Measurement and Prediction of Solid-Liquid Equilibria in the Ternary System (KCl-$SrCl_2$-H_2O) at 273 and 308 K

Lan-Rong Zhao Investigation; Data curation; Formal analysis; Writing - original draft ,
Xiao-Ping Li Supervision; Validation ,
Shi-Hua Sang Funding acquisition; Project administration; Validation; Writing - review & editing ,
Yun-Yun Gao Resources; Software ,
Chun-Xia He Methodology; Visualization

PII: S0378-3812(20)30459-3
DOI: https://doi.org/10.1016/j.fluid.2020.112910
Reference: FLUID 112910

To appear in: *Fluid Phase Equilibria*

Received date: 1 September 2020
Revised date: 26 October 2020
Accepted date: 18 November 2020

Please cite this article as: Lan-Rong Zhao Investigation; Data curation; Formal analysis; Writing - original draft , Xiao-Ping Li Supervision; Validation , Shi-Hua Sang Funding acquisition; Project administration; Validation; Writing Yun-Yun Gao Resources; Software , Chun-Xia He Methodology; Visualization , Measurement and Prediction of Solid-Liquid Equilibria in the Ternary System (KCl-$SrCl_2$-H_2O) at 273 and 308 K, *Fluid Phase Equilibria* (2020), doi: https://doi.org/10.1016/j.fluid.2020.112910

Measurement and Prediction of Solid-Liquid Equilibria in the Ternary System (KCl-$SrCl_2$-H_2O) at 273 and 308 K

Lan-Rong Zhao [1], Xiao-Ping Li [1], Shi-Hua Sang [1, 2*], Yun-Yun Gao [1], Chun-Xia He [1]

（[1]College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, Sichuan, China）

（[2]Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu 610059, Sichuan, China）

Abstract: Solubilities of ternary system (KCl-$SrCl_2$-H_2O) were determined using the isothermal dissolution equilibrium method at 273 and 308 K. According to the obtained experimental results, the phase diagrams of the system at 273 and 308 K were potted respectively. The results show that the ternary system has a invariant point, two univariate solubility curves and two crystallization regions corresponding to KCl and $SrCl_2 \cdot 6H_2O$ at 273 and 308 K, no solid solution was found in the phase diagram. Based on Pitzer and H-W model, the Pitzer single salt parameters of KCl ($\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ}) and $SrCl_2$ ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ}) and the interaction parameters of mixed ions ($\theta_{K, Sr}$, $\Psi_{K, Sr, Cl}$) were used to calculate the solubilities of the ternary system at 273 and 308 K, and the results show that the calculated values agree well with the experimental values in this work.

Keywords: Solid-liquid equilibrium; Pitzer model; Solubility; Strontium chloride; Potassium chloride

***Corresponding Author:** Prof. Shihua Sang, College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology**.** Tel: 13032845233 E-mail: sangshihua@sina.com.cn, sangsh@cdut.edu.cn

1 Introduction

The unique chemical properties of strontium are widely used in battery, metallurgy, new material ceramics, military industry, energy and other fields [1]. Potassium is one of the three most important elements in agricultural production, and is also an important industrial raw material for printing and dyeing, textiles, medicine, glass, etc. [2]. In Sichuan Basin of China's the underground brine are rich in various elements such as potassium, magnesium, lithium, strontium and bromine, which mostly reach the industrial grade needed for comprehensive and single exploitation. The content of potassium in Sichuan underground brine is 6.376 ~ 53.267 $g \cdot L^{-1}$, and the concentration range of strontium is 166.00 ~ 597.00 $mg \cdot L^{-1}$ [3]. For example, the concentration of potassium and strontium of the brines in the Sichuan Xuanda salt basin are 25.960 $g \cdot L^{-1}$ and 597.00 $mg \cdot L^{-1}$ respectively [4]. In addition, the underground brine resources are distributed in different brine layers, accordingly the temperature varies with brine layers. Solid-liquid phase equilibria reveal the basic rules of various brine salinization and mineralization. Therefore, multi-temperature phase equilibria study is of great significance for guiding the comprehensive exploitation and utilization of potassium and strontium resources in underground brine of Sichuan Basin in China.

The ternary system (KCl-$SrCl_2$-H_2O) has been investigated by many researchers at some different temperatures. For instance, Assarsson [5] studied the phase equilibria of quaternary system (NaCl-KCl-$SrCl_2$-H_2O) and its subsystems at partial temperatures between 291.15 and 378.15 K, and pointed out that the transition temperatures of strontium chloride hexahydrate-dihydrate in the binary system ($SrCl_2$-H_2O) was 334.15 K. Simultaneously, detailed solubility data of the ternary system (KCl-$SrCl_2$-H_2O) were given at 291.15, 333.15 and 373.15 K. Meng et al. [6] and Li et al. [7] determined the solubilities in the ternary system (KCl-$SrCl_2$-H_2O) at 288.15 K with the isothermal dissolution method, based on the Pitzer model, Pitzer mixed ions interaction parameters (θ, Ψ) and the solubility product constants (ln K_{sp}) of the solid salts were also fitted with the obtained solubility data, and solubilities of

the system were predicted by the former. Filippov et al. [8] and Shi et al. [9] investigated phase equilibria in the ternary system (KCl-$SrCl_2$-H_2O) at 298.15 K. They found that there is one invariant point, two univariant curves and two regions of crystallization: KCl and $SrCl_2 \cdot 6H_2O$. Han et al. [10] and Zhang et al. [11] studied the phase equilibria of the ternary system at 323.15 K, but the former further measured water activities for the ternary system of (KCl-$SrCl_2$-H_2O) and its binary system ($SrCl_2$-H_2O) by using an isopiestic method. Based on the previous work, the Pitzer-Simonson-Clegg model was used to correlate the measured water activity and solubility data, simulate the thermodynamic properties, and predict the solubility of the ternary system. Li et al. [12] investigated solid-liquid equilibria in the ternary system (KCl-$SrCl_2$-H_2O) at 348 K and found that $SrCl_2$ crystallized in the shape of dehydrates. In addition to phase equilibrium studies, scholars have also studied other thermodynamic properties of the ternary system. Downes [13] determined the osmotic coefficients at 298.15 K for (KCl-$SrCl_2$-H_2O) by the isopiestic method and the activity coefficients were calculated by Scatchard treatment. Reddy et al. [14] measured the activity coefficient of (KCl-$SrCl_2$-H_2O) at 298.15, 308.15 and 318.15 K using electromotive force method, and applied the Pitzer model to obtain single salt parameters and mixed ions interaction parameters of the Pitzer model under three temperature conditions. Although researchers have done lots of work about the ternary system (KCl-$SrCl_2$-H_2O) at some temperatures, the solubility data of the system at 273 K and 308 K has not been previously reported. The solubilities of the ternary system (KCl-$SrCl_2$ -H_2O) at 273 and 308 K are displayed in this paper.

The thermodynamic model based on the theory of electrolyte solution has been widely used in the prediction of phase equilibria of water-salt system. It can well describe the thermodynamic properties and state of solution. A large number of previous studies based on thermodynamic model have been carried out. Pitzer [15, 16] and co-workers proposed a semi-empirical equation for the thermodynamics of aqueous electrolyte solutions. Harvie and Weare [17] developed a chemical equilibrium model was grounded in the Pitzer model. The thermodynamic model was applied to predict the solubilities of minerals in seawater and natural water, and the

reliability of the model was well verified [17-19]. Kim and Frederick [20, 21] refitted Pitzer ion interaction parameters, and 304 single salts parameters and 43 mixing ions parameters were obtained at 298.15 K. Based on the Pitzer model, Moller and Greenberg [22, 23] predicted the solubility of the system Na-Ca-Cl-SO_4-H_2O at high temperature (0~250℃) and high concentration (I ~18. m), and established a correlation between model parameters and temperatures. The previous work makes us realize that the thermodynamic model has a good application prospect in the theoretical calculation of phase equilibria of water-salt system, especially in the comprehensive utilization of brine in China.

Based on the Pitzer and H-W model, the Pitzer parameters and the solubility equilibrium constant reported by predecessors[23-25] were adopted in this work, and the solubility data of ternary system (KCl-$SrCl_2$-H_2O) at 273 and 308 K were calculated.

2 Experimental Sections

2.1 Reagents and Apparatus

The reagents for the experiments with the mass-fraction purity of 0.995 are listed in Table 1. Ultrapure water was used in the whole study with resistivity >18 MΩ·cm (Sichuan Youpu Chaochun Technology Co. Ltd., UPT-II-20T).

Table 1 Chemical sample information

Chemical name	Source	mass-fraction purity	Purity grade
KCl	Chengdu Cologne Chemical Co. Ltd.	0.995	analytical
$SrCl_2·6H_2O$	Chengdu Cologne Chemical Co. Ltd.	0.995	analytical

The samples were evaluated by the electronic balance (Mettler Toledo Instruments Co. Ltd., AL104, accuracy value 0.0001 g). A thermostatic water bath oscillator (Harbin Donglian Electronic Technology Development Co. Ltd., HZS-HA type, ± 0.1 K) was used to control temperature at 308 ± 0.1 K. An incubator (Chongqing Yingbo Experimental Instrument Co. Ltd., SHH-250, ± 0.1 K) was used to control the temperature at 273 ± 0.1 K. An oscillator (Jintan Kexi Instrument Co. Ltd., HY-5) was employed for accelerating the establishment of equilibrium. The

solid-phases were identified by X-ray diffractometer (Dandong Fangyuan Instrument Co. Ltd., DX-2700).

2.2 Experimental Method

The isothermal equilibrium method was adopted to study the stable phase equilibrium of (KCl-$SrCl_2$-H_2O) systems. Based on the solubility data of each single salt at a certain temperature, a certain proportion of blend salts and 30 mL water were mixed in the Grinding mouth glass bottle with stopper (3 cm in diameter and 12 cm in height), the closed vessels with samples were placed in the thermostatic water bath oscillator (HZSHA type, ± 0.1 K) or incubator (SHH-250, ± 0.1 K) with oscillator (HY-5), The temperature was controlled at 308 ± 0.1 K or 273 ± 0.1 K for the isothermal dissolution equilibrium.

2.3 Analytical Methods

The content of chloride-ion (Cl^-) was determined by titration with a silver nitrate standard solution in a near-neutral solution using potassium chromate as an indicator (maximum relative standard uncertainty: 0.003). The concentration of potassium ion (K^+) was analyzed by a sodium tetra-phenyl borate (STPB)-hexadecyltrimethyl ammonium bromide (CTAB) back titration (maximum relative standard uncertainty: 0.005). At pH = 10 and introducing magnesium ions by adding a small amount of Mg-EDTA solution, the concentration of strontium ion (Sr^{2+}) was titrated with an EDTA standard solution and Eriochrome Black T as the indicator (maximum relative standard uncertainty: 0.005).

3 Results and Discussion

3.1 The Ternary System KCl-$SrCl_2$-H_2O at 273 K

The measured data of the ternary system KCl-$SrCl_2$-H_2O at 273 K was listed in Table 2. The isothermal solubility phase diagram was plotted with the determined data, as shown in Fig. 1. The phase diagram contains one invariant point (E_1), two solubility curves (A_1E_1 and B_1E_1) and two solids solid phase crystallization zones: $SrCl_2 \cdot 6H_2O$ and KCl, respectively. There are KCl and $SrCl_2 \cdot 6H_2O$ co-saturations at the invariant point E_1 and the mass fraction of the equilibrium liquid phase is w(KCl)

= 6.98%, $w(SrCl_2)$ = 27.11%. The invariant point E_1 with equilibrium solids KCl and $SrCl_2 \cdot 6H_2O$ were identified by the X-ray powder diffraction diagram in Fig. 2. The Extended connected lines of the composition points of a solution and its corresponding solid phase crystallization with wet liquid phase meet at the composition points of the coexisting solid phase. At the same time, $SrCl_2$ has strong salting out effect on KCl.

Table 2 Solubilities of salts in the ternary system KCl-$SrCl_2$-H_2O at 273 K and 0.1 MPa [a]

No.	Composition of liquid phase 100·w(b) [b]		Composition of wet solid phase 100·w(b)		Equilibrium solid phase
	w(KCl)	$w(SrCl_2)$	w(KCl)	$w(SrCl_2)$	
1, A_1	22.04	0.00	-	-	KCl
2	20.27	3.30	64.28	1.20	KCl
3	18.23	5.52	63.51	2.45	KCl
4	16.52	8.39	64.14	3.56	KCl
5	14.15	12.27	62.53	5.51	KCl
6	11.74	16.72	61.37	7.08	KCl
7	9.52	20.76	60.06	9.16	KCl
8, E_1	6.98	27.11	30.48	28.74	$SrCl_2 \cdot 6H_2O$+KCl
9, E_1	7.02	27.11	29.52	30.66	$SrCl_2 \cdot 6H_2O$+KCl
10	6.95	27.58	21.63	35.23	$SrCl_2 \cdot 6H_2O$
11	5.91	27.50	2.81	45.65	$SrCl_2 \cdot 6H_2O$
12	4.63	28.50	2.19	45.29	$SrCl_2 \cdot 6H_2O$
13	2.79	28.99	1.35	44.91	$SrCl_2 \cdot 6H_2O$
14, B_1	0.00	30.31	-	-	$SrCl_2 \cdot 6H_2O$

[a] The standard uncertainties u are u(T) = 0.1 K, u(P) = 0.005 MPa, Maximum relative standard uncertainties $u_r(w(KCl))$ = 0.005, $u_r(w(SrCl_2))$ = 0.005; [b] w(b): mass fraction.

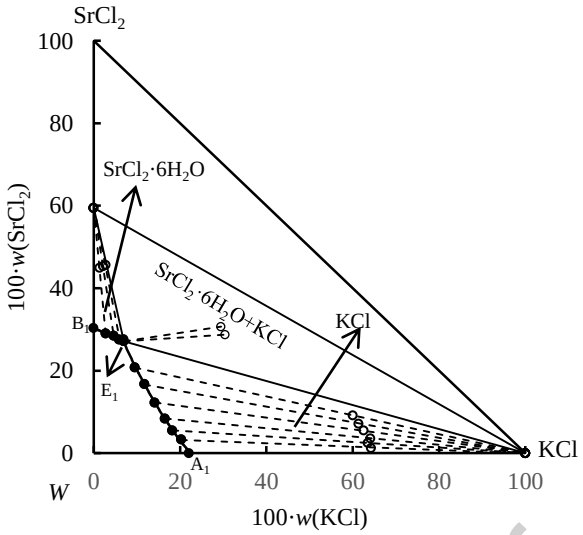

Fig. 1 Phase diagram of the ternary system KCl-$SrCl_2$-H_2O at 273 K

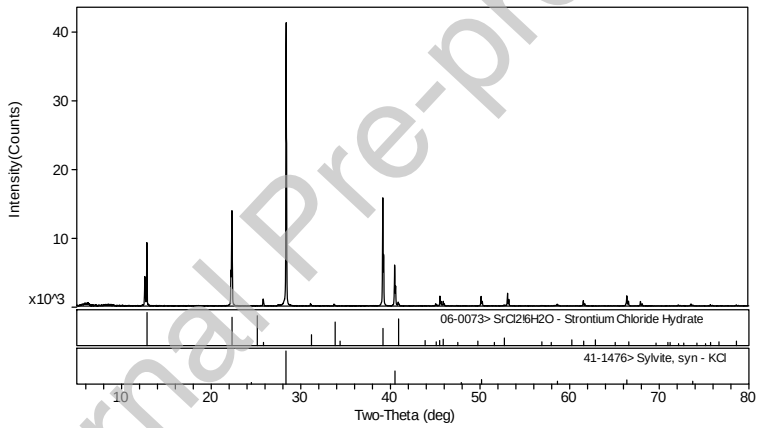

Fig. 2 X-ray diffraction photograph of the invariant point E_1 ($SrCl_2·6H_2O$ + KCl) in the ternary system KCl-$SrCl_2$-H_2O at 273 K

3.2 The Ternary System KCl-$SrCl_2$-H_2O at 308 K

The experimental determined data of the ternary system KCl-$SrCl_2$-H_2O at 308 K was listed in Table 2. Based on the liquid phase composition obtained, the isothermal solubility phase diagram of the system was plotted, as shown in Fig. 3. The isothermal solubility diagram contains one invariant point (E_2), two solubility curves (A_2E_2 and B_2E_2, corresponding to the crystallization of $SrCl_2·6H_2O$ and KCl, respectively). The invariant point E_2 is saturated with KCl and $SrCl_2·6H_2O$ and the composition of the point is w(KCl) = 7.24%, w($SrCl_2$) = 34.79%. Fig. 4 is the X-ray powder diffraction

diagram at the invariant point E_2, where equilibrium solids KCl and $SrCl_2 \cdot 6H_2O$ were identified, and wet solid phase analysis further verified the accuracy of the data. The results showed that $SrCl_2$ has a strong salting-out effect on KCl.

Table 3 Solubilities of salts in the ternary system KCl-$SrCl_2$-H_2O at 308 K and 0.1 MPa [a]

No.	Composition of liquid phase 100·w(b) [b]		Composition of wet solid phase 100·w(b)		Equilibrium solid phase
	w(KCl)	w($SrCl_2$)	w(KCl)	w($SrCl_2$)	
1, A_2	27.78	0.00	-	-	KCl
2	26.89	1.43	98.39	0.22	KCl
3	25.75	2.31	97.24	0.31	KCl
4	24.67	3.93	97.35	0.15	KCl
5	21.91	8.33	98.54	0.01	KCl
6	19.47	12.36	96.93	0.43	KCl
7	15.19	18.10	93.51	1.23	KCl
8	12.16	24.28	95.64	1.51	KCl
9	8.19	32.10	92.86	2.09	KCl
10, E_2	7.24	34.79	57.06	21.55	$SrCl_2 \cdot 6H_2O$+KCl
11	7.13	34.63	1.03	56.34	$SrCl_2 \cdot 6H_2O$
12	4.84	35.27	0.27	57.21	$SrCl_2 \cdot 6H_2O$
13	3.3	35.95	0.1	58.14	$SrCl_2 \cdot 6H_2O$
14	1.95	36.16	0.03	60.07	$SrCl_2 \cdot 6H_2O$
15, B_2	0.00	38.41	-	-	$SrCl_2 \cdot 6H_2O$

[a] The standard uncertainties u are u(T) = 0.1 K, u(P) = 0.005 MPa, Maximum relative standard uncertainties $u_r(w(KCl)) = 0.005$, $u_r(w(SrCl_2)) = 0.005$; [b] w(b): mass fraction.

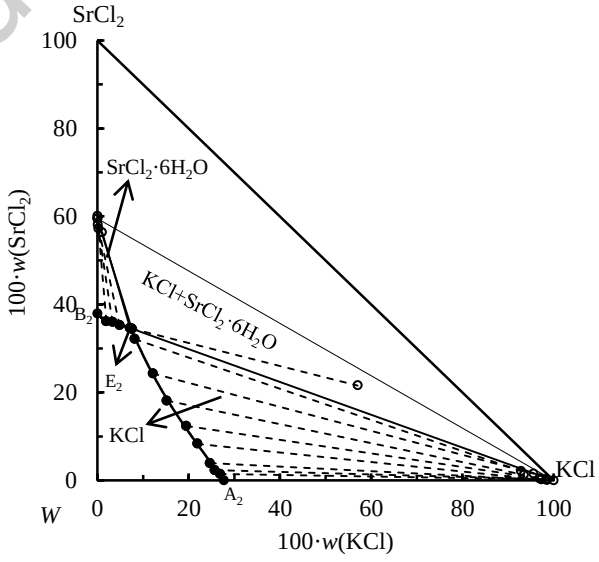

Fig. 3 Phase diagram of the ternary system KCl-$SrCl_2$-H_2O at 308 K

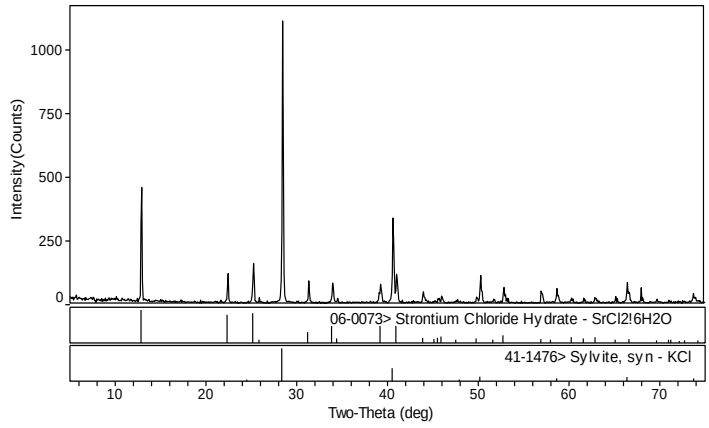

Fig. 4 X-ray diffraction photograph of the invariant point E_2 ($SrCl_2 \cdot 6H_2O$ + KCl) in the ternary system KCl-$SrCl_2$-H_2O at 308 K

3.3 Comparison and discussion of the ternary system at multi-temperatures

Assarsson [5] studied the solubilities of the ternary system KCl-$SrCl_2$-H_2O at 291-387 K, and gave the detailed solubility data at 291 K, 333 K and 373 K. Meng et al. [6], Li et al. [7], Shi et al. [9] and Han et al. [10] investigated phase equilibria in this system at temperatures of 288.15, 298.15 and 323.15 K, respectively. In the previous study, our group also determined the solubilities of ternary system KCl-$SrCl_2$-H_2O at 348 and 373 K[11,12]. Comparisons of the solubility data at invariant point were showed Table 4, and the contrast chart at multi-temperatures is displayed in Fig. 5. We can find that the solubility curve trends are consistent ranging from 273 to 373 K. There are two invariant points at 333 K, and strontium hexahydrate coexisted with strontium dihydrate are found. The other temperatures we have listed contain only one invariant point, the equilibrium solids of invariant point are KCl and $SrCl_2 \cdot 6H_2O$ at 273-323 K, the difference is that the equilibrium solids of invariant point are KCl and $SrCl_2 \cdot 2H_2O$ at 348 K and 373 K. At lower temperatures (273-333 K), the mass fraction of potassium chloride in the equilibrium liquid phase does not change much with increasing temperature. At higher temperatures (333-373 K), the mass fraction of potassium chloride changes more obviously with increasing temperature.

Table 4 Solubilities of invariant point in the ternary system KCl-$SrCl_2$-H_2O at different temperatures

T/K	Compositions of liquid phase at the invariant points 100·*w*(b) [a]		Equilibrium solid phase [b]	Ref	Invariant points
	w(KCl)	*w*($SrCl_2$)			
273	6.98	27.11	S6+K	This work	E_1
288	7.38	30.24	S6+K	Meng et al., 2018[6]	F_1
291	7.20	31.00	S6+K	Assarsson, 1953[5]	G_1
298	7.22	32.31	S6+K	Shi et al., 2010[9]	H_1
308	7.24	34.79	S6+K	This work	E_2
323	7.12	39.25	S6+K	Han et al., 2017[10]	I_1
333	7.20	43.50	S2+K	Assarsson, 1953[5]	J_1
	2.70	45.60	S2+S6		J_2
348	8.57	44.04	S2+K	Li et al., 2015[12]	K_1
373	10.8	46.70	S2+K	Assarsson, 1953[5]	L_1

[a] *w*(b): mass fraction; [b] S6: $SrCl_2 \cdot 6H_2O$, S2: $SrCl_2 \cdot 2H_2O$, K: KCl.

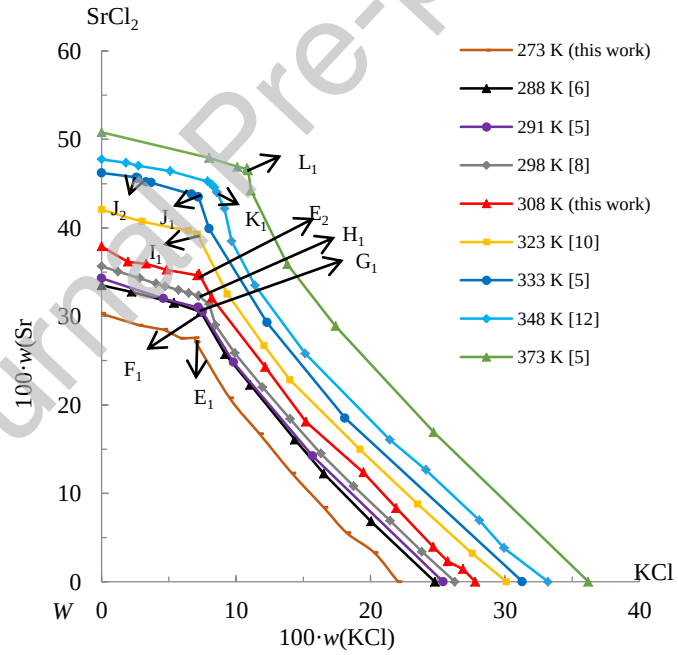

Fig. 5 Phase diagram of the ternary system KCl-$SrCl_2$-H_2O at different temperatures

4 Solubility Calculations

4.1 Model parameterization

In this study, we used the Pitzer and H-W model to calculate the composition of

equilibrium liquid phase of the ternary system KCl-$SrCl_2$-H_2O at 273 and 308 K based on a series of reported parameters. These parameters include the single salt parameters of KCl ($\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ}) and $SrCl_2$ ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$,C^{ϕ}), and the interaction parameters of mixed ions ($\theta_{K,\ Sr}$, $\Psi_{K,\ Sr,\ Cl}$) reported in the literature [23-25]. The single-salt parameters in the solution were shown in Table 5, and the values of the mixing ion-interaction parameters, Debye-Hückel constant A^{ϕ} and the solubility product constants of salts in the ternary system were shown in Table 6.

Table 5 Single-salt parameters required for calculation of ternary system KCl-$SrCl_2$-H_2O at (273 and 308) K

Salt	T/K	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	Reference
KCl	273	0.029151	0.16949	–	0.00125880	23
KCl	308	0.053231	0.23140	–	-0.00134299	23
$SrCl_2$	273	1.148028	1.509654	-1.352879	-0.0255777	24
$SrCl_2$	308	1.304448	1.756975	-1.209874	-0.0331849	24

Table 6 Mixing ion-interaction parameters, solubility product constants of salts required for calculation of ternary system KCl-$SrCl_2$-H_2O and values of Debye-Hückel constant (A^{ϕ}) at (273 and 308) K

	$\theta_{K,\ Sr}$	$\Psi_{K,\ Sr,\ Cl}$	A^{ϕ}	ln$K$(KCl)	ln$K$($SrCl_2 \cdot 6H_2O$)
273 K	-0.005053121	-0.0204632	0.37663	1.37910	3.41883
308 K	0.1015023	-0.029756	0.39842	2.32102	4.62217
References	25	25	23	23	24

4.2 Solubility calculation

Based on the Pitzer and H-W model, the Pitzer parameters listed in Tables 5 and 6 were used to calculate the solubilities of the ternary system KCl-$SrCl_2$-H_2O at 273 and 308 K. The comparisons of isothermal experimental and calculated phase diagrams are shown in Figs. 6 and 7. It was found that the calculated values are in good agreement with the experimental values, the reliability of the parameters selected in this work is proved well. And we calculated the relative error and standard deviation of 273 K and 308 K respectively. As shown in Tables 7 and 8. The relative error at 273 K is Er_1 = 0.08%, the relative error at 308 K is Er_2 = 1.31%. According to

the following standard deviation formula, we have calculated the standard deviation of the two temperatures respectively. The standard deviation is U_{A1} = 0. 26% at 273 K and U_{A2} = 0.53% at 308 K.

$$u_A\ (\bar{c}) = \frac{\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(c_i-\bar{c})^2}}{\sqrt{n}}$$

Table 7 Relative error between calculated value and experimental value in the ternary system KCl-$SrCl_2$-H_2O at 273 K

No.	Experimental composition of liquid phase 100·*w*(b) [b]	Calculated composition of liquid phase 100·*w*(b) [b]	Er%
1	22.04	21.96	-0.36
2	20.27	19.89	-1.87
3	18.23	18.54	1.70
4	16.52	16.79	1.63
5	14.15	14.50	2.47
6	11.74	11.96	1.87
7	9.52	9.84	3.36
8	6.98	6.89	-1.29
9	7.02	6.89	-1.85
10	6.95	7.01	0.86
11	5.91	5.91	0.00
12	4.63	4.66	0.65
13	2.79	2.79	0.00
14	3.3	3.32	0.61
15	5.52	5.50	-0.36
16	8.39	8.36	-0.36
17	12.27	12.22	-0.41
18	16.72	16.68	-0.24
19	20.76	20.69	-0.34
20	27.11	26.99	-0.44
21	27.11	26.99	-0.44
22	27.58	26.93	-2.36
23	27.5	27.47	-0.11
24	28.5	28.10	-1.40
25	28.99	29.04	0.17
26	30.31	30.49	0.59

Table 8 Relative error between calculated value and experimental value in the ternary system KCl-$SrCl_2$-H_2O at 308 K

No.	Experimental composition of liquid phase 100·*w*(b) [b]	Calculated composition of liquid phase 100·*w*(b) [b]	Er%

1	27.78	28.10	1.15
2	26.89	27.12	0.86
3	25.75	26.53	3.03
4	24.67	25.43	3.08
5	21.91	22.45	2.46
6	19.47	19.74	1.39
7	15.19	16.15	6.32
8	12.16	12.46	2.47
9	8.19	8.88	8.42
10	7.24	7.87	8.70
11	7.13	7.06	-0.98
12	4.84	4.78	-1.24
13	3.3	3.26	-1.21
14	1.95	1.91	-2.05
15	1.43	1.43	0.00
16	2.31	2.29	-0.87
17	3.93	3.89	-1.02
18	8.33	8.27	-0.72
19	12.36	12.32	-0.32
20	18.1	17.90	-1.10
21	24.28	24.20	-0.33
22	32.1	31.86	-0.75
23	34.79	34.95	0.46
24	34.63	35.23	1.73
25	35.27	36.11	2.38
26	35.95	36.73	2.17
27	36.16	37.31	3.18
28	38.41	38.17	-0.62

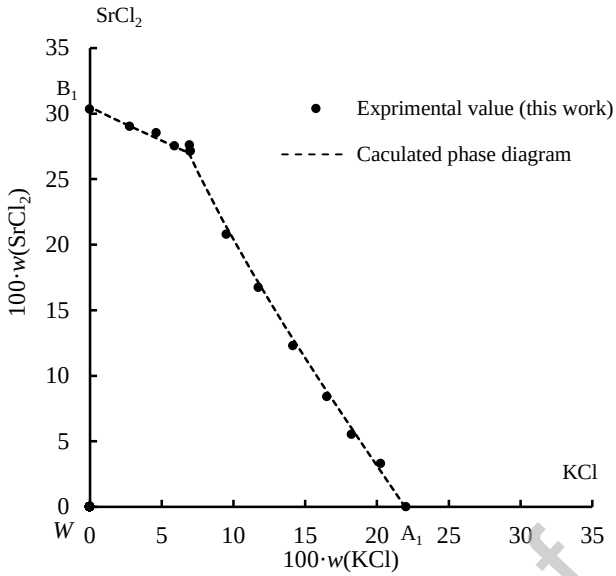

Fig. 6 Calculated and experimental phase diagram of of the ternary system KCl-$SrCl_2$-H_2O at 273 K

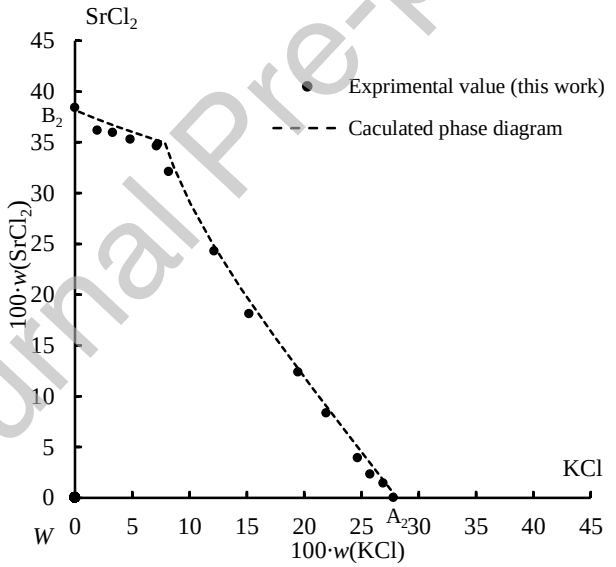

Fig. 7 Calculated and experimental phase diagram of of the ternary system KCl-$SrCl_2$-H_2O at 308 K

5 Conclusions

The ternary system KCl-$SrCl_2$-H_2O at 273 K and 308 K were studied by using the isothermal dissolution equilibrium method. The solubility of the salts and **t**he equilibrium solid phases were obtained, and the phase diagrams were drawn based on

the experimental results. The results show that the system belongs to hydrate I type co-saturated system, and the crystalline solid phases are KCl and $SrCl_2 \cdot 6H_2O$ at both temperatures. After multi-temperature comparison, it is found that the crystallization region of $SrCl_2 \cdot 6H_2O$ gradually became smaller as the temperature increased below 333 K. Based on Pitzer and H-W model, the single salt parameters KCl ($\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ}) , $SrCl_2$ ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ}) and the interaction parameters of mixed ions ($\theta_{K, Sr}$, $\Psi_{K, Sr, Cl}$) in the literatures were used to calculate the solubilities of at 273 and 308 K, and results show that the calculated results agree well with the experimental results in this work.

Author Information

Corresponding Author

*Tel: 13032845233. E-mail: sangshihua@sina.com.cn.

ORCID

Shi-Hua Sang: 0000-0002-5948-3882

Acknowledgments

This project was supported by the National Natural Science Foundation of China (41873071, 41373062) and the scientific research and innovation team in Universities of Sichuan Provincial Department of Education (15TD0009).

Notes

The authors declare no competing financial interest.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit author statement

Lan-Rong Zhao: Investigation; Data curation; Formal analysis; Writing - original draft;

Xiao-Ping Li: Supervision; Validation;

Shi-Hua Sang: Funding acquisition; Project administration; Validation; Writing - review & editing;

Yun-Yun Gao: Resources; Software;

Chun-Xia He: Methodology; Visualization;

References

[1] Y. L. Gao. Utilization and development of strontium. Qinghai People's Press. 1995.

[2] W. C. Du, N. Song. Overview of potassium resources and its utilization in China. China Chem. Trade. 3 (2012) 22.

[3] Y. T. Lin. Distribution types of characters of potassium bearing brine resources in Sichuan Basin. Geo. Chem. Minerals. 24 (2002) 215-221 + 247.

[4] Y. T. Lin, Y. C. Yao, Z. H. Kang, N. J. Wang. Study on the geochemical characteristics and resource significance of the highly mineralized potassium-rich brine in the Sichuan Xuanda salt basin. J. Salt Lake Res. 12 (2004) 8-18.

[5] G. O. Assarsson. Equilibria in aqueous systems containing Na^+, K^+, Sr^{2+} and Cl^-. J. Phys. Chem. 57 (1953) 207-210.

[6] L. Z. Meng, X. Wang, D. Li, T. L. Deng, Y. F. Guo, L. Yang. Experimental Determination and Thermodynamic Modeling of Solid–Liquid Equilibria in the Quaternary System NaCl-KCl-$SrCl_2$-H_2O at 288.15 K. J. Chem. Eng. Data. 63 (2018) 4410-4417.

[7] D. C. Li, R. Fan, S. N. Yang, Z. Zhang. Solid-liquid Equilibria in the Ternary Systems (NaCl-$SrCl_2$-H_2O) and (KCl-$SrCl_2$-H_2O) at 288.15 K and 0.1 MPa. Chem. Res. Chinese Uni. 34 (2018) 803-807.

[8] V. K. Filippov, Y. A. Fedorov, N. A. Charykov. Thermodynamics of phase equilibria in the potassium, strontium, sodium, chloride, water (K^+, Sr^{2+}/Cl^--H_2O, Na^+, Sr^{2+}/ Cl^--H_2O and Na^+, K^+, Sr^{2+}/ Cl^--H_2O) system at 25 °C. Zh. Obshch. Khim. 60 (1990) 492-499.

[9] L. J. Shi, B. Sun, X. P. Ding, P. S. Song. Phase Equilibria in Ternary System KCl-$SrCl_2$-H_2O at 25 °C. Chinese J. Inorg. Chem. 26 (2010) 333-338.

[10] H. J. Han, L. J. Guo, D. D. Li, Y. Yao. Water Activity and Phase Equilibria Measurements and Model Simulation for the KCl-$SrCl_2$-H_2O System at 323.15 K. J. Chem. Eng. Data. 62 (2017) 3753-3757.

[11] X. Zhang, S. H. Sang, S. Y. Zhong, W. Y. Huang. Equilibria in the ternary system $SrCl_2$-KCl-H_2O and the quaternary system $SrCl_2$-KCl-NaCl-H_2O at 323 K. Rus. J. Phys. Chem. A. 89 (2015) 2322-2326.

[12] D. W. Li, S. H. Sang, R. Z. Cui, C. Wei. Solid-liquid equilibria in the ternary systems NaCl-$SrCl_2$-H_2O and KCl-$SrCl_2$-H_2O at 348 K. J. Chem. Eng. Data. 60 (2015) 1227-1232.

[13] C. J. Downes. Osmotic and activity coefficients for mixtures of potassium chloride and strontium chloride in water at 298.15 K. J. Chem. Thermodyn. 6 (1974) 317-323.

[14] D. C. Reddy, J. Ananthaswamy. Thermodynamic properties of aqueous electrolyte solutions: an e.m.f. study of {KCl(mA)-$SrCl_2$(mB)} (aq) at the temperature 298.15 K, 308.15 K, and 318.15 K. J. Chem. Thermodyn. 22 (1990) 1015-1023.

[15] K. S. Pitzer. Thermodynamics of electrolytes. I. theoretical basis and general equations. J. Phys. Chem. 77 (1973) 268-277.

[16] K. S. Pitzer, G. Mayorga. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. J. Phys. Chem. 77 (1973) 2300-2308.

[17] C. E. Harvie, J. H. Weare. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO_4-H_2O system from zero to high concentrationat 25° C. Geochim. Cosmochim. Acta. 44 (1980) 981-997.

[18] C. E. Harvie, H. P. Eugster, J. H. Weare. Mineral equilibria in the six-component seawater system, Na-K-Mg-Ca-SO_4-Cl-H_2O at 25°C II: Compositions of the saturated solutions. Geochim. Cosmochim. Acta. 46 (1982) 1603-1618.

[19] C. E. Harvie, N. Moller, J. H. Weare. The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system to high ionic strengths at 25°C. Geochim. Cosmochim. Acta. 48 (1984) 723-751.

[20] H. T. Kim, W. J. Frederick. Evaluation of Pitzer ion interaction parameters of aqueous

electrolytes at 25 °C 1. Single salt parameters. J. Chem. Eng. Data. 33 (1988) 177-184.

[21] H. T. Kim, W. J. Frederick. Evaluation of Pitzer ion interaction parameters of aqueous mixed electrolyte solutions at 25 °C. 2. Ternary mixing parameters. J. Chem. Eng. Data. 33 (1988) 278-283.

[22] N. Moller. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO_4-H_2O system, to high temperature and concentration. Geochim. Cosmochim. Acta. 52 (1988) 821-837.

[23] J. P. Greenberg, N. Møller. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO_4-H_2O system to high concentration from 0 to 250 °C. Geochim. Cosmochim. Acta. 53 (1989) 2503-2518.

[24] M. Steiger. Thermodynamic properties of $SrCl_2$ (aq) from 252 K to 524 K and phase equilibria in the $SrCl_2$-H_2O system: Implications for thermochemical heat storage. J. Chem. Thermody. 120 (2018) 106-115.

[25] D. Li, Q. F. Meng, L. Z. Meng, X. X. Fan. Solid-liquid equilibria in the NaCl-$SrCl_2$-H_2O system at 288.15 K. Rus. J. Phys. Chem. A. 90 (2016) 368-373.