

Experimental and thermodynamic modeling study of solid-liquid equilibrium in ternary systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O at 288.15 K and 0.1 MPa

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ABSTRACT

The solubilities and refractive indices of the NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O systems at 288.15 K were investigated with the isothermal dissolution method. The phase diagrams and refractive index diagrams were plotted for the two systems at 288.15 K. The phase diagrams consist of one two-salt cosaturated invariant point, two univariant solubility isotherms, and two stable crystallization fields. The two systems belong to the simple eutectic type, and neither double salt nor solid solution was found. The refractive indices change regularly with the strontium bromide concentration increasing in solution, and reach the maximum value at the eutectic point. On the basis of Pitzer and Harvie-Weare (HW) model, the binary and mixing Pitzer parameters and solubility equilibrium constants of equilibrium solid salts for the two ternary systems at 288.15 K were acquired. And then, the solubilities for the ternary systems at 288.15 K were demonstrated. A comparison shows that the calculated solubilities agree well with the experimental data.

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1. Introduction

Recently, bromine and strontium have been widely used in the technology fields and pharmaceuticals fields. The oilfield brines in Nanyishan Section in the Qaidam Basin of the Qinghai-Tibet Plateau, which belong to the CaCl₂ type, have high contents of lithium, potassium, strontium, bromine, as well as accompanying sodium, calcium, boron, and many other useful components. The concentration of bromine in the brines is up to 0.281 g·L⁻¹, and 4.45 g·L⁻¹ for strontium, which is much higher than those in the salt lake brines in Qinghai-Tibet Plateau [1,2]. These brines largely consist of the complex system (Li–Na–K–Ca–Sr–Cl–Br–borate–H₂O). It is well-known that phase equilibria and phase diagrams (solubility data) of brine systems are both the theoretical foundation for the exploitation of the brine resources [3]. Therefore, the investigation of the phase equilibria and phase diagrams will provide the fundamental chemical engineering thermodynamic data for the finer separation and comprehensive exploitation of brine resources using salinity-gradient solar pond technology.

The ternary systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O containing strontium bromine are important subsystems of the above complex system. Although the equilibria of the quaternary system NaBr–KBr–SrBr₂–H₂O at 348.15 K have been reported [4], the equilibria of the above

ternary systems at 288.15 K, which is nearly the same as the temperature for brine exploitation, has not been reported in the literature. Computer models on the aqueous solutions of electrolytes are reliable on predicting solution behavior and (solid + liquid) equilibria. The Pitzer and Harvie-Weare (HW) model, which is described in our study, was widely used in calculating the solubilities of the salt-water systems [5–8]. The models for the quinary system Na–K–Mg–Ca–Br–H₂O and Na–K–Ca–Br–SO₄–H₂O containing bromine have been constructed over a wide temperature range (273.15 to 373.15) K [9,10]. The thermodynamic properties of the system SrBr₂–H₂O, which can be used for Pitzer model construction, have been reported from 303.15 K to 343.15 K [11]. The mean activity coefficients of NaBr in NaBr–SrBr₂–H₂O system at 298.15 K were shown in the literature [12]. However, the models for the systems containing strontium bromine are still lacking in the literature. In this study, the solubilities and the refractive indices of the ternary systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O at 288.15 K were determined, and the solubilities for the ternary systems were also calculated on the basis of Pitzer and Harvie-Weare (HW) model.

2. Experimental section

2.1. Apparatus and reagents

The phase equilibrium has been done in a magnetic stirring thermostatic bath (HXC-500-12A, Shanghai Baidian Experimental Instrument

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Table 1
Chemical sample information.

Chemical name	Source	Initial purity (mass fraction)	Purity grade
NaBr	Aladdin Industrial Corp.	0.99	Analytical purity
KBr	Aladdin Industrial Corp.	0.99	Analytical purity
SrBr ₂ ·6H ₂ O	Aladdin Industrial Corp.	0.98	Analytical purity

Ltd., temperature uncertainty ± 0.1 K). An X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands) was used to identify the solid phase minerals. The chemicals used in this work were analytical purity grade, as shown in Table 1. The water used in the experiments such as chemical analysis was double distilled water (DDW) with conductivity $\leq 1.2 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$ and pH ≈ 6.60 at 298.15 K.

2.2. Experimental methods

The isothermal dissolution method, which was described in our previous study [5], was used to measure the solubility of the systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O in this study. According to the estimated solubilities of the ternary system, a series of artificial synthesized brines by mixing appropriate amount of salts and DDW were prepared, and loaded into clean glass bottles, which were placed in the thermostatic bath, with the temperature at (288.15 ± 0.1) K and stirring speed at 300 rpm to quicken the equilibrium of those brines. The solid phase in the bottle should always exist during the equilibrium process. The stirring would stop for 2 h to make the solid and liquid phases stratification, and then a sample of approximately 3.0 cm³ of the clarified solution was taken, weighed accurately, diluted in a 250.0 cm³ volumetric flask with DDW and measured periodically. If the difference between the concentrations of the two samples taken from the same glass bottle was within $\pm 0.3\%$ in mass fraction, then the equilibrium state achieved. Otherwise, the solution was stirred continually until the equilibrium state achieved. The average of the concentrations of the two samples was the solubility data of this point. Generally, it took approximately 15 days to reach the equilibrium state at 288.15 K for the two systems. Meanwhile, some of the liquid phases were taken out for refractive index measurement. And the solid phases were also sampled and identified by Schreinemaker's wet residue method [13] (the liquid phase point, the wet residue point and the solid phase mineral point in the phase diagrams are in a line) and the X-ray diffraction. The remainder of the solid and liquid phases in the bottles was used to synthesize another system point.

2.3. Analytical method

The Sr²⁺ ion concentration was measured by titration with an EDTA standard solution in the presence of MgCl₂ and ammonia buffer solution with the indicator Eriochrome Black-T [14]. The Br[−] ion concentration determined was by titration with a standard solution of Hg(NO₃)₂ in the presence of mixed indicator of diphenylcarbazone and bromophenol blue [15]. The relative deviation for the Sr²⁺ and Br[−] concentrations was less than ± 0.003 . The concentration for Na⁺ and K⁺ was calculated in view of the charge balance of ions with relative deviation no more than ± 0.006 . The refractive indices (n_D) of liquid phases were measured with a WZS-1 type abbe refractometer at (288.15 ± 0.1) K, with an uncertainty of ± 0.0001 .

3. Results and discussion

The solubilities for the binary systems NaBr–H₂O and KBr–H₂O at different temperatures have been studied in many references, the difference between the solubilities at the same temperature have been reported in more detail [16]. The solubilities for the two systems at 288.15 K in this study are nearly the same as those in the literature, so the difference between experimental data in this study and those in

the literature for the binary systems were not discussed any more. The solubility for the SrBr₂–H₂O system was reported in many literature. There are solubility data from 273.15 to 373.15 K listed in the CRC Handbook of Chemistry and Physics [17]. The solubility data at 298.15 K agree well with the data (0.5160 in mass fraction) from Harkins and Pearce [18], but are higher than these from Milikan (0.4979 in mass fraction) [19], Scott and Durham (0.4993 in mass fraction) [20]. Ropp also give the solubility data for the SrBr₂–H₂O system from 273.15 to 363.15 K [21], which are the same as these in the handbook at 273.15 and 283.15 K, but higher at other temperatures. In this study, the equilibrium time for this system at 288.15 K was more than one month, and the solubility of SrBr₂ was carefully checked several times. The solubility data is 0.4927, which is close to the interpolated solubility data from the Handbook. A comparison between the solubility data at different temperatures are presented in Fig. 1. It is shown that the solubility data for SrBr₂ increases with increasing temperature.

The experimental solubility data and refractive indices of the NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O systems at 288.15 K are listed in Tables 2 and 3. w_i in Tables 2 and 3 is the concentration (mass fraction) for the mineral *i*. According to the experimental solubility data of Tables 2 and 3, the phase diagrams of the systems were shown in Figs. 2 and 3.

The points A and B in Table 2 and Fig. 2 represent the solubilities of the binary systems NaBr–H₂O and SrBr₂–H₂O at 288.15 K. The phase diagram in Fig. 2 has one invariant point E cosaturated with NaBr·2H₂O and SrBr₂·6H₂O, two univariant solubility curves AE and EB, and two crystallization fields for NaBr·2H₂O and SrBr₂·6H₂O. The crystallization area of NaBr·2H₂O is relatively large, while the crystallization area of SrBr₂·6H₂O are relatively small, which shows strontium bromide has a higher solubility than sodium bromide. The concentration of sodium bromide decreases with strontium bromide concentration increasing, which shows that strontium bromide has a strong salt-out effect on sodium bromide.

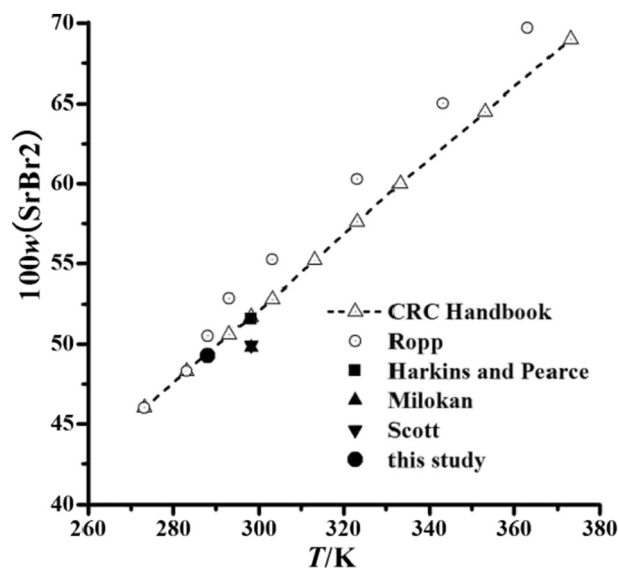


Fig. 1. Comparison of the experimental solubilities of SrBr₂ at different temperatures. Δ , Ref. 17; \circ , Ref. 21; \blacksquare , Ref. 18; \blacktriangle , Ref. 19; \blacktriangledown , Ref. 20; \bullet , this study.

Table 2

Experimental solubilities and refractive indices of the NaBr–SrBr₂–H₂O system at 288.15 K and pressure $p = 0.1$ MPa.^a

No.	Liquid phase, 100w ^b		Wet residue, 100w		Refractive index, n_D	Equilibrium solid phase
	NaBr	SrBr ₂	NaBr	SrBr ₂		
1, A	47.04	0.00	– ^c	–	1.4196	NaBr·2H ₂ O
2	43.07	4.48	–	–	1.4229	NaBr·2H ₂ O
3	41.63	5.99	50.88	4.43	1.4241	NaBr·2H ₂ O
4	38.36	9.78	–	–	1.4268	NaBr·2H ₂ O
5	34.23	13.89	–	–	1.4324	NaBr·2H ₂ O
6	32.12	16.78	45.13	11.58	1.4347	NaBr·2H ₂ O
7	27.24	22.74	–	–	1.4391	NaBr·2H ₂ O
8	24.05	27.41	34.28	21.67	1.4420	NaBr·2H ₂ O
9, E	20.49	32.08	25.37	39.48	1.4447	NaBr·2H ₂ O + SrBr ₂ ·6H ₂ O
10	13.5	37.21	–	–	1.4433	SrBr ₂ ·6H ₂ O
11	8.79	41.06	6.27	49.20	1.4428	SrBr ₂ ·6H ₂ O
12	5.37	43.27	–	–	1.4421	SrBr ₂ ·6H ₂ O
13	2.38	47.52	1.75	55.36	1.4415	SrBr ₂ ·6H ₂ O
14, B	0.00	49.27	–	–	1.4413	SrBr ₂ ·6H ₂ O

^a Standard uncertainties u , $u(T) = 0.1$ K, $u(p) = 0.005$ MPa, $u(w(\text{NaBr})) = 0.0077$, $u(w(\text{SrBr}_2)) = 0.0084$ and $u(n_D) = 0.0001$.

^b w , mass fraction.

^c –, not determined.

The points C and D in Table 3 and Fig. 3 represent the solubilities of the binary systems KBr–H₂O and SrBr₂–H₂O at 288.15 K. There is one invariant point F cosaturated with KBr and SrBr₂·6H₂O, two univariant solubility isotherms CF and FD, and two crystallization fields of KBr and SrBr₂·6H₂O in Fig. 3. The solubility of strontium bromide is higher than that of potassium bromide in Fig. 3. Strontium bromide has a strong salt-out effect on potassium bromide. It can be concluded that the systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O belong to the simple eutectic type, and neither double salt nor solid solution was found.

Using the refractive index data in Tables 2 and 3, the refractive index diagrams between the refractive indices and $w(\text{SrBr}_2)$ for the systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O were plotted in Fig. 4. The refractive indices in Fig. 4 firstly increase, and then decrease with the $w(\text{SrBr}_2)$ increasing after reaching the maximum value at the eutectic point E in NaBr–SrBr₂–H₂O system, and F in KBr–SrBr₂–H₂O system. Fig. 4 shows

Table 3

Experimental solubilities and refractive indices of the KBr–SrBr₂–H₂O system at 288.15 K and pressure $p = 0.1$ MPa.^a

No.	Liquid phase, 100w ^b		Wet residue, 100w		Refractive index, n_D	Equilibrium solid phase
	KBr	SrBr ₂	KBr	SrBr ₂		
1, C	38.49	0.00	– ^c	–	1.3888	KBr
2	32.28	6.39	–	–	1.3930	KBr
3	25.77	14.44	–	–	1.4028	KBr
4	23.11	17.81	–	–	1.4055	KBr
5	22.46	18.81	54.71	10.88	1.4067	KBr
6	21.45	20.7	45.41	14.11	1.4085	KBr
7	18.25	23.83	–	–	1.4131	KBr
8	17.01	25.64	–	–	1.4164	KBr
9	15.01	29.5	39.45	20.90	1.4227	KBr
10	10.76	35.83	–	–	1.4319	KBr
11	8.96	39.64	23.51	33.49	1.4382	KBr
12, F	6.97	43.09	21.15	47.29	1.4463	KBr + SrBr ₂ ·6H ₂ O
13	5.72	44.21	3.78	52.87	1.4452	SrBr ₂ ·6H ₂ O
14	3.04	45.73	1.57	58.45	1.4430	SrBr ₂ ·6H ₂ O
15	1.23	47.25	–	–	1.4419	SrBr ₂ ·6H ₂ O
16, D	0.00	49.27	–	–	1.4413	SrBr ₂ ·6H ₂ O

^a Standard uncertainties u , $u(T) = 0.1$ K, $u(p) = 0.005$ MPa, $u(w(\text{KBr})) = 0.0089$, $u(w(\text{SrBr}_2)) = 0.0084$ and $u(n_D) = 0.0001$.

^b w , mass fraction.

^c –, not determined.

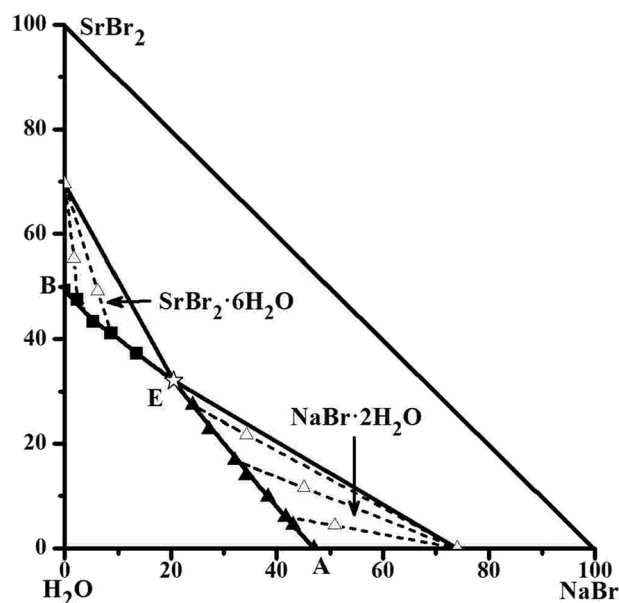


Fig. 2. Phase diagram of the ternary system NaBr–SrBr₂–H₂O at 288.15 K. \blacktriangle , liquid phase points for NaBr·2H₂O; \blacksquare , liquid phase for SrBr₂·6H₂O; \star , invariant point of NaBr·2H₂O and SrBr₂·6H₂O; —, experimental solubility isotherm; Δ , wet residue points; ..., wet residue curve; A, B and E, invariant point for the systems NaBr–H₂O, SrBr₂–H₂O and NaBr–SrBr₂–H₂O.

the refractive indices changed regularly with the changing of $w(\text{SrBr}_2)$ in the systems.

4. Solubility calculation

The Pitzer and HW model was used for the solubility calculation in this study. These equations in the model are based on the excess free energy, all the activity expressions are consistent, which will be ready for parameter evaluations and other thermodynamic property calculation.

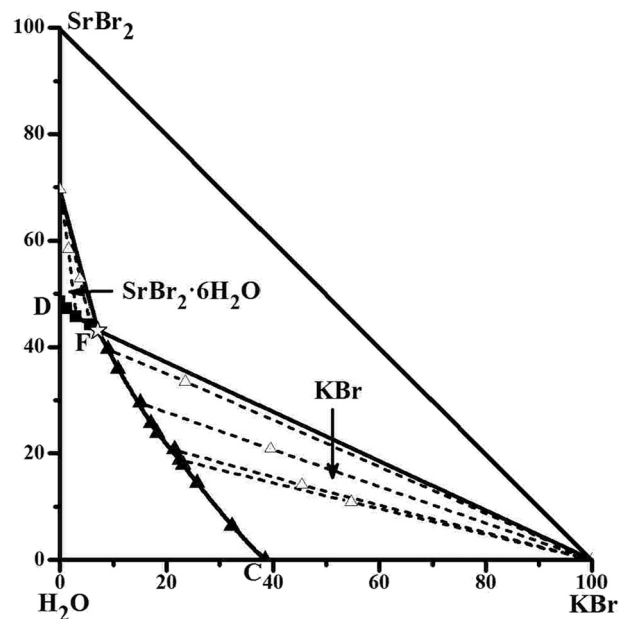


Fig. 3. Phase diagram of the ternary system KBr–SrBr₂–H₂O at 288.15 K. \blacktriangle , liquid phase points for KBr; \blacksquare , liquid phase for SrBr₂·6H₂O; \star , invariant point of KBr and SrBr₂·6H₂O; —, experimental solubility isotherm; Δ , wet residue points; ..., wet residue curve; C, D and F, invariant point for the systems KBr–H₂O, SrBr₂–H₂O and KBr–SrBr₂–H₂O.

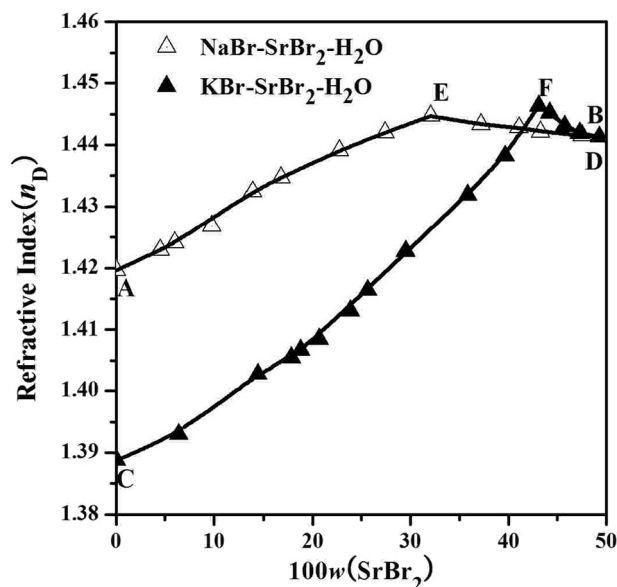


Fig. 4. The refractive index diagrams of the systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O at 288.15 K. Δ , experimental data for NaBr–SrBr₂–H₂O system; \blacktriangle , experimental data for KBr–SrBr₂–H₂O system. A, B and E, invariant point for the systems NaBr–H₂O, SrBr₂–H₂O and NaBr–SrBr₂–H₂O; C, D and F, invariant point for the systems KBr–H₂O, SrBr₂–H₂O and KBr–SrBr₂–H₂O.

The solubilities can be calculated with the Pitzer parameters and the solubility products of the equilibrium solid phases.

4.1. Model parameterization

The Debye–Hückel parameter $A^\theta = 0.385646$ and Pitzer binary parameters of NaBr and KBr at 288.15 K were calculated with the temperature-dependent equations presented in the literature [16]. The osmotic coefficients for SrBr₂–H₂O system at 288.15 K were measured in our laboratory with the isopiestic method, which are listed in Table S1 in electronic Supplementary information (ESI). And then, the Pitzer binary parameters of SrBr₂ were fitted with the least-squares method. The solubility data in the curve AE saturated with NaBr·2H₂O for the ternary system NaBr–SrBr₂–H₂O in this study were used to fit the mixing parameters $\theta_{Na,Sr}$ and $\Psi_{Na,Sr,Br}$. The parameters $\theta_{K,Sr}$ and $\Psi_{K,Sr,Br}$ were also fitted with the solubility data of the system KBr–SrBr₂–H₂O. All the parameters used in the prediction are presented in Table 4. The equilibrium constants ($\ln K_{sp}$) of equilibrium solid salts NaBr·2H₂O and KBr were also obtained from the literature [16]. The $\ln K_{sp}$ for SrBr₂·6H₂O was calculated by the activity product constant method with the parameters and the solubility data in this study. Take the solid phase SrBr₂·6H₂O for example, the solubility product constant ($\ln K_{sp}$) of SrBr₂·6H₂O at a stated temperature and pressure can be shown in Eq. (2).

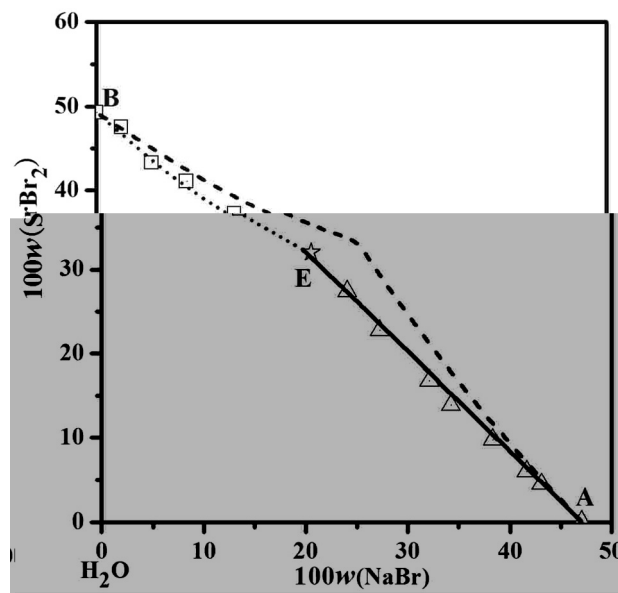
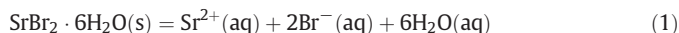


Fig. 5. Comparison of calculated and experimental phase diagrams of the NaBr–SrBr₂–H₂O system at 288.15 K. Δ , experimental solubility data for NaBr·2H₂O; \square , experimental solubility data for SrBr₂·6H₂O; \star , invariant point of NaBr·2H₂O and SrBr₂·6H₂O; ---, calculated solubility isotherm for NaBr·2H₂O with binary parameters only; -·-, calculated solubility isotherm for NaBr·2H₂O with binary parameters and mixing parameters; ···, calculated solubility isotherm for SrBr₂·6H₂O with binary parameters and mixing parameters; A, B and E, invariant point for the systems NaBr–H₂O, SrBr₂–H₂O and NaBr–SrBr₂–H₂O.

$$\begin{aligned} \ln K_{sp} &= \ln(m_{Sr}\gamma_{Sr}) + 2\ln(m_{Br}\gamma_{Br}) + 6\ln\alpha_w \\ &= \ln m_{Sr} + 2\ln m_{Br} + 3\ln\gamma_{\pm} + 6\ln\alpha_w \end{aligned} \quad (2)$$

The activity coefficient γ and water activity α_w can be calculated with the Pitzer and HW model. These equilibrium constants ($\ln K_{sp}$) for the equilibrium solid salts of NaBr·2H₂O, KBr and SrBr₂·6H₂O are 4.4286, 2.3996, and 2.0871, respectively.

4.2. Solubility calculation

The Pitzer and HW model were used for the solubility prediction in the two ternary systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O in this study. The unsaturated solutes were fixed at continuous molalities, and then the saturated solutes' solubilities were calculated.

Applying the binary parameters only, the solubilities of the two ternary systems were predicted, as shown in Figs. 5 and 6 (dash lines). The predicted solubility isotherms deviate remarkably from the experimental data, which shows that the model with binary parameters only is insufficient in calculating the solubilities of the ternary system, and mixture model parameters are needed. Applying both the binary and the mixing parameters, the solubility isotherms were predicted again, as shown by dotted–solid lines in Figs. 5 and 6. The relative deviations ($100 \times (\text{calculated mass fraction} - \text{measured mass fraction}) /$

Table 4
Pitzer parameters of the systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O at 288.15 K.

Species	$\beta^{(0)}$	$\beta^{(1)}$	$C^{(\theta)}$	θ	Ψ	Ref.
NaBr	0.115716	0.061669	−0.002143			16
KBr	0.045483	0.290291	−0.000129			16
SrBr ₂	0.408961	−3.461831	−0.029171			This work
Na ⁺ , Sr ²⁺				0.070668		This work
K ⁺ , Sr ²⁺				0.024708		This work
Na ⁺ , Sr ²⁺ , Br [−]					−0.001082	This work
K ⁺ , Sr ²⁺ , Br [−]					0.010018	This work

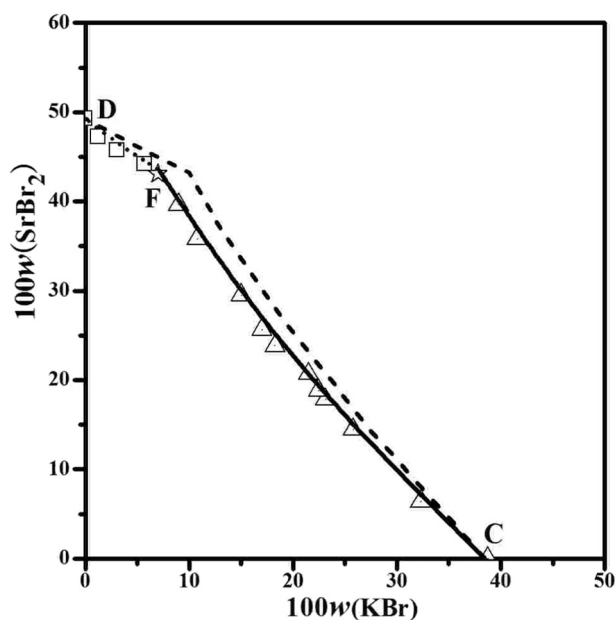


Fig. 6. Comparison of calculated and experimental phase diagrams of the KBr–SrBr₂–H₂O system at 288.15 K. Δ , experimental solubility data for KBr; \square , experimental solubility data for SrBr₂·6H₂O; \star , invariant point of KBr and SrBr₂·6H₂O; —, calculated solubility isotherm with binary parameters only; —, calculated solubility isotherm for KBr with binary parameters and mixing parameters; —, calculated solubility isotherm for SrBr₂·6H₂O with binary parameters and mixing parameters; C, D and F, invariant point for the systems KBr–H₂O, SrBr₂–H₂O and KBr–SrBr₂–H₂O.

measured mass fraction) are <5%. The calculated phase diagrams and the experimental phase diagrams are found to be in good agreement, which confirms that the Pitzer binary and mixing parameters and the equilibrium constants of equilibrium solid salts obtained in this work are reliable for predicting the solubilities of the systems containing the strontium bromide. That comparison shown in Figs. 5 and 6 means that the interaction between the NaBr (KBr) and SrBr₂ salts is quite strong in the framework of the Pitzer model. The interaction between the two ions Na⁺ (K⁺) and Sr²⁺, and three ions Na⁺ (K⁺), Sr²⁺ and Br[−] in the solution, which are represented with the mixing parameters $\theta_{\text{Na,Sr}}$ ($\theta_{\text{K,Sr}}$) and $\psi_{\text{Na,Sr,Br}}$ ($\psi_{\text{K,Sr,Br}}$) in the Pitzer and HW model, are quite strong on the molecular-level.

The salt-out effect can be illustrated using the Pitzer and HW model on the molecular-level. Take the system NaBr–SrBr₂–H₂O for example. When adding NaBr(s) into the solution saturated with SrBr₂·6H₂O, the Br[−] concentration will increase as NaBr dissolving, the activity coefficients for Sr²⁺ and Br[−], and water activity can be considered as stable in a very short period of time, so the Sr²⁺ concentration will decrease because K_{sp} of SrBr₂·6H₂O is a constant at a stated temperature and pressure. The dissolution process results can be illustrated with Eq. (3).

$$K_{\text{sp}} = m_{\text{Sr}}\gamma_{\text{Sr}} \times (m_{\text{Br}}\gamma_{\text{Br}})^2 \times \alpha_{\text{w}}^6 = (m_{\text{Sr}} - dm_{\text{Sr}})\gamma_{\text{Sr}} \times (m_{\text{Br}} + dm_{\text{Br}})^2 \gamma_{\text{Br}}^2 \times \alpha_{\text{w}}^6 \quad (3)$$

dm in Eq. (3) represents the small change for the concentration m . As the concentration of the ions changing in the solution, the activity coefficients for Sr²⁺ and Br[−] will change.

The mean activity coefficients (γ_{\pm}) of strontium bromide and water activities in mixed solutions up to the saturated concentration molality of the two systems at 288.15 K were acquired as shown in Fig. 7. In Fig. 7(a), the γ_{\pm} value of strontium bromide first increases, and then decreases as strontium bromide concentration increasing in the solution, and reaches the maximum value at the invariant points of the ternary systems. The curve in Fig. 7(b) shows the opposite trend. The water activity first decreases and then increases with strontium bromide concentration increasing, and gets the minimum value at the invariant points. In the univariant solubility isotherms saturated with SrBr₂·6H₂O, the γ_{\pm} values decrease and the α_{w} values increase as SrBr₂ concentration increasing. When adding NaBr(s) into the solution saturated with SrBr₂·6H₂O, the product $(\gamma_{\text{Sr}} \times (m_{\text{Br}}\gamma_{\text{Br}})^2 \times \alpha_{\text{w}}^6)$ increases, which can be calculated with the Pitzer and HW model. Therefore, the Sr²⁺ concentration decreases in the solution. On the molecular-level, the Sr²⁺, Br[−] and water molecule in the solution will combine together into SrBr·6H₂O molecule, and then the salt SrBr·6H₂O will precipitate out from the saturated solution.

5. Conclusions

The solubilities, refractive indices and thermodynamic models of the ternary systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O at 288.15 K were studied in this work. The phase diagrams of the two systems at 288.15 K were plotted with the experimental solubility data. There is one invariant point, two univariant solubility curves, and two crystallization fields in the phase diagrams. The two systems belong to the simple saturation

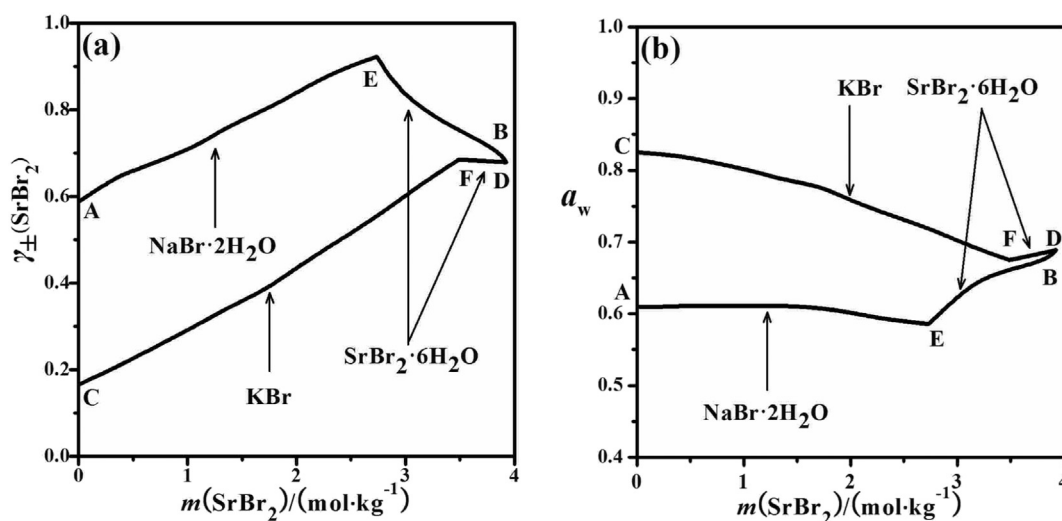


Fig. 7. Mean activity of strontium bromide (a) and water activity (b) calculated from the model of the systems NaBr–SrBr₂–H₂O and KBr–SrBr₂–H₂O at 288.15 K. A, B and E, invariant point for the systems NaBr–H₂O, SrBr₂–H₂O and NaBr–SrBr₂–H₂O; C, D and F, invariant point for the systems KBr–H₂O, SrBr₂–H₂O and KBr–SrBr₂–H₂O.

type, and neither double salt nor solid solution was found. The refractive indices change regularly with the strontium bromide concentration in solution, and reach the maximum value at the eutectic point. On the basis of Pitzer and HW model, the binary and mixing Pitzer parameters and solubility equilibrium constants of equilibrium solid salts for the two ternary systems at 288.15 K were obtained, and the solubilities of the two ternary systems at 288.15 K were calculated. The calculated solubilities agree well with the experimental data, which shows the binary parameters, mixing parameters and equilibrium constants of equilibrium solid salts for the two ternary systems obtained in this work are reliable.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2018.01.020>.

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