

---



---

 PHYSICAL CHEMISTRY  
OF SOLUTIONS
 

---



---

# Solid–Liquid Equilibria in the NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O System at 288.15 K<sup>1</sup>

Dan Li<sup>a</sup>, Qing-fen Meng<sup>b</sup>, Ling-zong Meng<sup>a, \*</sup>, and Xiu-xiu Fan<sup>a</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Linyi University, Linyi 276000, China

<sup>b</sup> Key Laboratory of Salt Lake Resources and Chemistry, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China

\*e-mail: menglingzong@lyu.edu.cn

Received December 23, 2014

**Abstract**—The phase equilibria in the ternary system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15 K were studied with the isothermal equilibrium solution method. The phase diagram and refractive index diagram were plotted for this system at 288.15 K. The phase diagram contains one invariant solubility point, two univariant solubility curves, and two crystallization fields of NaCl and SrCl<sub>2</sub> · 6H<sub>2</sub>O. The refractive indices of the equilibrium solution change regularly with *w*(NaCl) increase. The calculated refractive index data are in good agreement with the experimental data. Combining the experimental solubility data of the ternary system, the Pitzer binary parameters for NaCl at 288.15 K and SrCl<sub>2</sub> at 298.15 K, the Pitzer mixing parameters  $\theta_{\text{Na, Sr}}$ ,  $\Psi_{\text{Na, Sr, Cl}}$  and the solubility equilibrium constants  $K_{\text{sp}}$  of solid phases existing in the ternary system at 288.15 K were fitted using the Pitzer and Harvie-Weare (HW) models. The mean activity coefficients of sodium chloride and strontium chloride, and the solubilities for the ternary system at 288.15 K were presented. A comparison between the calculated and measured solubilities shows that the predicted data agree well with the experimental results.

**Keyword:** phase equilibrium, phase diagram, Pitzer and Harvie-Weare models, strontium chloride, solubility.

**DOI:** 10.1134/S0036024416020114

## INTRODUCTION

Strontium compounds are rather widely used in modern industry. The oil field brines in Nanyishan Section of the Qaidam Basin in Qinghai Province of China have high strontium content [1, 2]. The content of strontium in Nanyishan Section reaches 4.45 g L<sup>−1</sup>, so these brines have very high exploitation value. These brines, which belong to CaCl<sub>2</sub> type, can be regarded as Li–Na–K–Ca–Sr–Cl–Br–borate–H<sub>2</sub>O system. The phase diagrams and solubility data for the brine systems are important for utilizing the brine resources and describing their geochemical behavior [3]. Therefore, study of the phase diagrams and thermodynamics of Sr-rich brine systems is necessary both for industrial and scientific purposes.

A number of experimental and theoretical studies on strontium-containing systems at different temperatures have been carried out in recent decades. The phase equilibria in the NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O system, which is an important subsystem of the above oil field brine system, have been reported for 291.15, 298.15, 333.15, and 373.15 K temperatures [4, 5], but the data for 288.15 K, which is nearly the average summer temperature of the brine in Nanyishan Section are not yet published.

Computer models, which can predict the behavior of solutions and solid-liquid equilibria with close to experimental accuracy, have wide applicability. The Pitzer and Harvie-Weare (HW) models containing the Pitzer parameters and the equilibrium constants of salts, which is described in our study, was widely used in predicting the solubility data of the salt-water systems [6–8]. The three binary parameters for SrCl<sub>2</sub> at various temperatures were reported by Holmes [9–11]. Clegg [12] gave the isopiestic determination of the osmotic and activity coefficients of the ternary system at 298.15 K and representation with an extended ion-interaction model. Five binary parameters for SrCl<sub>2</sub>, which were different from that in the literature [9–11], were fitted from isopiestic data. Moreover, the mixing parameters  $\theta_{\text{Na, Sr}}$  and  $\Psi_{\text{Na, Sr, Cl}}$  were fitted at different ionic strengths. However, studies on modeling the ternary system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15 K are not reported in the literature.

In this paper, the phase diagram (solubility data) and refractive index diagram of the NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O system at 288.15 K were presented together with the calculated mean activity coefficients of sodium chloride and strontium chloride in the solutions, the predictive solubilities on the basis of the Pitzer and HW models after acquiring the lacking Pitzer mixing parameters at full ionic strengths and the solubility

<sup>1</sup> The article is published in the original.

**Table 1.** Solubility and physicochemical property data of the system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15 K

No.	Liquid phase composition, 10 <sup>2</sup> w <sub>b</sub>		Wet residue composition, 10 <sup>2</sup> w <sub>b</sub>		Equilibrium solid phase
	NaCl	SrCl <sub>2</sub>	NaCl	SrCl <sub>2</sub>	
1, A	0.00	33.50	0.00	48.79	SrCl <sub>2</sub> · 6H <sub>2</sub> O
2	3.46	31.03	2.24	38.28	SrCl <sub>2</sub> · 6H <sub>2</sub> O
3	6.48	27.76	3.14	43.55	SrCl <sub>2</sub> · 6H <sub>2</sub> O
4, E	9.36	24.90	12.36	34.72	SrCl <sub>2</sub> · 6H <sub>2</sub> O + NaCl
5, E	9.47	24.98	14.49	44.51	SrCl <sub>2</sub> · 6H <sub>2</sub> O + NaCl
6	10.99	22.56	26.33	18.64	NaCl
7	12.95	19.50	—	—	NaCl
8	13.58	17.47	—	—	NaCl
9	16.24	14.38	—	—	NaCl
10	17.98	11.37	—	—	NaCl
11	19.50	8.98	42.84	6.54	NaCl
12	21.89	5.29	—	—	NaCl
13	24.23	2.42	—	—	NaCl
14	25.04	1.14	—	—	NaCl
15, B	26.35	0.00	—	—	NaCl

— Not detected.

equilibrium constants  $K_{sp}$  of solid phases existing in the ternary system through fitting using the experimental solubility data of the ternary system at 288.15 K.

## EXPERIMENTAL

A DC0506 type low-temperature thermostat ( $\pm 0.1$  K accuracy) from Shanghai Baidian Experimental Instrument Ltd was employed in the equilibrium experiment. The solid phase minerals were indentified with by XRD (X'pert PRO, Spectris Pte. Ltd., the Netherlands). All reagents used were of analytical grade. Sodium chloride (NaCl, >99%) was produced by Shanghai Jufeng Chemical Reagent Ltd. Strontium chloride hexahydrate (SrCl<sub>2</sub> · 6H<sub>2</sub>O, >99%) was obtained from Sinopharm Chemical Reagent Co. Ltd. The purity (mass fraction) of the starting chemicals was checked by titration analysis [13]. Doubly deionized water (DDW) with conductivity less than  $1.2 \times 10^{-4}$  S m<sup>-1</sup> at 298.15 K was used to prepare the series of brines and for the chemical analysis.

The experiments were conducted using the isothermal equilibrium solution method. The samples were prepared by gradual addition of the second salt to the binary solution in 120 mL glass bottles. Then the bottles were sealed with plugs and placed in the thermostat container at a temperature of (288.15  $\pm$  0.1) K. The brine was stirred at 120 rpm by a stirring rod, which was inserted into the bottle through the plug. The experimental procedure is described in more details in our previous works [14]. After equilibrium settled, the liquid samples were taken for chemical analysis. The equilibrium solid phases were determined by the wet residue method [15] (the liquid

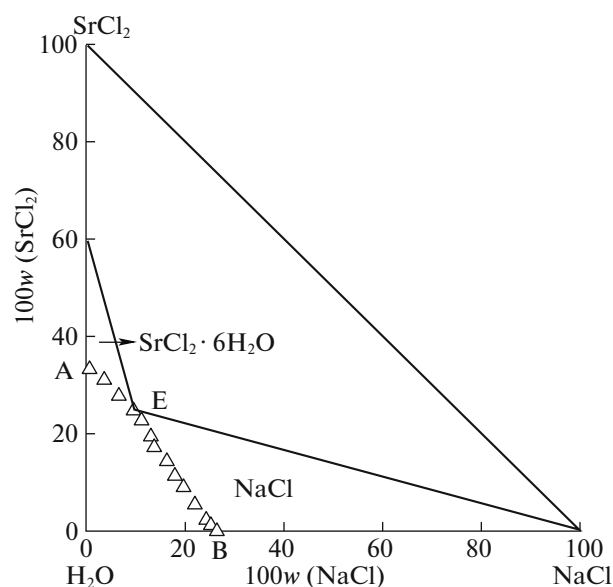
phase point, the wet residue point and the solid phase mineral point are in line) and further identified by X-ray powder diffraction. The remaining parts of the mixtures were used to produce another system points.

**Analytical method.** The Cl<sup>-</sup> ion concentration was determined by titration with a standard solution of Hg(NO<sub>3</sub>)<sub>2</sub> using diphenylcarbazone and bromophenol blue mixed indicator [13]. The concentration of Sr<sup>2+</sup> was determined by titration with an EDTA standard solution in the presence of MgCl<sub>2</sub> and ammonia buffer solution with the indicator Eriochrome Black T [16]. The uncertainty of concentrations determined using titrimetric analysis was no more than  $\pm 0.003$  in mass fraction. Na<sup>+</sup> content was calculated in view of the charge balance of ions with accuracy  $\pm 0.006$  in mass fraction. The compositions of NaCl and SrCl<sub>2</sub> were acquired with the Na<sup>+</sup> and Sr<sup>2+</sup> concentrations, so the precision of the SrCl<sub>2</sub> concentration was no more than  $\pm 0.003$ , and  $\leq \pm 0.006$  for NaCl concentration. AWZS-1 thermostatted Abbe refractometer was used for the liquid phase refractive index ( $n$ ) measurements at a 288.15  $\pm$  0.1 K temperature with an uncertainty of  $\pm 0.0001$ .

## RESULTS AND DISCUSSION

**NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O system at 288.15 K.** The measured solubilities in the NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O system at 288.15 K are presented in Table 1. According to these solubility data, the phase diagram of the studied system was plotted in Fig. 1.

The points A and B are the invariant points of the systems SrCl<sub>2</sub>–H<sub>2</sub>O and NaCl–H<sub>2</sub>O. The phase dia-



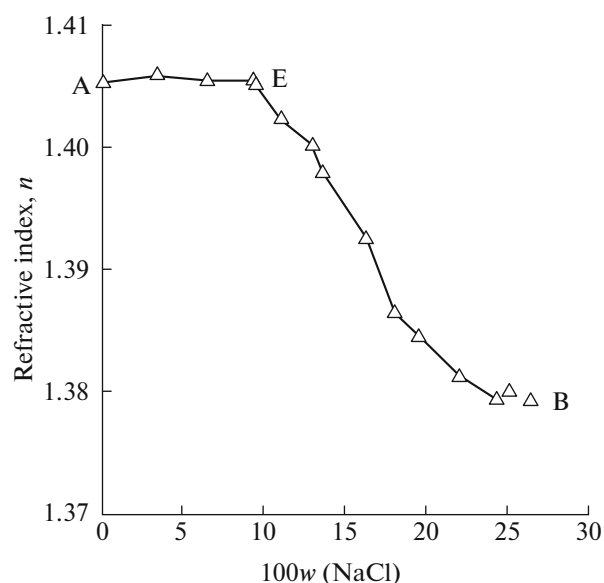
**Fig. 1.** Phase diagram of the system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15 K.

gram in Fig. 1 consists of one two-salt co-saturated invariant point E co-saturated with NaCl + SrCl<sub>2</sub> · 6H<sub>2</sub>O, two univariant curves AE and BE saturated with a single salt (SrCl<sub>2</sub> · 6H<sub>2</sub>O, NaCl), and two crystallization fields of NaCl and SrCl<sub>2</sub> · 6H<sub>2</sub>O. The crystallization area of NaCl is relatively large, while the crystallization area of SrCl<sub>2</sub> · 6H<sub>2</sub>O is relatively small. These results show that strontium chloride has a

**Table 2.** Calculated and experimental refractive index data of the system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15 K

No.	Refractive index, <i>n</i>		Relative error, %
	experimental	calculated	
1, A	1.4052	1.4052	0.00
2	1.4057	1.4060	0.02
3	1.4053	1.4043	-0.07
4, E	1.4052	1.4032	-0.14
5, E	1.4050	1.4036	-0.10
6	1.4022	1.4010	-0.08
7	1.4001	1.3978	-0.16
8	1.3978	1.3945	-0.23
9	1.3924	1.3926	0.01
10	1.3864	1.3891	0.20
11	1.3844	1.3866	0.16
12	1.3812	1.3829	0.12
13	1.3793	1.3808	0.11
14	1.3800	1.3795	-0.03
15, B	1.3794	1.3794	0.00

Relative error = 100% × (calculated value—experimental value)/experimental value.



**Fig. 2.** The refractive index diagram of the system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15 K.

higher solubility than sodium chloride. Moreover, the concentration of sodium chloride decreased with the increase of the strontium chloride concentration. This decrease is most likely caused by the strong salting-out effect of strontium chloride. From Fig. 1, it can be summarized that the system belongs to a simple eutectic type, and there are no solid solutions or double salts in this system.

Using the refractive index data (*n*) in Table 2, the relationship between the solution refractive indices and concentration of sodium chloride is plotted in Fig. 2. The sample numbers in the Table 2 are the same as in the Table 1. It can be seen that the solution refractive indices of the ternary system change regularly with the sodium chloride content change. The refractive index reaches its maximum value around the eutectic point E (SrCl<sub>2</sub> · 6H<sub>2</sub>O + NaCl). The minimum point in Fig. 2 corresponds to the point B saturated with the single salt NaCl.

#### Comparison of the system at different temperatures.

A comparison of the equilibrium phase diagrams for the NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O system at 288.15, 291.15, 298.15, 333.15, and 373.15 K is presented in Fig. 3 [4, 5]. The solubility of SrCl<sub>2</sub> changes from 33.50 at 288.15 K to 50.80 wt % at 373.15 K, and for NaCl, only from 26.35 to 28.50 wt %. This solubility information can be applied in extraction of strontium chloride due to wide variation of its solubility. The shapes of the solubility curves at these five temperatures are nearly the same. The crystallization regions of strontium chloride hydrate and sodium chloride decrease with temperature increase, especially for strontium chloride, which indicates that the solubilities have a positive correlation with temperature. With this information,

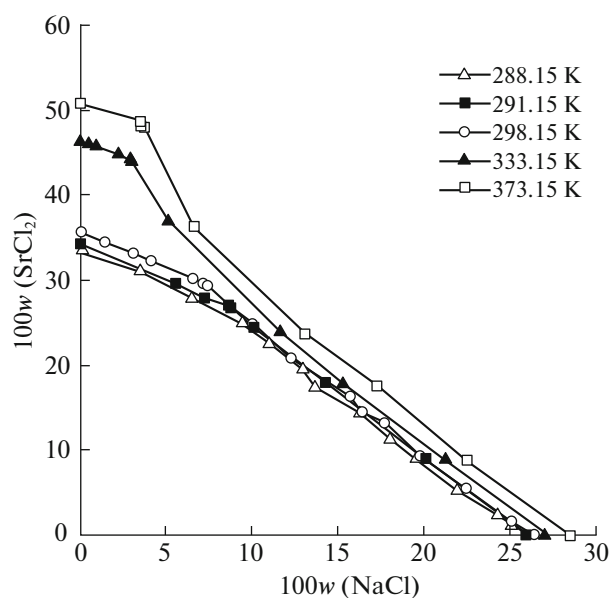


Fig. 3. Comparison of the phase diagrams of the system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15, 291.15, 298.15, 333.15, and 373.15 K.

the mixture of strontium chloride and sodium chloride can be separated and purified. It should be emphasized that the equilibrium solid phases for strontium chloride hydrate differ with temperature. The equilibrium solid phase SrCl<sub>2</sub> · 6H<sub>2</sub>O will transform to SrCl<sub>2</sub> · 2H<sub>2</sub>O at the temperatures between 333.95 and 334.55 K in the binary system SrCl<sub>2</sub>–H<sub>2</sub>O. However, there is only SrCl<sub>2</sub> · 2H<sub>2</sub>O at 333.15 K in the ternary system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O. SrCl<sub>2</sub> · 6H<sub>2</sub>O phase exists at the lower temperatures, while SrCl<sub>2</sub> · 2H<sub>2</sub>O exists at higher temperatures. New temperature solubilities are needed to acquire the exact transition temperature between SrCl<sub>2</sub> · 6H<sub>2</sub>O and SrCl<sub>2</sub> · 2H<sub>2</sub>O in this system. The differences between the system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at different temperatures were not further developed because of lack of more data.

**Refractive index calculation.** On the basis of the following empirical equation of the refractive index in electrolyte solutions developed in the previous study [17, 18], the refractive indices of the solutions were calculated.

$$\ln(n/n_0) = \sum B_i w_i, \quad (1)$$

where  $n$  and  $n_0$  (1.333390) are the refractive indices of the ternary solution and pure water at 288.15 K, and  $w_i$  is the mass fraction of the salt  $i$ .  $B_i$  is the coefficients of the salt  $i$  and can be found using the refractive index and solubility data in this study at 288.15 K. The  $B_i$  for NaCl and SrCl<sub>2</sub> were fitted as 0.001287 and 0.001566, respectively. Combining the coefficients  $B_i$  and the solubility data in Table 1, the refractive index data of the system points were demonstrated. The calculated and measured values are compared in Table 2, and the maximum relative error is about 0.23%. The calculated values agree well with the experimental data, confirming that the coefficients  $B_i$  obtained in this work are reliable for more complicated system containing NaCl and SrCl<sub>2</sub>.

### Solubility Prediction

**Model parameterization.** The Pitzer and HW model, which incorporate the concentration dependent equations showing the specific interactions of the solutes [19–22], was applied to the aqueous solutions in this study. Using the Pitzer single-salt parameters, the mixing ion-interaction parameters and the solubility products of the equilibrium solid phase allowed us to identify the coexisting solid phases and their compositions at equilibrium. The Debye–Hückel parameter  $A^\circ = 0.385646$  and Pitzer binary parameters for NaCl at 288.15 K were obtained using the temperature dependencies equations from the literature [23]. The Pitzer binary parameters  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^{(0)}$  for SrCl<sub>2</sub> at 288.15 K which were calculated according to [11], were  $-1.7730$ ,  $-0.2799$ , and  $-0.0437$ , respectively. Then the single salt parameters were used to calculate the solubility equilibrium constant for SrCl<sub>2</sub> · 6H<sub>2</sub>O, but no result can be obtained. Moreover, the data are also very different from that at 298.15 K in the literature [9, 12]. Therefore, the single salt parameters for SrCl<sub>2</sub> used in prediction were the data at 298.15 K in [12]. The solubility data for the ternary system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O in this study were used to fit the mixing parameters  $\theta_{\text{Na, Sr}}$  and  $\Psi_{\text{Na, Sr, Cl}}$  at full ion strength via a multiple linear regression procedure. All parameters used in the prediction are presented in Table 3. Note that in the mixed system model parameterization we used only raw experimental minerals solubility and the single salt parameters for SrCl<sub>2</sub> at 298.15 K. The results may be fitted more precisely by

Table 3. Single-salt and mixing ion-interaction parameters of the ternary system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15 K

Species	$\beta^{(0)}$	$\beta^{(1)}$	$C^{(0)}$	$\theta$	$\Psi$	Ref.
NaCl	0.068440	0.268838	0.02373	0.421001	-0.037910	23
SrCl <sub>2</sub>	0.282700	1.562500	-0.000225			12
Na <sup>+</sup> , Sr <sup>2+</sup>						This work
Na <sup>+</sup> , Sr <sup>2+</sup> , Cl <sup>-</sup>						This work

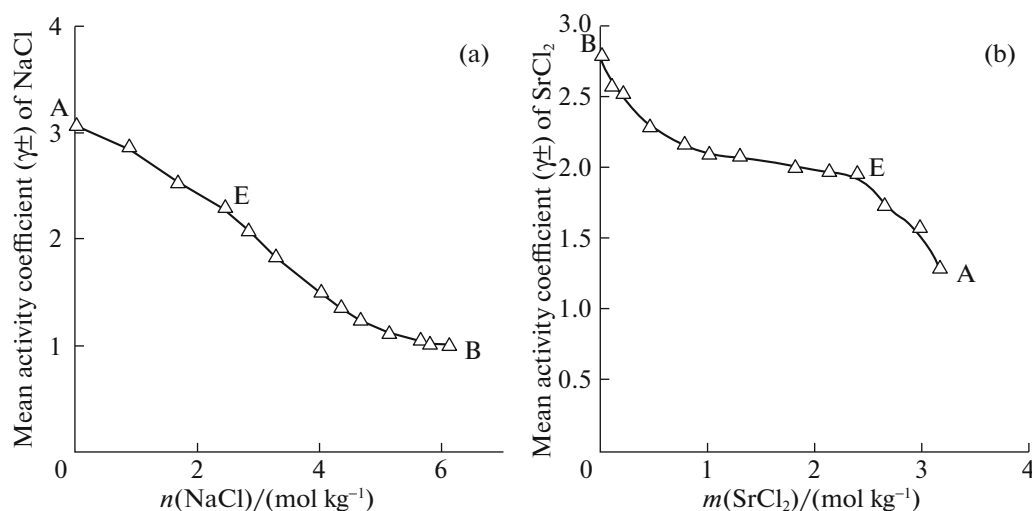


Fig. 4. Mean activity ( $\gamma_{\pm}$ ) of sodium chloride and strontium chloride in the system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15 K; (a) NaCl, (b) SrCl<sub>2</sub>.

applying more thermodynamic data. Using the parameters and the solubility data of the ternary system in this work, the equilibrium constants of the minerals in the ternary system at 288.15 K were calculated for each equilibrium solution with the method of the activity product constant. These average equilibrium constants ( $\ln K_{\text{aver}}$ ) for the equilibrium solid salts of SrCl<sub>2</sub> · 6H<sub>2</sub>O and NaCl are 4.2196 and 3.8753, respectively.

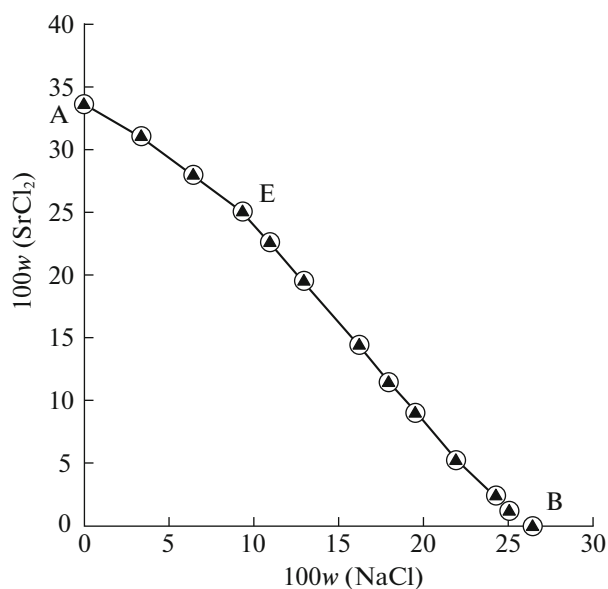


Fig. 5. Comparison of the experimental and calculated phase diagrams of the ternary system NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 288.15 K; ▲, experimental data; ○, calculated data; —, calculated isotherm curve.

**Model validation and application.** To affirm the model validity, combining the parameters and solubility data of the ternary system, the mean activity coefficients ( $\gamma_{\pm}$ ) of sodium bromide and calcium bromide in mixed solutions up to the saturated concentration molality at 288.15 K were acquired, as shown in Fig. 4. The mean activity coefficients of sodium chloride and strontium chloride decrease with increasing concentration of sodium chloride and strontium chloride. The shape of the mean activity coefficient curves for strontium chloride on Fig. 4a is very different from the shape of the curves in binary solutions [9], moreover, the  $\gamma_{\pm}$  of sodium chloride and strontium chloride are not 1 at infinite dilution in Fig. 4, which also differs from the values in binary solutions. A similar situation has been described for MgBr<sub>2</sub>–MgSO<sub>4</sub>–H<sub>2</sub>O system in [8]. It can be concluded that the mean activity coefficients become complicated for mixed solutions and vary greatly in different solutions. The curves for mean activity coefficients change significantly in the invariant point, especially in Fig. 4b, so the invariant point can be found easily from Fig. 4.

The solubilities in the NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O system at 288.15 K were predicted to affirm the model validity. It should be noted that the molalities of unsaturated solute in the solution were fixed at its experimental values, and then the solubilities of the saturated solute were predicted. Based on the experimental and the calculated data, the phase diagrams were constructed in Fig. 5. The calculated phase diagram and the experimental phase diagram are found to be in good agreement, which confirms that the obtained Pitzer mixing parameters  $\theta_{\text{Na, Sr}}$ ,  $\Psi_{\text{Na, Sr, Cl}}$  and the solubility equilibrium constants of minerals existing in the ternary system at 333.15 K are reliable for predicting the solubilities of the system containing strontium chloride.

## CONCLUSIONS

The phase equilibrium of the NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O system at 288.15 K was investigated using the isothermal equilibrium solution method. Using the solubility and the refractive index data for this system, the phase diagram and refractive index diagram were plotted. It was found that there are one two-salt co-saturated invariant point, two univariant solubility isotherms, and two crystallization fields in the ternary system. Neither solid solutions nor double salts were found. The system belongs to a simple eutectic type. The refractive indices of the solutions change regularly with the sodium chloride content change. No significant differences were found among the diagrams of the ternary system at different temperatures except the size of crystallization fields. The calculated refractive indices are in good accordance with the experimental results.

Using the experimental solubility data of the ternary system, the single-salt parameters for NaCl at 288.15 K obtained from the temperature-dependent equations, and SrCl<sub>2</sub> at 298.15 K, the Pitzer mixing parameters  $\theta_{\text{Na, Sr}}$ ,  $\Psi_{\text{Na, Sr, Cl}}$  and the solubility equilibrium constants ( $\ln K_{\text{sp}}$ ) of solid phases existing in the ternary system at 333.15 K were fitted using the Pitzer and HW model. Then, the mean activity coefficients of sodium chloride and strontium chloride, and the solubilities in the ternary system at 288.15 K were demonstrated. A comparison of the calculated and experimental solubilities of the ternary system shows that the predicted solubilities agree well with experimental values, which confirms that the Pitzer mixing parameters and the solubility equilibrium constants of minerals in the ternary system are reliable for predicting the solubilities of the system containing strontium chloride.

## ACKNOWLEDGMENTS

Financial support from the NNSFC (grant no. 21406104) and the Key Laboratory of Salt Lake Resources and Chemistry, Qinghai Institute of Salt

Lake, Chinese Academy of Sciences (grant no. KLSLRC-KF-13-HX-4) is greatly acknowledged.

## REFERENCES

1. Y. F. Ma, Z. H. Zhang, and Y. D. Zhang, *J. Salt Chem. Ind.* **38**, 1 (2009).
2. Q. S. Fan, H. Z. Ma, H. B. Tan, and T. W. Li, *J. Salt Lake Res.* **15**, 6 (2007).
3. L. Z. Meng, D. Li, Y. F. Guo, et al., *J. Chem. Eng. Data* **58**, 3499 (2013).
4. G. O. Assarsson, *J. Phys. Chem.* **57**, 207 (1953).
5. X. P. Ding, B. Sun, L. J. Shi, et al., *Inorg. Chem. Ind.* **42**, 9 (2010).
6. L. Z. Meng, D. Li, T. L. Deng, et al., *CALPHAD* **43**, 105 (2013).
7. T. L. Deng, *J. Chem. Eng. Data* **49**, 1295 (2004).
8. L. Z. Meng, T. L. Deng, Y. F. Guo, et al., *Fluid Phase Equilib.* **342**, 88 (2013).
9. H. F. Holmes and R. E. Mesmer, *J. Chem. Thermodyn.* **13**, 1025 (1981).
10. H. F. Holmes and R. E. Mesmer, *J. Chem. Thermodyn.* **28**, 1325 (1996).
11. H. F. Holmes, J. M. Simonson, and R. E. Mesmer, *J. Chem. Thermodyn.* **29**, 1363 (1997).
12. S. M. Clegg, *J. Chem. Eng. Data* **50**, 1162 (2005).
13. S. J. Cao, *Analytical Methods of Brines and Salts*, 2nd ed. (Science, Beijing, 1988).
14. L. Z. Meng, D. Li, T. L. Deng, et al., *J. Chem. Eng. Data* **59**, 4193 (2014).
15. P. S. Song, *J. Salt Lake Res.* **1**, 42 (1991).
16. X. Y. Lai, *Ferro-Alloys* **6**, 33 (1988).
17. P. S. Song, X. H. Du, and H. C. Xu, *Kexue Tongbao* **29**, 1072 (1984).
18. P. S. Song and X. H. Du, *Chin. Sci. Bull.* **3**, 209 (1986).
19. K. S. Pitzer, *J. Phys. Chem.* **77**, 268 (1973).
20. K. S. Pitzer, *Thermodynamics*, 3rd ed. (McGraw-Hill, New York, 1995).
21. C. E. Harvie and J. H. Weare, *Geochim. Cosmochim. Acta* **44**, 981 (1980).
22. C. E. Harvie, N. Moller, and J. H. Weare, *Geochim. Cosmochim. Acta* **48**, 723 (1984).
23. R. J. Spencer, N. Moller, and J. H. Weare, *Geochim. Cosmochim. Acta* **54**, 575 (1990).