Phase Equilibria in the Quaternary Systems NaOH + Na₂CO₃ + Na₂SO₄ + H₂O, Na₂CO₃ + NaOH + NaCl + H₂O, and NaOH + Na₂SO₄ + NaCl + H₂O at 363.15 K

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ABSTRACT: The solid–liquid equilibrium data of the aqueous NaOH–Na₂CO₃–Na₂SO₄–H₂O, NaOH–Na₂CO₃–NaCl–H₂O, and NaOH–Na₂SO₄–NaCl–H₂O quaternary systems at 363.15 K were measured. The equilibrium solid phases and solubilities of salts in the three systems and its subsystems were determined. The densities of the saturated solutions were also determined. The experimental data are used to plot the solubility diagrams and water content diagrams of the systems. It was found that the NaOH–Na₂CO₃–Na₂SO₄–H₂O system contains the solid solution of γ-salt (mNa₂SO₄·nNa₂CO₃) and the other two systems Na₂CO₃–NaOH–NaCl–H₂O and NaOH–Na₂SO₄–NaCl–H₂O have the complex salts S1 (Na₂SO₄·2NaOH) and S3 (Na₂SO₄·NaCl·NaOH). On the basis of Xu’s activity coefficient model, a model was constructed for the correlation of solid–liquid equilibrium in electrolyte solutions to calculate the solubilities of salts in these systems at 363.15 K. The calculated solubilities are in agreement with the experimental values.

1. INTRODUCTION

There are abundant resources of natural soda in Inner Mongolia and Henan Province in China. The major components of natural soda include sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃), sodium sulfate (Na₂SO₄), and sodium chloride (NaCl). Based on these components, natural soda can be used to produce caustic soda. After natural soda is dissolved in water, insoluble impurities can be removed through the flocculation clarification process. When lime milk is added, which reacts with sodium carbonate to form a caustic solution, the NaOH concentration in caustic liquor is usually approximately 8–10%. Considering the economic efficiency and equilibrium conversion rate, the causticization rate is generally controlled at approximately 90%, as well as the fact that only a very small amount of sodium bicarbonate (NaHCO₃) is retained, diluted caustic soda liquid can be regarded as a quinary system of NaOH–NaCl–Na₂CO₃–Na₂SO₄–H₂O.

To obtain caustic soda products that meet quality standards, the caustic soda liquid should be concentrated, and Na₂SO₄, NaCl, and a small amount of Na₂CO₃ impurities should be removed. The evaporation method for producing caustic soda through the causticizing process generally involves three-effect evaporation. The first-effect temperature is approximately 423.15 K, at which the concentration of caustic soda can be controlled at 11–12% and the diluted caustic soda liquid is concentrated; the second-effect temperature is approximately 393.15 K, at which the concentration of caustic soda is generally controlled at approximately 19–20% to achieve partial removal of the impurities; and the third-effect temperature is approximately 363.15 K, at which the concentration of caustic soda is controlled at 45–48%. At the third-effect temperature, Na₂SO₄ and NaCl are removed to concentrate the diluted caustic soda liquid and remove impurities; then, the caustic soda liquid is allowed to cool to achieve separation, dehydration, and solidification to form solid caustic soda that meets the quality requirements. In the actual production process, only the third-effect temperature is controlled at 363.15 K; at this point, the evaporated liquor has reached saturation and salting-out. Therefore, 363.15 K was chosen as the research temperature in this paper.

Liu et al. systematically studied the phase diagram of the quinary system NaOH–NaCl–Na₂CO₃–Na₂SO₄–H₂O at 423.15 K. Stephen et al. collected detailed phase equilibrium data for the quaternary subsystems of the quinary system under consideration at 363.15 K. Su et al. studied a related quaternary system and obtained partial solubility data. To date, the phase equilibrium data for the quaternary subsystems of the quinary system NaOH–NaCl–Na₂CO₃–Na₂SO₄–H₂O, including NaOH–Na₂CO₃–Na₂SO₄–H₂O, NaOH–NaCl–Na₂CO₃–H₂O,
electrolyte solutions and mixed electrolyte solution systems, the reference state of activity coefficients; literature data for single salt systems; the solubilities of these substances at 363.15 K are calculated using Xu’s activity coefficient model.

2. EXPERIMENTAL SECTION

2.1. Reagents and Instruments. Distilled water with a conductivity of less than 1.3 × 10^-4 S·m^-1 and a pH of 6 was used for solubility measurements and chemical analysis. All chemicals used were of analytical purity grade and recrystallized before use. The sources, purity, and CAS numbers are listed in Table 1.

A thermostatic water bath (76-1, Jiangsu Tianyou Co., Ltd.) with a precision of ±0.1 K was used for the solid–liquid equilibrium (SLE) measurements. In addition, we used a thermostatic water bath (KSA-II thyristor dc governor, 2.2 kW, Ningbo Beilun District Zhitou Electronic Control Equipment Factory), circulating heated water, to achieve a uniform mixture of the solid and liquid phases. An analytical balance, with an accuracy of ±0.001 g (ALC-110.4, Sartorius AG, Germany), was used for weighing; a muffle furnace (SX-1300 °C, Tianjin Zhonghuan Experimental Electric Furnace Co., Ltd.) was used to burn the precipitate; and an intelligent temperature controller (XMTG-6000, Jiangsu Taizhou Haige Instrument Co., Ltd.), which was calibrated against a temperature calibrator, was used.

2.2. Experimental Methods. The system points were prepared as follows. For the ternary systems, the system points were prepared by gradually adding the second component on the basis of the single salt saturation points. For the quaternary systems, the system points were prepared by adding the third component on the basis of the double salt cosaturation points. Each solubility curve was prepared using 5–15 groups, and an appropriate number of points

Table 1. Purity and Suppliers of Chemicals

| chemicals name       | molecular formula | mass fraction purity (%) | recrystallization conditions | CAS no. | source                                      |
|----------------------|-------------------|--------------------------|------------------------------|---------|---------------------------------------------|
| sodium chloride      | NaCl              | ≥99.5                    | dried in an oven at 723.15 K | 7647-14-5 | Tianjin Yongsheng Chemical Reagent Co., Ltd, China |
| sodium hydroxide     | NaOH              | ≥96.0                    |                              | 1310-73-2 | Tianjin Yongsheng Chemical Reagent Co., Ltd, China |
| sodium carbonate     | Na₂CO₃            | ≥99.8                    | dried in an oven at 543.15 K | 497-19-8 | Tianjin Yongsheng Chemical Reagent Co., Ltd, China |
| sodium sulfate       | Na₂SO₄            | ≥99.0                    | dried in an oven at 423.15 K | 7757-82-6 | Tianjin Yongsheng Chemical Reagent Co., Ltd, China |
| potassium chromate   | K₂CrO₄            | ≥99.5                    |                              | 7789-00-6 | Tianjin Yongsheng Chemical Reagent Co., Ltd, China |
| silver nitrate       | AgNO₃             | ≥99.8                    |                              | 7761-88-8 | Sinopharm Chemical Regent Co., Ltd |
| phenolphthalein      | C₂₀H₁₄O₄          | ≥98.0                    |                              | 77-09-8 | Tianjin Yongsheng Chemical Reagent Co., Ltd, China |
| methyl orange indicator | C₁₅H₁₅N₃O₂       | ≥96.0                    |                              | 547-58-0 | Tianjin Chemical Reagent 3rd Factory |
| methyl red indicator  | C₁₃H₁₃N₃O₂       | AR                       |                              | 493-52-7 | Tianjin Tianxin Chemical Development Center |
| barium chloride      | BaCl₂             | ≥99.5                    |                              | 10361-37-2 | Tianjin Chemical Reagent 1st Factory |
| hydrochloric acid    | HCl               | ≥38.0                    |                              | 7647-01-0 | Tianjin Chemical Reagent 3rd Factory |

“Stated by the suppliers.

Abbreviations: Cl: NaCl; S: Na₂SO₄; OH: NaOH; S1: NaOH–Na₂SO₄; and C: Na₂CO₃.

Table 2. Determination of the Experimental Results with the Equilibrium Time and Static Time

| no. | fluid, w(B) × 10⁰% | equilibrium phase solids | equilibrium time | static time |
|-----|--------------------|--------------------------|-------------------|-------------|
| 1   |                    |                          |                   |             |
| 2   |                    |                          |                   |             |
amount of distilled water was added to each group of mixtures. The matched experimental solutions were put into glass bottles (30 mL, 3.5 cm in diameter, and 6.5 cm high), sealed with rubber plugs and aluminum caps, placed in a thermostatic water bath (363.15 \pm 0.1 K) with a rotating drum, and rotated at a constant speed in the thermostatic water bath to achieve phase equilibrium.9

The experimental setup, which was established in accordance with the characteristics of the studied system, is shown in Figure 1. The balancing device could also be used for static and sampling

Table 3. Repeatability of Data of Phase Equilibria Measured at \( T = 363.15 \text{ K} \) and \( P = 88.94 \text{ kPa} \)\(^a\)

| cosaturated points | serial number | Na\(_2\)CO\(_3\) | NaCl | Na\(_2\)SO\(_4\) | NaOH | H\(_2\)O | equilibrium phase solids\(^c\) |
|--------------------|---------------|-----------------|------|-----------------|------|--------|----------------|
| Table 5 | 9(E\(_1\)) | 1 | 0 | 0 | 2.21 | 34.18 | 63.61 | S + S1 |
| | | 2 | 0 | 0 | 2.30 | 34.21 | 63.49 | |
| | | 3 | 0 | 0 | 2.16 | 34.16 | 63.68 | |
| | | average value | 0 | 0 | 2.22 | 34.18 | 63.60 | |
| | 15(E\(_2\)) | 1 | 0 | 0 | 2.71 | 71.62 | 25.67 | S1 + OH |
| | | 2 | 0 | 0 | 2.74 | 71.59 | 25.67 | |
| | | 3 | 0 | 0 | 2.79 | 71.64 | 25.75 | |
| | | average value | 0 | 0 | 2.75 | 71.62 | 25.63 | |
| | Table 6 | 12(E) | 1 | 0 | 2.85 | 0 | 68.89 | 28.26 | Cl + OH |
| | | 2 | 0 | 2.89 | 0 | 68.92 | 28.19 | |
| | | 3 | 0 | 2.87 | 0 | 68.81 | 28.32 | |
| | | average value | 0 | 2.87 | 0 | 68.87 | 28.26 | |
| | Table 7 | 14(E\(_1\)) | 1 | 2.22 | 0.00 | 6.54 | 26.98 | 64.26 | S + γ + S1 |
| | | 2 | 2.34 | 0.00 | 6.59 | 27.07 | 64.00 | |
| | | 3 | 2.31 | 0.00 | 6.70 | 27.04 | 63.95 | |
| | | average value | 2.29 | 0.00 | 6.61 | 26.92 | 64.07 | |
| | | Table 15(E\(_2\)) | 1 | 4.89 | 0.00 | 1.83 | 61.82 | 31.46 | OH + C1 + γ |
| | | 2 | 4.79 | 0.00 | 1.77 | 61.83 | 31.61 | |
| | | 3 | 4.98 | 0.00 | 1.75 | 61.89 | 31.38 | |
| | | average value | 4.89 | 0.00 | 1.81 | 61.85 | 31.48 | |
| | Table 16(E\(_1\)) | 1 | 2.89 | 0.00 | 0.83 | 51.66 | 44.62 | C1 + C + OH |
| | | 2 | 2.88 | 0.00 | 0.86 | 51.69 | 44.57 | |
| | | 3 | 2.81 | 0.00 | 0.82 | 51.64 | 44.73 | |
| | | average value | 2.86 | 0.00 | 0.84 | 51.66 | 44.64 | |
| | | Table 17(E\(_1\)) | 1 | 2.05 | 0.00 | 1.63 | 55.79 | 40.53 | OH + S1 + γ |
| | | 2 | 2.12 | 0.00 | 1.68 | 55.76 | 40.44 | |
| | | 3 | 2.10 | 0.00 | 1.75 | 56.01 | 40.14 | |
| | | average value | 2.09 | 0.00 | 1.69 | 55.85 | 40.37 | |
| | | Table 8 | 5(E\(_1\)) | 1 | 2.05 | 3.99 | 0.00 | 51.04 | 42.92 | C + OH + Cl |
| | | 2 | 2.11 | 4.03 | 0.00 | 50.97 | 42.89 | |
| | | 3 | 1.99 | 4.00 | 0.00 | 51.00 | 43.01 | |
| | | average value | 2.05 | 4.01 | 0.00 | 51.00 | 42.94 | |
| | | Table 9 | 4(E\(_1\)) | 1 | 1.66 | 4.35 | 0.00 | 34.18 | 59.81 | C + C1 + Cl |
| | | 2 | 1.71 | 4.37 | 0.00 | 34.22 | 59.70 | |
| | | 3 | 1.69 | 4.29 | 0.00 | 34.23 | 59.79 | |
| | | average value | 1.69 | 4.34 | 0.00 | 34.21 | 59.76 | |
| | | Table 10 | 4(E\(_1\)) | 1 | 0.00 | 0.71 | 3.12 | 41.85 | 54.32 | S + S1 + S3 |
| | | 2 | 0.00 | 0.69 | 3.12 | 41.79 | 54.40 | |
| | | 3 | 0.00 | 0.73 | 3.15 | 41.92 | 54.20 | |
| | | average value | 0.00 | 0.71 | 3.13 | 41.85 | 54.31 | |
| | | Table 11 | 6(E\(_1\)) | 1 | 0.00 | 4.51 | 3.50 | 60.36 | 31.63 | S + Cl + S3 |
| | | 2 | 0.00 | 4.66 | 3.43 | 60.40 | 31.51 | |
| | | 3 | 0.00 | 4.62 | 3.34 | 60.55 | 31.49 | |
| | | average value | 0.00 | 4.60 | 3.42 | 60.44 | 31.54 | |
| | | Table 12 | 9(E\(_1\)) | 1 | 0.00 | 2.38 | 2.58 | 81.31 | 13.73 | Cl + S3 + OH |
| | | 2 | 0.00 | 2.37 | 2.51 | 81.29 | 13.83 | |
| | | 3 | 0.00 | 2.25 | 2.64 | 81.25 | 13.86 | |
| | | average value | 0.00 | 2.33 | 2.58 | 81.28 | 13.81 | |
| | | Table 13 | 11(E\(_1\)) | 1 | 0.00 | 1.07 | 3.71 | 78.12 | 17.10 | S1 + S3 + OH |
| | | 2 | 0.00 | 1.07 | 3.68 | 78.11 | 17.14 | |
| | | 3 | 0.00 | 1.06 | 3.72 | 78.13 | 17.09 | |
| | | average value | 0.00 | 1.07 | 3.70 | 78.12 | 17.11 | |

\(^a\)Standard uncertainties \( u(T) = 0.1 \text{ K}, u(P) = 0.5 \text{ kPa}, \) and \( u(Na_2CO_3) = u(Na_2SO_4) = u(NaCl) = u(NaOH) = 0.05.\(^b\)\(w(B)\) is the mass fraction of the component (B).\(^c\)Abbreviations: S, Na\(_2\)SO\(_4\); OH, NaOH; Cl, NaCl; C\(_1\), Na\(_2\)CO\(_3\)·H\(_2\)O; S\(_1\), Na\(_2\)SO\(_4\)·NaOH; γ, m\(Na_2SO_4\)·n\(Na_2CO_3\); and S\(_3\), Na\(_2\)SO\(_4\)·NaCl·NaOH.
almost no liquid and solid phases. Accordingly, the formation of CO2 had volumes of the vapor phases were much smaller than those of the 0.25%. In addition, the experimental systems were sealed and the to the total pressure in the equilibrium vapor phase was only 0.09.

Table 5. Equilibrium Solubilities of the Ternary System NaOH—Na2SO4—H2O at T = 363.15 K and P = 88.94 kPa

| subject | Na2CO3 | NaCl | Na2SO4 | NaOH | Cl + OH | Cl + OH | data sources |
|---------|--------|------|--------|------|---------|---------|-------------|
| Table 6 12(E) measured results | 0 | 2.87 | 0 | 68.87 | | | |
| literature data | 0 | 2.90 | 0 | 65.00 | | | |
| relative error (%) | 0 | 0.01 | 0 | 0.06 | | | |
| absolute error | 0 | 0.03 | 0 | 3.87 | | | |

"Standard uncertainties u are u(T) = 0.1 K, u(P) = 0.5 kPa, and u(Na2CO3) = u(Na2SO4) = u(NaCl) = u(NaOH) = 0.05. (b) Data source: Stephen et al. (1963). (c) Abbreviations: OH, NaOH and Cl, NaCl."

Table 6.12(E) measured results 0 2.87 0 68.87 Cl + OH this work

Table 5. Equilibrium Solubilities of the Ternary System NaOH—Na2SO4—H2O at T = 363.15 K and P = 88.94 kPa

| composition of liquid phase, w(B) × 100 | composition of wet residue, w(B) × 100 | solution density ρ/g cm⁻³ | equilibrium phase solids |
|----------------------------------------|----------------------------------------|---------------------------|-------------------------|
| NaOH | Na2SO4 | H2O | NaOH | Na2SO4 | H2O | | |
| 1 | 0.00 | 29.91 | 70.09 | 0.00 | 32.01 | 67.99 | 1.1984 | S |
| 2 | 6.47 | 22.86 | 70.67 | 4.67 | 65.08 | 30.25 | 1.2034 | S |
| 3 | 10.95 | 16.25 | 72.80 | 9.99 | 46.34 | 43.67 | 1.2522 | S |
| 4 | 14.79 | 12.41 | 72.80 | 14.52 | 35.32 | 50.16 | 1.2146 | S |
| 5 | 17.12 | 9.65 | 73.23 | 14.99 | 22.41 | 63.60 | 1.2190 | S |
| 6 | 20.84 | 6.07 | 73.09 | 14.99 | 46.34 | 43.67 | 1.2195 | S |
| 7 | 25.44 | 4.97 | 69.59 | 16.99 | 46.34 | 39.89 | 1.2522 | S |
| 8 | 30.24 | 2.49 | 67.27 | 22.30 | 27.86 | 49.84 | 1.2930 | S |
| 9(E1) | 34.18 | 2.22 | 63.60 | 22.61 | 35.32 | 40.16 | 1.3122 | S + S1 |
| 10 | 37.39 | 2.49 | 60.12 | 31.93 | 27.86 | 40.16 | 1.3657 | S |
| 11 | 37.34 | 2.31 | 59.95 | 31.93 | 27.86 | 40.16 | 1.3686 | S |
| 12 | 41.63 | 1.66 | 56.71 | 40.63 | 31.04 | 28.33 | 1.4048 | S |
| 13 | 43.74 | 2.22 | 54.04 | 41.87 | 35.72 | 46.89 | 1.4279 | S |
| 14 | 63.39 | 2.49 | 34.12 | 54.67 | 23.45 | 22.06 | 1.5884 | S |
| 15(E2) | 71.62 | 2.75 | 25.63 | 51.01 | 35.72 | 17.68 | 1.5884 | S |
| 16 | 76.28 | 0.00 | 23.72 | 72.26 | 6.81 | 19.38 | 1.5884 | S + OH |

"Standard uncertainties u are u(T) = 0.1 K, u(P) = 0.5 kPa, and u(Na2CO3) = u(Na2SO4) = u(NaCl) = u(NaOH) = 0.05. (b) w(B) is the mass fraction of the component (B). (c) Abbreviations: S, Na2SO4; OH, NaOH; and S1, Na2SO4 NaOH."

operations to prevent temperature changes in the external environment from disturbing the balance of the samples. A micro ac constant-speed motor made of plexiglass was used at a speed of 60 rpm to achieve liquid—solid phase equilibrium. The equilibrium time was approximately three days; after equilibrium was achieved, the supernatant liquid was removed from the balanced bottle every few hours and chemical analysis was conducted. If the relative error among the three consecutive sampling was below 0.003, the equilibrium could be considered to be achieved. It was determined using the experimental results with the equilibrium time and static time in Table 2. At equilibrium, the sample solutions were allowed to rest for 3 days to separate the solid and liquid phases and kept in a constant-temperature oil bath. The upper portion of the sealed bottles was kept above the liquid level to prevent oil from entering the balanced bottles during sampling and then affecting the experimental results. After reaching equilibrium, the sampling tubes were preheated in an oven to avoid disturbing the equilibrium, and then the supernatant used to determine the chemical composition of the equilibrium liquid phase via chemical analysis.

To prevent effects from CO2 in the air, the samples were collected in a nitrogen cabinet. The contents of CO2 in the vapor phase were quite small in most cases: the ratio of the partial pressure to the total pressure in the equilibrium vapor phase was only 0.09—0.25%. In addition, the experimental systems were sealed and the volumes of the vapor phases were much smaller than those of the liquid and solid phases. Accordingly, the formation of CO2 had almost no effect on the equilibrium fluid composition.

2.3. Analytical Methods. 2.3.1. Liquid-Phase Analytical Methods. According to a previously reported method,11,12 the total alkali (sodium carbonate and sodium hydroxide) content was titrated with standard hydrochloric acid using methyl orange solution as an indicator. The content of NaOH was determined by excess alkaliometry using phenolphthalein solution as an indicator. The chlorine ion concentration was measured by silver nitrate titration. The content of sulfate ions was determined by a
gravimetric method. The details of the abovementioned analytical methods can be found in the literature.13 The solution density was measured by the density bottle method with a precision of ±0.0002 g. Each experiment was performed three times in parallel, and a relative standard uncertainty of 0.05 was achieved.14−17,21 The results of the repeatability experiments shown in Table 3 confirmed that the phase equilibrium data measured by the setup in this work had good repeatability.

2.3.2. Identification of the Solid Phase. The solids were analyzed by the wet residue method. The wet residue point and the liquid phase point were on the same line, and the equilibrium solid point was on the extension line. The solids were then analyzed by the abovementioned method to obtain the composition of the solid phases. In addition, the crystalloid form could be identified by an auxiliary method; that is, the wet solid sample was further prepared by drying with filter paper and studied by X-ray powder diffraction (XRD).18 To confirm the reliability of the experimental apparatus and method utilized in this article, before the formal experiment, we measured the data for one cosaturation point of the system NaCl−NaOH−H2O with the experimental apparatus developed. The results

Table 6. Equilibrium Solubilities of the Ternary System NaCl−NaOH−H2O at T = 363.15 K and P = 88.94 kPa

| no. | NaCl  | NaOH  | H2O  | NaCl  | NaOH  | H2O  | ρ/g·cm⁻³ | equilibrium phase solids¹ |
|-----|-------|-------|------|-------|-------|------|---------|--------------------------|
| 1   | 27.80 | 0.00  | 72.2 | 46.34 | 0.00  | 53.66 | 1.1723  | Cl                       |
| 2   | 24.09 | 4.65  | 71.26| 63.49 | 2.31  | 34.20 | 1.1935  | Cl                       |
| 3   | 20.28 | 9.95  | 69.77| 67.11 | 3.67  | 29.22 | 1.2195  | Cl                       |
| 4   | 16.65 | 14.72 | 68.63| 47.89 | 9.18  | 42.93 | 1.2445  | Cl                       |
| 5   | 11.96 | 24.28 | 63.76| 45.78 | 14.80 | 39.42 | 1.3170  | Cl                       |
| 6   | 7.16  | 34.34 | 58.50| 40.49 | 21.58 | 37.93 | 1.3708  | Cl                       |
| 7   | 5.30  | 39.91 | 54.79| 39.47 | 25.17 | 35.16 | 1.4139  | Cl                       |
| 8   | 3.67  | 49.18 | 47.15| 56.67 | 22.15 | 17.28 | 1.5019  | Cl                       |
| 9   | 2.63  | 55.81 | 41.56| 57.78 | 23.77 | 18.45 | 1.5444  | Cl                       |
| 10  | 2.13  | 60.04 | 37.83| 54.38 | 28.22 | 17.40 | 1.5763  | Cl                       |
| 11  | 2.09  | 65.61 | 32.30| 68.99 | 21.85 | 9.16  | 1.5831  | Cl                       |
| 12(E)| 2.87  | 68.87 | 28.26| 41.55 | 41.42 | 17.03 | 1.5831  | Cl + OH                  |
| 13  | 2.30  | 70.17 | 27.53| 57.89 | 74.64 | 23.12 | 1.5831  | OH                       |
| 14  | 2.32  | 71.56 | 26.12| 1.74  | 75.65 | 22.61 | 1.5831  | OH                       |
| 15  | 1.60  | 73.52 | 24.88| 1.48  | 75.20 | 23.32 | 1.5831  | OH                       |
| 16  | 0.00  | 76.28 | 23.72| 0.00  | 76.42 | 23.58 | 1.5884  | OH                       |

¹Standard uncertainties are: u(T) = 0.1 K, u(P) = 0.5 kPa, and u_r(NaCl) = u_r(NaOH) = 0.05. b w(B) is the mass fraction of the component (B).

Abbreviations: OH, NaOH and Cl, NaCl.

Figure 3. X-ray diffraction photograph of the cosaturation points E₁ and E₂ of the ternary system NaOH−Na₂SO₄−H₂O at 363.15 K.

Figure 4. Equilibrium phase diagrams of the ternary system NaCl−NaOH−H₂O at 363.15 K and 88.94 kPa; (•) measured solubility; (—) solubility curve.

(Shown in Table 4) were in good accordance with the data in the literature.4,5
3. RESULTS AND DISCUSSION

3.1. Solid−Liquid Phase Equilibrium. 3.1.1. Ternary System NaOH−Na2SO4−H2O at 363.15 K. The measured solubilities of the ternary system NaOH−Na2SO4−H2O at 363.15 K are listed in Table 5. The solubility of the equilibrated liquid phase is expressed as the mass fraction, and the corresponding phase diagram is plotted in Figure 2. There are two cosaturation points, E1 and E2, and two solubility curves, DE1 and E1E2. Figure 3 shows the XRD patterns of the cosaturation points in this system. According to this figure, points E1 and E2 correspond to the cosaturation points of Na2SO4 + NaOH·Na2SO4 and NaOH·Na2SO4 + NaOH, respectively.

Table 7. Experimental Values of Solubility and Dry Salt of the Quaternary System NaOH−Na2CO3−Na2SO4−H2O at T = 363.15 K and P = 88.94 kPa

| no. | NaOH | Na2CO3 | Na2SO4 | H2O | NaOH | Na2CO3 | Na2SO4 | H2O mass (g/100 g dry salt) | solution density ρ/g/cm−3 | equilibrium phase solids |
|-----|------|--------|--------|-----|------|--------|--------|-------------------------------|--------------------------|-------------------------|
| 1   | 0.00 | 0.00   | 29.91  | 70.09 | 0.00 | 0.00   | 100.00 | 234.34                       | 1.1984                   | S                        |
| 2   | 34.18 | 2.22   | 0.00   | 93.60 | 63.60 | 30.00  | 0.00   | 174.73                       | 1.3321                   | S1 + S                  |
| 3   | 71.62 | 2.75   | 0.00   | 25.63 | 96.30 | 3.70   | 0.00   | 31.10                        | 1.5884                   | OH                      |
| 4   | 76.28 | 0.00   | 0.00   | 23.72 | 100.00| 0.00   | 0.00   | 102.68                       | 1.4696                   | C + OH                  |
| 5   | 48.79 | 0.55   | 0.00   | 50.66 | 98.88 | 1.12   | 0.00   | 255.49                       | 1.3239                   | C1 + C                  |
| 6   | 17.14 | 10.99  | 0.00   | 71.87 | 60.93 | 39.07  | 0.00   | 227.87                       | 1.3112                   | C1                      |
| 7   | 0.00  | 30.50  | 0.00   | 69.50 | 0.00 | 100.00 | 0.00   | 227.87                       | 1.3112                   | C1                      |
| 8   | 0.00  | 20.65  | 6.40   | 72.95 | 0.00 | 76.34  | 23.66  | 227.87                       | 1.3112                   | C1                      |
| 9   | 0.00  | 4.41   | 25.99  | 69.60 | 0.00 | 14.51  | 85.49  | 228.95                       | 1.2248                   | S + γ                   |
| 10  | 3.85  | 3.60   | 23.08  | 69.47 | 12.61 | 11.79  | 75.60  | 228.95                       | 1.2248                   | S1 + OH                 |
| 11  | 8.81  | 2.96   | 19.79  | 68.44 | 27.92 | 9.37   | 62.71  | 226.80                       | 1.2193                   | S + γ                   |
| 12  | 12.07 | 3.54   | 17.23  | 67.16 | 36.93 | 10.78  | 52.29  | 226.80                       | 1.2193                   | S + γ                   |
| 13  | 21.89 | 2.29   | 10.22  | 65.60 | 63.64 | 6.66   | 29.70  | 203.66                       | 1.2547                   | S + γ                   |
| 14(E1) | 27.03 | 2.29   | 66.1   | 64.07 | 75.23 | 6.37   | 18.40  | 178.38                       | 1.2869                   | S + C1                  |
| 15(E2) | 55.85 | 2.09   | 1.69   | 40.37 | 93.60 | 3.51   | 2.83   | 67.71                        | 1.5477                   | OH + S1 + γ             |
| 16(E3) | 51.66 | 2.86   | 0.84   | 44.64 | 93.32 | 5.16   | 1.52   | 80.66                        | 1.5102                   | C1 + C + OH             |
| 17(E4) | 61.85 | 4.89   | 1.78   | 31.48 | 90.27 | 7.14   | 2.59   | 45.94                        | 1.5885                   | OH + C1 + γ             |
| 18  | 21.55 | 5.08   | 2.23   | 71.12 | 74.62 | 17.58  | 7.80   | 246.24                       | 1.2525                   | C1 + γ                  |
| 19  | 11.80 | 13.16  | 4.28   | 70.76 | 40.36 | 45.00  | 14.64  | 242.08                       | 1.2192                   | C1 + γ                  |
| 20  | 10.64 | 13.86  | 4.54   | 70.96 | 36.65 | 47.72  | 15.63  | 244.39                       | 1.2203                   | C1 + γ                  |
| 21  | 8.64  | 15.02  | 5.05   | 71.29 | 30.10 | 52.32  | 17.58  | 248.29                       | 1.2216                   | C1 + γ                  |

*aStandard uncertainties u are u(T) = 0.1 K, u(P) = 0.5 kPa, and u(\(\text{Na}_2\text{CO}_3\)) = u(\(\text{Na}_2\text{SO}_4\)) = u(\(\text{NaOH}\)) = 0.05. bAbbreviations: S, Na2SO4; OH, NaOH; C1, Na2CO3·H2O; S1, Na2SO4·NaOH; and γ, mNa2SO4·nNa2CO3.

Figure 5. X-ray diffraction photograph of the cosaturation point E of the ternary system NaCl−NaOH−H2O at 363.15 K.

Figure 6. Dry salt and water diagrams of the quaternary system NaOH−Na2CO3−Na2SO4−H2O at 363.15 K and 88.94 kPa: (●) measured solubility; (---) solubility curve.
3.1.2. Ternary System NaOH−NaCl−H₂O at 363.15 K.

The measured solubilities of the ternary system NaCl−NaOH−H₂O at 363.15 K are presented in Table 6. The compositions of the saturated solution and wet solid phase are expressed as mass fractions. The corresponding phase diagram is shown in Figure 4. There is one cosaturation point, E, and two crystallization regions, CDE and EBF. Point E corresponds to the cosaturation of NaCl + NaOH. The two solubility curves of this ternary system are represented by curves DE and FE. The crystallization field of NaCl (EBFE) is larger than that of NaOH (CDEC). The XRD pattern of the cosaturation point (point E) is given in Figure 5.

Table 8. Solubilities of Solutions in the Quaternary System NaCl−Na₂CO₃−NaOH−H₂O at T = 363.15 K and P = 88.94 kPa

| no. | NaOH  | Na₂CO₃ | NaCl  | H₂O   | NaOH | Na₂CO₃ | NaCl  | H₂O   | H₂O mass (g/100 g dry salt) | solution density ρ/g·cm⁻³ | equilibrium phase solids¹ |
|-----|-------|--------|-------|-------|------|--------|-------|-------|-----------------------------|-----------------------------|--------------------------|
| 1   | 0.00  | 0.00   | 27.80 | 72.20 | 0.00 | 0.00   | 100.00| 0.00  | 259.71                      | 1.1723                      | Cl                       |
| 2   | 68.87 | 0.00   | 2.87  | 28.26 | 96.00| 0.00   | 4.00  | 0.00  | 39.39                       | 1.5831                      | Cl + OH                  |
| 3   | 76.28 | 0.00   | 0.00  | 23.72 | 100.00| 0.00  | 0.00  | 0.00  | 31.10                       | 1.5884                      | OH                       |
| 4   | 48.79 | 0.55   | 0.00  | 50.66 | 98.88| 1.12   | 0.00  | 0.00  | 102.68                      | 1.4696                      | OH + C                   |
| 5(F₁) | 51.00| 2.05   | 4.01  | 42.94 | 89.38| 3.59   | 7.03  | 0.00  | 75.26                       | 1.5215                      | Cl + OH + Cl             |
| 6   | 36.51 | 1.95   | 3.64  | 57.90 | 86.72| 4.64   | 8.64  | 0.00  | 137.52                      | 1.3868                      | C + Cl                   |
| 7(F₂) | 34.21| 1.69   | 4.34  | 59.76 | 85.02| 4.20   | 10.78 | 0.00  | 148.51                      | 1.3680                      | C + C₁ + Cl              |
| 8   | 17.14 | 10.99  | 0.00  | 71.87 | 60.93| 39.07  | 0.00  | 0.00  | 255.49                      | 1.2339                      | C + C₁                   |
| 9   | 0.00  | 30.50  | 0.00  | 69.50 | 0.00 | 100.00 | 0.00  | 0.00  | 227.87                      | 1.3112                      | C₁                      |
| 10  | 0.00  | 9.97   | 21.09 | 68.94 | 0.00 | 32.10  | 67.90 | 0.00  | 221.96                      | 1.2031                      | C₁ + Cl                  |
| 11  | 8.65  | 3.17   | 15.54 | 72.64 | 31.61| 11.57  | 56.82 | 0.00  | 265.62                      | 1.2084                      | C₁ + Cl                  |
| 12  | 16.42 | 2.57   | 10.71 | 70.30 | 55.28| 8.67   | 36.05 | 0.00  | 236.73                      | 1.2453                      | C₁ + Cl                  |
| 13  | 28.46 | 3.15   | 9.47  | 58.92 | 69.29| 7.65   | 23.06 | 0.00  | 143.42                      | 1.3418                      | C₁ + Cl                  |
| 14  | 24.67 | 1.58   | 7.14  | 66.61 | 73.88| 4.73   | 21.39 | 0.00  | 199.44                      | 1.2940                      | C₁ + Cl                  |
| 15  | 30.11 | 1.65   | 4.6   | 63.64 | 82.81| 4.54   | 12.65 | 0.00  | 175.06                      | 1.3286                      | C₁ + Cl                  |

¹Standard uncertainties are u(T) = 0.1 K, u(P) = 0.5 kPa, and u_r(Na₂CO₃) = u_r(NaCl) = u_r(NaOH) = 0.05. ²Abbreviations: OH, NaOH; Cl, NaCl; C, Na₂CO₃; and C₁, Na₂CO₃·H₂O.

3.1.2. Ternary System NaOH−NaCl−H₂O at 363.15 K. The measured solubilities of the ternary system NaCl−NaOH−H₂O at 363.15 K are presented in Table 6. The compositions of the saturated solution and wet solid phase are expressed as mass fractions. The corresponding phase diagram is shown in Figure 4. There is one cosaturation point, E, and two crystallization regions, CDE and EBF. Point E corresponds to the cosaturation of NaCl + NaOH. The two solubility curves of this ternary system are represented by curves DE and FE. The crystallization field of NaCl (EBFE) is larger than that of NaOH (CDEC). The XRD pattern of the cosaturation point (point E) is given in Figure 5.
3.1.3. NaOH−Na₂SO₄−H₂O System at 363.15 K.

The experimental solubilities and equilibrium solids of the quaternary system NaOH−Na₂SO₄−H₂O at 363.15 K are listed in Table 7. Based on the Jänecke dry salt indices, the dry salt solubility and water diagrams are plotted in Figure 6. A solid solution \( \gamma \text{Na}_2\text{SO}_4 \cdot n\text{Na}_2\text{CO}_3 \) without complex salt was formed. Points E₁, E₂, E₃, and E₄ are the cosaturation points representing the saturation of Na₂SO₄ + \( \gamma \) + Na₂SO₄·NaOH, NaOH + Na₂SO₄·NaOH + \( \gamma \), NaOH + Na₂CO₃ + Na₂SO₄·H₂O, and NaOH + Na₂CO₃·H₂O + \( \gamma \), respectively. The system also contains six crystallization fields, which are represented by NaOH, Na₂CO₃, Na₂CO₃·H₂O, Na₂SO₄, S₁(Na₂SO₄·NaOH), and \( \gamma \)-salt. The \( \gamma \)-salt has the largest crystallization field, indicating that it has the lowest solubility and thus can be readily crystallized out. The XRD patterns of points E₁, E₂, E₃, and E₄ are given in Figure 7.

3.1.4. Na₂CO₃−NaOH−NaCl−H₂O System at 363.15 K.

The experimental solubility data for the quaternary system Na₂CO₃−NaOH−NaCl−H₂O at 363.15 K were determined and combined with the literature data. These data are presented in Table 8 in 15 groups, and the solution composition of the equilibrium liquid phase is expressed in terms of the mass fraction and Jänecke index (g/100 g dry salt). The corresponding phase and water diagrams of the system are shown in Figure 8. The phase diagram consists of two points, E₁ and E₂, which are the cosaturation points of NaOH + Na₂CO₃ + NaCl and Na₂CO₃·H₂O + Na₂CO₃ + NaCl, respectively; and four crystallized regions, AGE₂FA, FBDE₁E₂F, GE₂E₁CG, and E₁DCH, which correspond

![Figure 8. Equilibrium phase/water diagrams of the quaternary system NaCl−Na₂CO₃−NaOH−H₂O at 363.15 K and 88.94 kPa (●) measured solubility; (—) solubility curve.](https://dx.doi.org/10.1021/acsomega.9b03703)

![Figure 9. X-ray diffraction photograph of the cosaturation point E₁ and E₂ of the quaternary system NaCl−Na₂CO₃−NaOH−H₂O at 363.15 K.](https://dx.doi.org/10.1021/acsomega.9b03703)

Table 9. Experimental Values of Solubilities and Dry Salt of the Quaternary System NaOH−Na₂SO₄−NaCl−H₂O at T = 363.15 K and P = 88.94 kPa

| no. | NaOH | Na₂SO₄ | NaCl | H₂O | NaOH | Na₂SO₄ | NaCl | H₂O mass (g/100 g dry salt) | solution density ρ/(g·cm⁻³) | equilibrium phase solids |
|-----|------|--------|------|-----|------|--------|------|-----------------------------|---------------------------|--------------------------|
| 1   | 76.28| 0.00   | 0.00 | 23.72| 100.00| 0.00   | 0.00 | 31.10                       | 1.5884                    | OH                       |
| 2   | 71.62| 2.75   | 0.00 | 25.63| 96.30 | 3.70   | 0.00 | 34.46                       | 1.5884                    | S₁ + OH                  |
| 3   | 34.18| 2.22   | 0.00 | 63.60| 93.90 | 6.10   | 0.00 | 118.87                      | 1.3321                    | S₁ + S                   |
| 4   | 41.85| 3.13   | 0.71 | 54.31| 91.59 | 8.41   | 0.94 | 114.5                    | 1.5831                    | S + S₁ + S₃             |
| 5   | 49.07| 3.64   | 2.65 | 44.64| 88.63 | 5.37   | 1.85 | 80.59                       | 1.5831                    | Cl + S₃                  |
| 6   | 60.44| 4.24   | 4.60 | 31.54| 88.28 | 5.00   | 6.72 | 46.07                       | 1.5831                    | Cl + S₃                  |
| 7   | 64.73| 3.27   | 3.98 | 28.02| 89.92 | 4.55   | 5.33 | 38.92                       | 1.5832                    | Cl + S + OH             |
| 8   | 74.98| 2.91   | 3.12 | 18.99| 92.56 | 3.59   | 3.85 | 23.44                       | 1.5831                    | Cl + S + OH             |
| 9   | 81.28| 2.58   | 2.33 | 13.81| 94.30 | 2.99   | 2.71 | 16.03                       | 1.5832                    | Cl + S + OH             |
to Na₂CO₃·H₂O, NaCl, Na₂CO₃, and NaOH, respectively. Among the crystallization fields, the crystallization field of Na₂CO₃·H₂O is the largest, suggesting that this salt is very easily crystallized because of its lower solubility in the quaternary system. Neither a solid solution nor a complex salt was formed. The XRD patterns of the crystallization solution are expressed in terms of the mass fraction and Jahnke index of its lower solubility in the quaternary system. Neither a solid solution nor a complex salt was formed. The XRD patterns of the cosaturation points in this system without the formation of a solid solution. Figure 11 shows the XRD patterns of the cosaturation points in this system. According to this figure, points E₁, E₂, E₃, and E₄ correspond to the cosaturation points of S₁ + S₃ + S, Cl + S + S₃, OH + S + Cl, and S₁ + S₃ + OH, respectively.

### 4. SOLUBILITY PREDICTIONS

For SLEs, Xu²⁻¹⁻¹⁻¹⁻¹ proposed a new hypothesis for the reference state of activity coefficients with respect to solubility predictions. In the model, he assumed that the new reference state of activity coefficients is the activity of the solute: \( a_i (=m_i \times \gamma_i) \to 1 \) as \( m_i \to 0 \). This reference is meaningful only for SLE, not other situations.

For the calculation, water–salt parameters for electrolyte solutions are shared in single salt systems and mixed salt systems. The excess Gibbs energy is described as follows

\[
G^e = G^e_w + G^e_x
\]

\[
\frac{n_i G^e_w}{RT} = m_i E_i
\]

\[
\frac{n_i G^e_x}{RT} = \sum (m_m F_{ij} + m_j F_{ij})
\]

\[
RT \ln \gamma_i = \left( \frac{\partial n_i G^e}{\partial n_i} \right)
\]

The function of \( G^e_w \) is based on the excess Gibbs energy function of the Pitzer model and \( G^e_w \) is adopted to account for the electrostatic interaction term between single electrolyte and water. The function of \( G^e_x \) is based on the excess Gibbs energy function of the Pitzer model and \( G^e_w \) is the electrostatic interaction term between salt and salt, which is usually used in multicomponent electrolyte solutions. It is assumed that solubility of every dissolved solid is affected by other solutes in multicomponent electrolyte solutions, where \( m_i \) and \( m_j \) are the molalities of the solution; \( E_{ij} \), \( F_{ij} \), and \( G_{ij} \) are the interaction parameters at a particular temperature; \( \kappa \) is \( 0.5 \).

We obtain the activity coefficient expression of the solute from eqs 1–4, the expression for the solute is as follows

\[
\ln \gamma_i = p_{a_i} T + p_{a_i} T^{1.5} + p_{a_i} T / T + \sum (p_{a_i} T + p_{a_i} T^{1.5} m_j + p_{a_i} T + p_{a_i} T^{1.5} m_j)
\]
Figure 11. X-ray diffraction photograph of the cosaturation points E₁, E₂, E₃, and E₄ of the quaternary system NaOH−Na₂SO₄−NaCl−H₂O at 363.15 K.

Table 10. Salt−Salt Parameters for Electrolyte Solutions

| System | Crystal | Salts | p[^b] | p[^b] | p[^a] |
|--------|---------|-------|-------|-------|-------|
| NaCl−NaOH−H₂O | NaCl | NaOH | −0.0149 | 0.4133 | −2.1404 |
| | NaOH | NaCl | 0.7917 | −0.4974 | −4.3871 |
| | Na₂SO₄ | NaOH | −2.1514 | 2.0314 | −4.3869 |
| | Na₂SO₄−NaOH | Na₂SO₄ | 0.0704 | −1.0505 | 3.1256 |
| | | Na₂CO₃ | −1.9303 | −6.1879 | −1.0298 |
| | | Na₂CO₃ | 0.1633 | −0.1272 | |
| | | Na₂CO₃−H₂O | −4.3639 | 3.2865 | −1.2025 |
| | | Na₂CO₃−H₂O | −0.0428 | 0.3725 | |
| | | Na₂SO₄ | −0.9579 | 0.9387 | −1.1008 |
| | | Na₂SO₄ | 0.1688 | −0.0149 | |
| NaOH−Na₂SO₄−H₂O | Na₂SO₄ | NaOH | −2.5062 | 2.7415 | |
| | | Na₂SO₄ | 0.9340 | −4.0026 | 6.2569 |
| | | Na₂SO₄ | 1.0652 | −4.2955 | |
| | | Na₂SO₄ | −0.0042 | 0.0349 | |
| | Na₂CO₃ | NaOH | 3.2472 | −3.7620 | −1.7964 |
| | | Na₂CO₃ | −0.1235 | 1.1247 | |
| | | NaOH | −7.5784 | 6.1927 | −4.3869 |
| | | Na₂CO₃ | 0.1839 | −0.0306 | |
| Na₂CO₃−Na₂SO₄−NaOH−H₂O | Na₂CO₃ | NaOH | −0.9737 | 8.2281 | −14.6524 |
| | | Na₂CO₃ | 4.8361 | −6.4716 | |
| | | Na₂CO₃ | −0.1109 | 0.5905 | −1.2514 |
| | | Na₂CO₃ | −1.0737 | 2.7899 | |
| | | NaCl | −0.7166 | 0.2424 | −1.8233 |
We obtain the activity expression from Eq. 6, and the activity of the solute is as follows

\[ a_i = m_i^{0.5} \]

We obtain the activity expression from Eq. 6, and the activity of the solute is as follows

\[ a_i = m_i^{0.5} \]

\[ + \sum_{j \neq i} (Ph_{j} T + p_{c_{j}} T^{0.5}) \]

Then, based on the reference state of activity coefficients \((a_i \rightarrow 1)\) and \((m_i \rightarrow \text{solubility})\) in this model, the solubility of the corresponding solute is obtained. The expression of the calculation is as follows

\[ m_s \exp \left( Ph_{i} T + p_{c_{i}} T^{0.5} \right) \]

\[ + \sum_{j \neq i} (Ph_{j} T + p_{c_{j}} T^{0.5}m_j + pd_{i_{j}} T + p_{c_{i_{j}}} T^{0.5}m_j^{0.5}) \]

\[ = 1 \]

where \(m_s\) is the solubility of the solute.

The main expressions of the ion activity coefficient and the osmotic coefficient of water for the equation are briefly shown above. In this work, we calculated the solubility \(m_s\) of the corresponding solute. The software used for this calculation was...
Table 12. continued

| T/K  | NaOH | Na2SO4 solid phases | NaOH | Na2SO4 | dP%/% |
|------|------|---------------------|------|--------|-------|
| 69.86 | 0.76 | Na2SO4 + Na2SO4·H2O | 69.82 | 0.75 | 0.76 | 0.06 |
| 80.40 | 0.00 | NaOH | 80.40 | 0.00 | 5.38 | 5.22 |

average

\[ dP = \frac{1}{N} \sum |P_{exp} - P_{cal}| / P_{exp} \times 100\% \]

Table 13. Error Analysis for the NaOH–Na2CO3–NaCl–H2O System

| T/K  | NaOH | Na2CO3 | NaCl solid phases | NaOH | Na2CO3 | NaCl | dP%/% |
|------|------|--------|---------------------|------|--------|------|-------|
| 363.15 | 0.00 | 0.00 | 6.55 Cl | 6.03 | 7.95 |
| 69.93 | 0.00 | 1.73 Cl + OH | 1.72 | 0.65 |
| 29.69 | 0.45 | 1.59 C + OH + Cl | 1.49 | 6.44 |
| 15.76 | 0.32 | 1.07 C + Cl | 1.18 | 10.42 |
| 14.31 | 0.27 | 1.24 C + C1 + Cl | 1.47 | 19.03 |
| 0.00 | 1.36 | 5.20 C1 + Cl | 5.81 | 11.74 |
| 2.98 | 0.41 | 3.64 C1 + Cl | 3.67 | 0.90 |
| 5.84 | 0.34 | 2.59 C1 + Cl | 2.43 | 6.12 |
| 12.08 | 0.50 | 2.73 C1 + Cl | 2.49 | 8.85 |
| 9.26 | 0.22 | 1.82 C1 + Cl | 1.77 | 2.98 |
| 11.83 | 0.24 | 1.23 C1 + Cl | 1.29 | 4.98 |
| 60.93 | 0.00 | 1.73 C1 + Cl | 60.93 | 0.00 |
| 80.40 | 0.00 | 0.00 OH | 80.40 | 0.00 |
| 24.08 | 0.10 | 0.00 OH + C | 24.08 | 0.00 |
| 29.69 | 0.45 | 1.59 C + OH + Cl | 29.69 | 0.00 |
| 24.08 | 0.10 | 0.00 OH + C | 0.10 | 0.00 |
| 29.69 | 0.45 | 1.59 C + OH + Cl | 0.45 | 0.00 |
| 15.76 | 0.32 | 1.07 C + Cl | 0.32 | 0.00 |
| 14.31 | 0.27 | 1.24 C + C1 + Cl | 0.27 | 0.00 |
| 5.96 | 1.44 | 0.00 C + C1 | 1.44 | 0.00 |
| 14.31 | 0.27 | 1.24 C + C1 + Cl | 0.28 | 5.42 |
| 5.96 | 1.44 | 0.00 C + C1 | 1.60 | 11.05 |
| 0.00 | 4.14 | 0.00 C1 | 3.86 | 6.71 |
| 0.00 | 1.36 | 5.20 C1 + Cl | 1.45 | 6.51 |
| 2.98 | 0.41 | 3.64 C1 + Cl | 0.43 | 3.68 |
| 5.84 | 0.34 | 2.59 C1 + Cl | 0.32 | 6.93 |
| 12.08 | 0.50 | 2.73 C1 + Cl | 0.43 | 14.24 |
| 9.26 | 0.22 | 1.82 C1 + Cl | 0.27 | 18.51 |
| 11.83 | 0.24 | 1.23 C1 + Cl | 0.29 | 18.31 |

average

\[ dP = \frac{1}{N} \sum |P_{exp} - P_{cal}| / P_{exp} \times 100\% \]

Abbreviations: OH, NaOH; Cl, NaCl; C, Na2CO3; and C1, Na2CO3·H2O.

Table 14. Error Analysis for the NaOH–Na2CO3–Na2SO4–H2O System

| T/K  | Na2CO3 | Na2SO4 | NaOH solid phases | Na2CO3 | Na2SO4 | NaOH | dP%/% |
|------|--------|--------|---------------------|--------|--------|------|-------|
| 363.15 | 0.00 | 3.00 | 0.00 S | 3.00 | 0.00 |
| 60.93 | 2.63 | 0.00 | S + γ | 2.58 | 1.88 |
| 49.04 | 2.34 | 1.39 | S + γ | 2.48 | 6.03 |
| 61.04 | 2.04 | 3.22 | S + γ | 2.01 | 1.20 |
| 50.05 | 1.81 | 4.49 | S + γ | 1.77 | 2.07 |
| 33.03 | 1.10 | 8.34 | S + γ | 1.03 | 5.77 |
| 34.07 | 0.73 | 10.55 | S + γ + S1 | 0.77 | 5.33 |
| 1.01 | 0.00 | 69.86 | S1 + OH | 66.02 | 5.49 |
| 0.00 | 0.00 | 80.40 | OH | 72.33 | 10.03 |
| 0.10 | 0.00 | 24.08 | C + OH | 26.86 | 11.55 |
| 49.04 | 0.29 | 34.59 | OH + S1 + γ | 33.47 | 3.23 |
| 60.06 | 0.13 | 28.93 | C1 + C + OH | 30.84 | 6.58 |
| 1.47 | 0.40 | 49.12 | OH + C1 + γ | 49.83 | 1.45 |
| 0.10 | 0.00 | 24.08 | C + OH | 0.10 | 0.00 |
Table 14. continued

| T/K | Na₂CO₃ | Na₂SO₄ | NaOH | solid phases | calculated results | dP²/% |
|-----|--------|--------|------|-------------|-------------------|-------|
|     |        |        |      |             | Na₂CO₃ | Na₂SO₄ | NaOH |     |
| 1.44 | 0.00   | 5.96   | C + C₁ | 1.44        | 0.00  |
| 0.60 | 0.13   | 28.93  | C₁ + C + OH | 0.60       | 0.00  |
| 1.44 | 0.00   | 5.96   | C + C₁ | 1.51        | 4.94  |
| 4.14 | 0.00   | 0.00   | C₁     | 3.74        | 9.57  |
| 2.67 | 0.62   | 49.12  | OH + C₁ + γ | 2.76       | 3.32  |
| 1.67 | 0.40   | 7.58   | C₁ + γ | 0.74        | 9.07  |
| 0.67 | 0.22   | 4.17   | C₁ + γ | 1.54        | 12.10 |
| 1.75 | 0.43   | 3.75   | C₁ + γ | 1.72        | 6.74  |
| 1.84 | 0.45   | 3.03   | C₁ + γ | 1.89        | 4.68  |
| 1.99 | 0.50   | 0.00   | C₁ + γ | 2.69        | 0.62  |
| 0.60 | 2.63   | 0.00   | S + γ  | 0.59        | 2.61  |
| 0.49 | 2.34   | 1.39   | S + γ  | 0.49        | 2.32  |
| 0.41 | 2.04   | 3.22   | S + γ  | 0.41        | 2.07  |
| 0.50 | 1.81   | 4.49   | S + γ  | 0.50        | 1.81  |
| 0.33 | 1.10   | 8.34   | S + γ  | 0.33        | 1.11  |
| 0.34 | 0.73   | 10.55  | S + γ  + S₁ | 0.33       | 0.71  |
| 0.49 | 0.29   | 34.59  | OH + S₁ + γ | 0.48       | 0.29  |
| 1.47 | 0.40   | 49.12  | OH + C₁ + γ | 1.48       | 0.40  |
| 0.67 | 0.22   | 7.58   | C₁ + γ | 0.69        | 0.23  |
| 1.75 | 0.43   | 4.17   | C₁ + γ | 1.74        | 0.42  |
| 1.84 | 0.45   | 3.75   | C₁ + γ | 1.83        | 0.45  |
| 1.99 | 0.50   | 3.03   | C₁ + γ | 1.97        | 0.50  |
| average | 3.42 | 3.38 |

*aP = (1/N) ∑|P_exp − P_calc|/P_exp × 100%. bAbbreviations: S, Na₂SO₄; OH, NaOH; C₁, Na₂CO₃·H₂O; S₁, Na₂SO₄·NaOH; and γ, mNa₂SO₄·nNa₂CO₃.

Table 15. Error Analysis for the NaOH−Na₂SO₄−NaCl−H₂O System

| T/K | NaOH | Na₂SO₄ | NaCl | solid phases | calculated results | dP²/% |
|-----|------|--------|------|-------------|-------------------|-------|
|     |      |        |      |             | NaOH | Na₂SO₄ | NaCl |     |
| 363.15 | 47.91 | 0.76 | 2.48 | S + Cl + S | 2.73 | 10.25 |
| 57.75 | 0.82 | 2.42 | Cl + S | 2.69 | 11.22 |
| 98.71 | 1.08 | 2.79 | Cl + S | 2.71 | 3.14 |
| 147.14 | 1.32 | 2.87 | Cl + S + OH | 2.72 | 5.36 |
| 60.93 | 0.00 | 1.73 | Cl + OH | 1.82 | 5.38 |
| 12.91 | 0.53 | 5.06 | S + Cl | 4.31 | 14.82 |
| 5.49 | 0.48 | 5.19 | S + Cl | 4.86 | 6.32 |
| 0.00 | 0.59 | 6.39 | S + Cl | 7.43 | 16.32 |
| 0.00 | 0.00 | 6.55 | Cl | 6.32 | 3.53 |
| 80.40 | 0.00 | 0.00 | OH | 80.40 | 0.00 |
| 69.86 | 0.76 | 0.00 | S₁ + OH | 69.86 | 0.00 |
| 147.14 | 1.32 | 2.87 | Cl + S + OH | 147.14 | 0.00 |
| 114.14 | 1.52 | 1.06 | S₁ + S + OH | 114.14 | 0.00 |
| 60.93 | 0.00 | 1.73 | Cl + OH | 60.93 | 0.00 |
| 13.44 | 0.25 | 0.00 | S₁ + S | 0.28 | 12.02 |
| 19.26 | 0.41 | 0.22 | S + S₁ + S | 0.44 | 9.55 |
| 27.48 | 0.57 | 1.01 | S + S₁ | 0.64 | 11.73 |
| 47.91 | 0.76 | 2.48 | S + Cl + S₁ | 0.74 | 3.56 |
| 12.91 | 0.53 | 5.06 | S + Cl | 0.45 | 15.17 |
| 5.49 | 0.48 | 5.19 | S + Cl | 0.44 | 7.95 |
| 0.00 | 0.59 | 6.39 | S + Cl | 0.60 | 2.42 |
| 0.00 | 3.00 | 0.00 | S | 2.57 | 14.42 |
| 69.86 | 0.76 | 0.00 | S₁ + OH | 69.86 | 0.76 |
| 13.44 | 0.25 | 0.00 | S₁ + S | 13.44 | 0.25 |
| 19.26 | 0.41 | 0.22 | S + S₁ + S | 19.26 | 0.41 |
| 132.06 | 2.13 | 1.49 | S₁ + S | 132.06 | 2.15 |
| 114.14 | 1.52 | 1.06 | S₁ + S + OH | 114.14 | 1.52 |

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Table 10 presents the values of the parameters introduced in eq 5; the solute−solute parameters are listed.

The predictive capability of the model was examined by calculating SLE in mixed electrolyte solution systems using the parameter values obtained from the correlations of binary electrolyte solution systems. The predicted SLE data for the solutions NaOH−NaCl−H2O, NaOH−Na2SO4−H2O, NaOH−Na2CO3−Na2SO4−H2O, NaOH−Na2CO3−NaCl−H2O, NaOH−Na2SO4−NaCl−H2O, and S3, Na2SO4, NaCl, NaOH.

Table 15. continued

| T/K  | NaOH   | Na2SO4 | NaCl   | solid phases | NaOH   | Na2SO4 | NaCl | dP*/% |
|------|--------|--------|--------|--------------|--------|--------|------|-------|
|      |        |        |        |              |        |        |      |       |
| 19.26| 0.41   | 0.22   | S + S1 + S3 | 19.27  | 0.41   | 0.22  | 0.04 | 0.00  | 0.00 |
| 27.48| 0.57   | 1.01   | S + S3    | 27.43  | 0.57   | 1.01  | 0.19 | 0.00  | 0.00 |
| 47.91| 0.76   | 2.48   | S + Cl + S3 | 47.88  | 0.76   | 2.48  | 0.05 | 0.00  | 0.00 |
| 57.75| 0.82   | 2.42   | Cl + S3   | 58.04  | 0.83   | 2.43  | 0.49 | 1.22  | 0.41 |
| 98.71| 1.08   | 2.79   | Cl + S3   | 98.24  | 1.07   | 2.78  | 0.47 | 0.94  | 0.36 |
| 147.14| 1.32  | 2.87   | Cl + S3 + OH | 147.35 | 1.32  | 2.87  | 0.14 | 0.00  | 0.00 |
| 132.06| 2.15  | 1.49   | S1 + S3   | 132.04 | 2.15  | 1.49  | 0.01 | 0.00  | 0.00 |
| 114.14| 1.52  | 1.06   | S1 + S3 + OH | 114.20 | 1.52  | 1.06  | 0.05 | 0.00  | 0.00 |

average

\[ dP = \frac{1}{N} \sum |P_{exp} - P_{cal}| \times 100\% \]

Abbreviations: Cl, NaCl; OH, NaOH; S, Na2SO4; S1, Na2SO4·NaOH; and S3, Na2SO4·NaCl·NaOH.

Figure 12. Correlation of experimental SLE data for NaOH−NaCl−H2O.

Figure 13. Correlation of experimental SLE data for NaOH−Na2SO4−H2O.

Figure 14. Correlation of experimental SLE data for Na2CO3−NaCl−NaOH−H2O.

Figure 15. Correlation of experimental SLE data for Na2CO3−Na2SO4−H2O.

1stopt 6.0, and the computational algorithm was the Universal Global Algorithm.

Table 10 presents the values of the parameters introduced in eq 5; the solute−solute parameters are listed.

The predictive capability of the model was examined by calculating SLE in mixed electrolyte solution systems using the parameter values obtained from the correlations of binary electrolyte solution systems. The predicted SLE data for the solutions.

NaOH−NaCl−H2O, NaOH−Na2SO4−H2O, NaOH−Na2CO3−Na2SO4−H2O, NaOH−Na2CO3−NaCl−H2O, and NaOH−Na2SO4−NaCl−H2O are shown in Tables 11–15 and Figures 12–16.

The simulation data for the system at 363.15 K were obtained using the model and the parameters in Table 10. Comparisons of the experimental and calculated values of the ternary and quaternary invariant points for the quaternary system at 363.15 K are given in Tables 11–15; the calculated phase diagram is plotted using the simulation data in Figures 12–16. The analysis of the model as presented in the figures and tables shows that the simulation data agree well with the experimental data.
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5. CONCLUSIONS

The solubilities of the quaternary systems (NaOH–Na₂CO₃–Na₂SO₄–H₂O, NaOH–Na₂CO₃–NaCl–H₂O, and NaOH–Na₂SO₄–NaCl–H₂O) at 363.15 K were determined using the isothermal solubility method. The solid minerals were identified using X-ray diffraction. According to the experimental data and the identification result, the isothermal phase diagrams were plotted. The phase diagrams determined for the quaternary systems were applied in the analysis of the vaporization process, laying the foundation for research on the phase equilibrium of the quinary system.

Combining the experimental solubility data of the systems, the corresponding parameters were fitted with Xu’s modified activity coefficient model. Then, the solubilities for the systems at 363.15 K were demonstrated. A comparison of the calculated and experimental solubilities of the systems showed that the predicted solubilities are in accordance with experimental values.

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