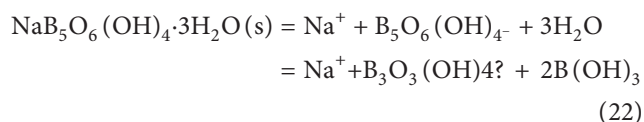
$$K_6 = \frac{(m_{B(OH)_3(aq)} \times \gamma_{B(OH)_3(aq)})^3 \times (m_{OH^-} \times \gamma_{OH^-})}{(m_{B(OH)_4^-} \times \gamma_{B(OH)_4^-})}, \quad (19)$$

$$K_7 = \frac{(m_{B_3O_3(OH)_4^-} \times \gamma_{B_3O_3(OH)_4^-}) \times (m_{OH^-} \times \gamma_{OH^-})^2 \times a_w^3}{(m_{B(OH)_4^-} \times \gamma_{B(OH)_4^-})^3}, \quad (20)$$

$$K_8 = \frac{(m_{B_4O_5(OH)_4^{2-}} \times \gamma_{B_4O_5(OH)_4^{2-}}) \times (m_{OH^-} \times \gamma_{OH^-})^2 \times a_w^5}{(m_{B(OH)_4^-} \times \gamma_{B(OH)_4^-})^4}. \quad (21)$$

In equations (18)–(21), K_5 , K_6 , K_7 , and K_8 represent the equilibrium constant equations for equations (18)–(21).

$B_5O_6(OH)_4^-$ cannot be neglected in the solution in the system $NaB_5O_6(OH)_4 \cdot H_2O$ when the concentration of $NaB_5O_6(OH)_4$ is not very low [7]. In the system $Na_2O-B_2O_3-H_2O$, the concentration of $B_5O_6(OH)_4^-$ may be not neglected when the solution is saturated with $NaB_5O_6(OH)_4 \cdot 3H_2O$. $B_5O_6(OH)_4^-$ will convert into $B(OH)_3$ and $B_3O_3(OH)_4^-$ when the concentration of $NaB_5O_6(OH)_4$ is low. Therefore, the dissolution equilibrium constant of $B_5O_6(OH)_4^-$ (K_9) can be calculated with equation (23) because of the lacking parameters for $B_5O_6(OH)_4^-$:



$$K_9 = (m_{Na^+} \times \gamma_{Na^+}) \times (m_{B_3O_3(OH)_4^-} \times \gamma_{B_3O_3(OH)_4^-}) \times (m_{B(OH)_3} \times \gamma_{B(OH)_3})^2. \quad (23)$$

According to the Pitzer model, the activity and osmotic coefficients are parametric functions of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^ϕ , $\theta_{aa'}$, $\psi_{aa'c}$, λ_{Na} , $\lambda_{Na'}$, and $\zeta_{Na'}$. $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ are the parameters of a single salt; $\theta_{aa'}$ represents the interaction between the two ions with the same sign, and $\psi_{aa'c}$ represents the interactions among the three ions, in which the sign of the third ion is different from the first two ions. Combining the charge conservation and matter conservation equations, the compositions of different species at equilibrium and solubilities for the system $Na_2O-B_2O_3-H_2O$ can be calculated with the above equations with the Pitzer parameters and standard chemical potentials (μ^\ominus/RT) of different species.

TABLE 1: Experimental and calculated solubilities of invariant points for the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K.

No.		Na_2O	B_2O_3	pH	Equilibrium solid phase	Ref.
A	Experimental data	0.00	3.06	4.27	H_3BO_3	[12]
	Experimental data	0.00	3.25	2.50	H_3BO_3	[27]
A	Calculated data	0.00	3.07	3.15	H_3BO_3	This work
E_1	Experimental data	1.69	10.26	—	$\text{H}_3\text{BO}_3 + \text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$	[12]
E_1	Experimental data	1.62	10.08	6.22	$\text{H}_3\text{BO}_3 + \text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$	[14]
E_1	Calculated data	1.83	10.27	6.50	$\text{H}_3\text{BO}_3 + \text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$	This work
E_2	Experimental data	2.73	12.73	7.18	$\text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O} + \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	[12]
E_2	Experimental data	2.82	12.70	—	$\text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O} + \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	[14]
E_2	Calculated data	2.87	13.10	6.83	$\text{NaB}_5\text{O}_8 \cdot 5\text{H}_2\text{O} + \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	This work
E_3	Experimental data	9.38	10.64	13.08	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{NaBO}_2 \cdot 4\text{H}_2\text{O}$	[12]
E_3	Calculated data	10.34	12.08	12.73	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{NaBO}_2 \cdot 4\text{H}_2\text{O}$	This work

3. Result and Discussion

The experimental and calculated solubilities of boundary point saturated with $\text{B}(\text{OH})_3$ and invariant points for the ternary system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K are shown in Table 1. The comparisons of experimental and calculated phase diagrams in the system at 298.15 K are shown in Figure 1. The point A, which is saturated with $\text{B}(\text{OH})_3$, is the boundary point in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. There are three invariant points (E_1 , E_2 , and E_3) and four solubility curves in the system. According to Table 1 and Figure 1, the calculated values are in agreement with the experimental values except point E_3 . The results show that the Pitzer model with four boron species is reliable for calculating the solubilities in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. From A to E_2 , $w(\text{B}_2\text{O}_3)$ increased as $w(\text{Na}_2\text{O})$ increases and reaches the maximum data at point E_2 . The point with minimum $w(\text{B}_2\text{O}_3)$ in Figure 1 is shown as point B. The solubility curve saturated with $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$ can be separated into two parts $E_2\text{B}$ and BE_3 . From E_2 to B, $w(\text{B}_2\text{O}_3)$ decreased sharply as $w(\text{Na}_2\text{O})$ decreased. However, $w(\text{B}_2\text{O}_3)$ increased relatively gently as $w(\text{Na}_2\text{O})$ increases from B to E_3 . In the solubility curve saturated with $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, $w(\text{B}_2\text{O}_3)$ decreased with $w(\text{Na}_2\text{O})$ increasing.

The H^+ or OH^- concentration cannot be neglected in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K. The calculated and experimental pH diagrams were plotted, as shown in Figure 2. The mass fractions (100w) of Na_2O were used as the abscissa in Figure 2. The calculated pH data are in accordance with the experimental results except some points. The pH datum for point A is 4.27 from Валяшко [12] and 2.50 from Li [27] in Table 1. Considering the experimental error, the calculated data for point A (3.15) can be considered to be in agreement with the experimental data. The pH data increased with increasing $w(\text{Na}_2\text{O})$. The changing trend varied in different curves saturated with different salts. With the calculated pH diagram, the invariant points in the system can be roughly judged.

The reasons about the difference between the calculated solubility and pH data with experimental results are complicated. On the one hand, only four boron species were considered in the solution of the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ in this model calculation. However, $\text{B}_5\text{O}_6(\text{OH})_4^-$ may exist in the solution in the system [7]. Moreover, the concentration

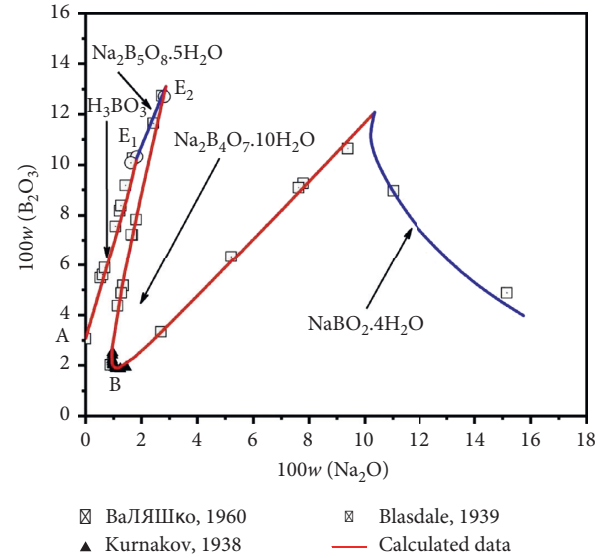


FIGURE 1: Experimental and calculated phase diagrams in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K. \square , data from ref.; \blacktriangle , data from ref.; \circ , data from ref.; —, calculated data.

of $\text{B}_5\text{O}_6(\text{OH})_4^-$ cannot be neglected as $m(\text{B})$ in the solution increases [7]. On the other hand, the lacking Pitzer parameters for boron ions cannot be considered as zero. Therefore, the difference between the experimental and calculated values is inevitable, and it was controlled to the minimum based on our current knowledge.

The mole fractions (x_i) for the four boron species in this ternary system calculated with the Pitzer model are shown in Figure 3. The mole fraction of the four boron species (x_i) can be calculated with equations (24)–(27), which is the same as our previous work [22]. In equations (24)–(27), B_4^{2-} , B_3^- , B^- , and B represent $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}(\text{OH})_4^-$, and $\text{B}(\text{OH})_3$.

$$x_{\text{B}_4^{2-}} = \frac{4m_{\text{B}_4^{2-}}}{4m_{\text{B}_4^{2-}} + 3m_{\text{B}_3^-} + m_{\text{B}^-} + m_{\text{B}}}, \quad (24)$$

$$x_{\text{B}_3^-} = \frac{3m_{\text{B}_3^-}}{4m_{\text{B}_4^{2-}} + 3m_{\text{B}_3^-} + m_{\text{B}^-} + m_{\text{B}}}, \quad (25)$$

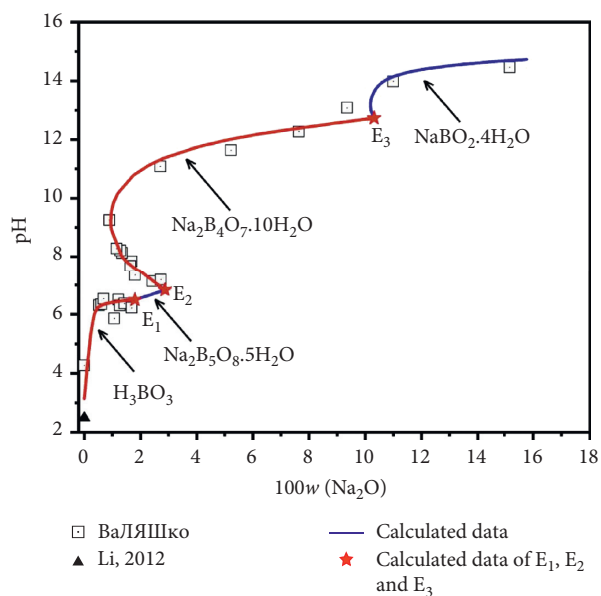


FIGURE 2: Experimental and calculated pH data in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K. \square , data from ref.; \blacktriangle , data from ref.; \star , calculated data in the invariant points; —, calculated data.

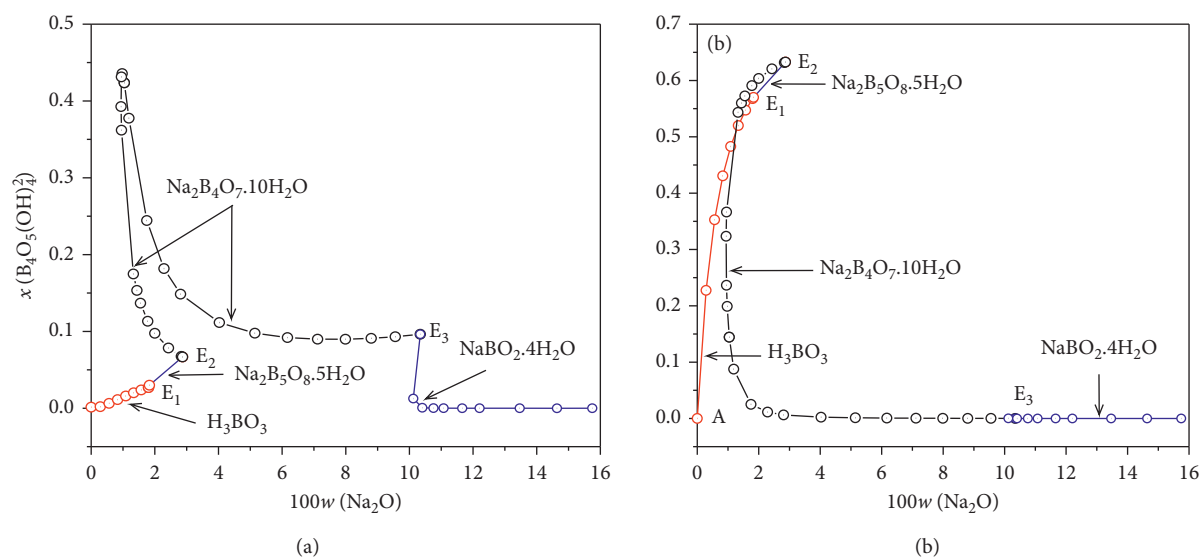


FIGURE 3: Continued.

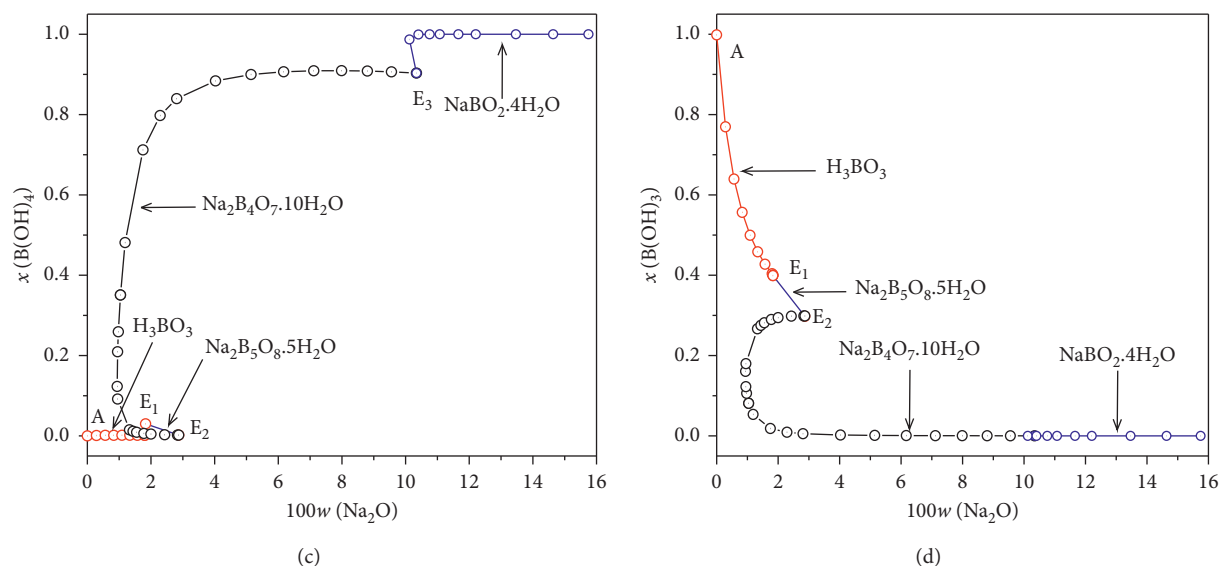


FIGURE 3: Variation in the distribution of boron species in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K: (a) $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$; (b) $\text{B}_3\text{O}_3(\text{OH})_4^-$; (c) $\text{B}(\text{OH})_4^-$; (d) $\text{B}(\text{OH})_3$.

$$x_B^- = \frac{m_B^-}{4m_{\text{B}_4^{2-}} + 3m_{\text{B}_3^-} + m_B^- + m_B}, \quad (26)$$

$$x_B = \frac{m_B}{4m_{\text{B}_4^{2-}} + 3m_{\text{B}_3^-} + m_B^- + m_B}. \quad (27)$$

The variation trends for the relationships between x_i and $w(\text{Na}_2\text{O})$ are different in Figure 3. With the difference, the invariant points can be judged. From Figure 3(a), $x(\text{B}_4\text{O}_5(\text{OH})_4^{2-})$ increased from point A to E_2 as $w(\text{Na}_2\text{O})$ increased. In the curve E_2E_3 saturated with $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, $x(\text{B}_4\text{O}_5(\text{OH})_4^{2-})$ firstly increased sharply as $w(\text{Na}_2\text{O})$ decreased, and then decreased sharply as $w(\text{Na}_2\text{O})$ increased. In the curve saturated with $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ in Figure 3(a), $x(\text{B}_4\text{O}_5(\text{OH})_4^{2-})$ decreased to nearly zero. In Figure 3(b), $x(\text{B}_3\text{O}_3(\text{OH})_4^-)$ increased from points A to E_2 . From points E_2 to E_3 , $x(\text{B}_3\text{O}_3(\text{OH})_4^-)$ decreased to nearly zero. $x(\text{B}_3\text{O}_3(\text{OH})_4^-)$ can be neglected in the curve saturated with $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. $x(\text{B}(\text{OH})_4^-)$ in Figure 3(c) is nearly zero in the curves AE_1 and E_1E_2 . $x(\text{B}(\text{OH})_4^-)$ increased from points E_2 to E_3 and reached the maximum data at E_3 . In the curve saturated with $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, $x(\text{B}(\text{OH})_4^-)$ increased sharply to the maximum and became stable with the mole fraction no less than 0.99. In Figure 3(d), $x(\text{B}(\text{OH})_3)$ decreased as $w(\text{Na}_2\text{O})$ increased from point A to E_2 . In the curve E_2E_3 , $x(\text{B}(\text{OH})_3)$ decreased to nearly zero. $x(\text{B}(\text{OH})_3)$ can be neglected if $w(\text{Na}_2\text{O})$ is more than 0.028. From Figure 3, the mole fraction of the four boron species is mainly affected by the ratio of B_2O_3 and Na_2O in the solution, which affects the equilibrium solid phase in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$.

From Figure 3, the dominant boron species in solutions saturated with different salts vary greatly. The main boron species are $\text{B}(\text{OH})_3$ and $\text{B}_3\text{O}_3(\text{OH})_4^-$ in the solution saturated with $\text{B}(\text{OH})_3$ or $\text{NaB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$. $\text{B}(\text{OH})_4^-$ is the

dominant boron species in the solution saturated with $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. The boron species are very different in the solution saturated with $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 3\text{H}_2\text{O}$. When $w(\text{Na}_2\text{O})$ is less than 0.028, the four boron species exist in the solution. However, the mass fraction of $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}(\text{OH})_3$ can be neglected if $w(\text{Na}_2\text{O})$ is more than 0.028. The dominant boron species is $\text{B}(\text{OH})_4^-$ in the solution if $w(\text{Na}_2\text{O})$ is more than 0.028.

4. Conclusions

The Pitzer model of boron species in the ternary system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 298.15 K was constructed. The solubilities; concentration of four boron species $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, and H^+ (OH^-) in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ were calculated with the Pitzer model. The boron species $\text{B}_5\text{O}_6(\text{OH})_4^-$ was not considered in the model calculation. The calculated solubility and pH data are in accordance with the experimental results. The Pitzer model can be used to describe the experimental values. The distributions of the four boron species in the solution were obtained. The mole fractions of the four boron species are mainly affected by the ratio of B_2O_3 and Na_2O in the solution. The dominant boron species in the solution saturated with different salts vary greatly. The main boron species are $\text{B}(\text{OH})_3$ and $\text{B}_3\text{O}_3(\text{OH})_4^-$ in the solution saturated with $\text{B}(\text{OH})_3$ or $\text{NaB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$. $\text{B}(\text{OH})_4^-$ is the dominant boron species in the solution saturated with $\text{NaB}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. The results can supply a theoretical reference for sodium borate separation from brine.

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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