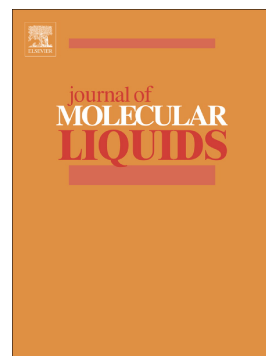


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# Isopiestic investigation and phase equilibrium of the high-efficient absorption refrigerants LiBr and SrBr<sub>2</sub> at 288.15 K

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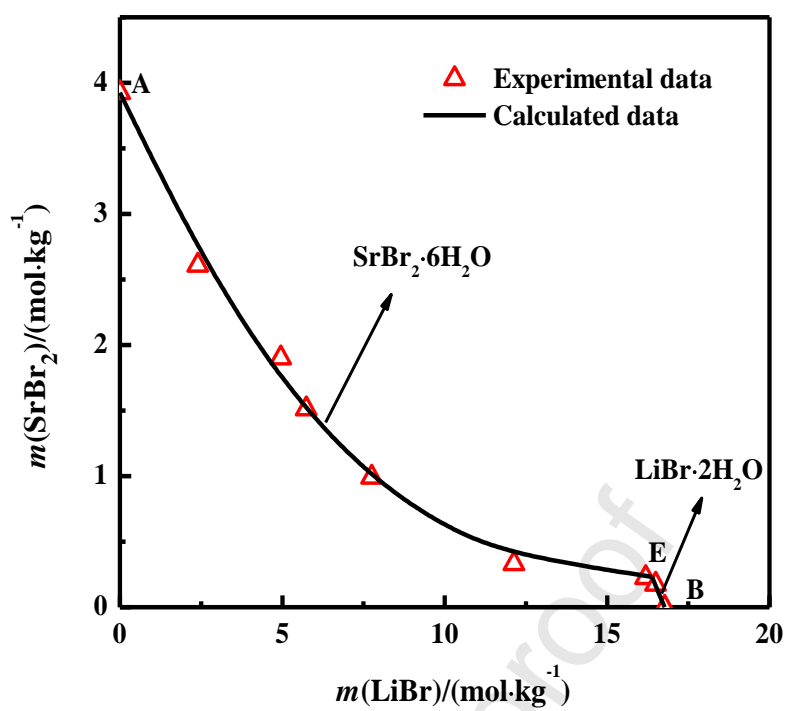
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## ABSTRACT

Isopiestic molalities and water activities for the commercial absorption refrigerants LiBr and SrBr<sub>2</sub> at 288.15 K were accurately measured using an improved isopiestic method. And the solubilities for the absorption refrigeration systems were determined by the isothermal dissolution equilibrium method, meanwhile, the refractive indices and densities were measured. The Pitzer and HW model was used to correlate the measured water activities and solubilities, simulate the thermodynamic properties and predict the data in the phase equilibrium process for the absorption refrigeration systems, and the predicted data agreed well with the experimental solubilities. On the basis of the Pitzer ion-interaction parameters and solubility product constant ( $K_{sp}$ ) obtained in this work, the ion-interactions between alkali metal ions with Sr<sup>2+</sup> and phase equilibrium behaviors were illustrated on the molecular level, which could give an essential guide for the designing of absorption refrigeration system.

**Keywords:** Absorption Refrigerant; Water Activity; Solubility; Pitzer Model; Ion-interaction



Graphic Abstract

## 1. Introduction

LiBr and SrBr<sub>2</sub> are both important chemical and energy storage materials, which were widely used in inorganic industry, absorption refrigeration system, battery production and so on for their excellent characteristics [1, 2]. Especially in the area of absorption refrigeration [3], due to the good performance for water absorption and heat storage, the aqueous LiBr and SrBr<sub>2</sub> solutions as commercial refrigerants were usually added in the energy-saving absorption heat pumps and chillers [4, 5], which could be easily driven by waste heat, solar energy and other low-grade thermal energy [6], so it was meaningful for the energy-saving and environmental protection. But in the actual process, as the evaporation of water, the concentration of LiBr and SrBr<sub>2</sub> refrigerants was sharply increased, meanwhile, the crystallization phenomenon would occur in refrigerants at low temperature, which seriously influenced the refrigerating performance for the refrigerants and strongly corroded the metal container [7]. In order to overcome this problem, it is desirable to study the fundamentals thermodynamic properties and phase behaviors such as solubilities, water activity and ion-interactions of aqueous LiBr, SrBr<sub>2</sub> and their mixtures to guide the actual design for industrial refrigeration system.

In recent years, lots of research for this absorption regeneration system has been done. To overcome the crystallization problem of LiBr aqueous solution at high concentration, some organic salts and ionic liquids were added in the refrigerants to adjust the interactions among ion and molecular, meanwhile, some thermodynamic parameters, such as heat capacity, vapor pressure, enthalpies of dilution and solubility were measured to explain the process [8, 9]. As for the thermodynamic properties of solvent, Meng studied the water activities, osmotic coefficients and vapor pressure for LiBr aqueous solution in wide ranges of concentration at 373.15 K using an improved isopiestic apparatus, and the results were related to the basis of Pitzer original and its extended model [10]. In order to deeply understand the crystallization phenomenon for the aqueous solutions containing LiBr and SrBr<sub>2</sub>, some phase equilibrium experiments were reported, the solubilities for the ternary system (LiCl + LiBr + H<sub>2</sub>O) and its subsystem at 288.15 K were measured by Li using the isothermal equilibrium dissolution method, and a new type of solid solution were discovered [11]. As for the system containing SrBr<sub>2</sub>, the phase diagram of the ternary systems (NaBr + SrBr<sub>2</sub> + H<sub>2</sub>O) and (KBr + SrBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K was obtained [12]. However, the thermodynamic properties of refrigerants containing LiBr and SrBr<sub>2</sub> at low

temperature are not reported in the literature up to now.

In this paper, the water activities and solubilities of the refrigerants including LiBr and SrBr<sub>2</sub> at 288.15 K were accurately measured using an improved isopiestic method and isothermal equilibrium dissolution method, respectively. And then, the Pitzer ion-interaction model was constructed to describe the thermodynamic properties and predict the solubilities of the absorption refrigeration systems at 288.15 K. Finally, the ion-interactions between alkali metal ions and Sr<sup>2+</sup> were discussed in the existence of Br<sup>-</sup>.

## 2. Experimental

### 2.1. Materials and apparatus

All the sources and purities of the chemicals used in this experiment were listed in Table 1, and all the salts were dried for 24h at 473.15 K in a vacuum drying box (STIK VOS-30A, China) before using. The deionized distilled water (DDW) as pure water was produced by ULUP-II-10T (China) with a conductivity less than  $1 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$  and pH  $\approx 6.60$  at 25°C. The pure stock solutions of NaCl, CaCl<sub>2</sub>, LiBr, and SrBr<sub>2</sub> used in this experiment were prepared with relative salts and dissolved by DDW in a Glove Box (UNILab Plus, MBraun, Germany) filled with nitrogen.

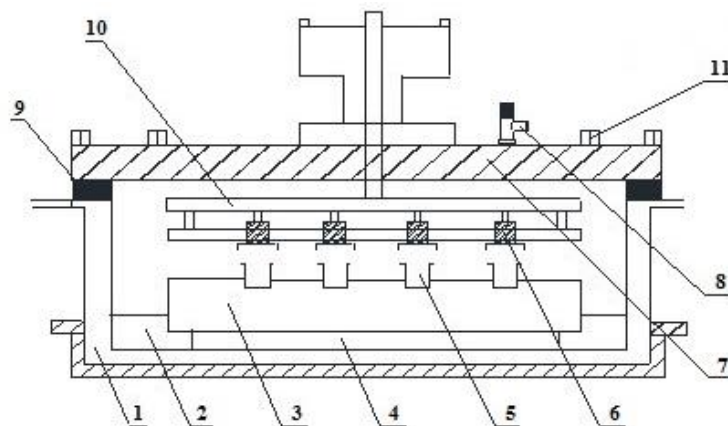
**Table 1**

Source and purity of chemicals used in this work

Chemicals	Source of chemicals	Purification method	Purity (in mass fraction)
NaCl	Aladdin Chemical	no further purification	0.9999
CaCl <sub>2</sub>	Aladdin Chemical	no further purification	0.9999
LiBr	Aladdin Chemical	no further purification	0.9999
SrBr <sub>2</sub>	Aladdin Chemical	no recrystallization	0.9995
AgNO <sub>3</sub>	Shanghai Tairuier Chemical	no further purification	0.9995

The isopiestic apparatus was consisted of an isopiestic chamber and a thermostatic system (Lauda DLK45, Germany) with the accuracy 0.01 K. The isopiestic chamber was mainly made of stainless steel. At the top of the chamber, an air controlling valve and a screwing capping device was fixed here to remove or add the dry air to the chamber and adjust the position of cap, respectively, in the isopiestic chamber, 14 sample cups made by titanium alloy were tightly fixed in a heat transferable plate, and the structure of the isopiestic chamber was described in detail in Fig. 1. The experiment of phase equilibrium was done by a magnetic stirring thermostatic apparatus (XHC-500-6, Beijing Fortunejoy Sci. Technol. Co. Ltd.) with the uncertainty of

temperature  $\pm 0.01$  K. The solid phase minerals were identified with X-ray powder diffractometer (MSAL XD-3, Beijing Purk. Instrument Co. Ltd., China). Density ( $\rho$ ) for the liquid phase was measured using an Anton Paar Digital vibrating-tube densimeter (DMA 4500, Anton Paar Co. Ltd., Austria) with an uncertainty less than  $\pm 0.15 \text{ mg}\cdot\text{cm}^{-3}$ . And the refractive index ( $n_D$ ) was measured by an Anton Paar automatic refractometer (Abbemat 550, Shanghai Trading Co.Ltd., China) with an uncertainty within  $\pm 0.0001$ .



**Fig. 1.** Diagram of isopiestic chamber. (1) stainless steel container; (2) Block supports; (3) Heat transfer plate; (4) Locating device; (5) Sample cup; (6) Capping device; (7) Chamber cover; (8) Needle valve; (9) Sealing washer; (10) Screwing capping device; (11) Fixing nuts.

## 2.2. Experimental and analytical method

The absorption refrigeration systems could be represented by the ternary system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) and binary systems ( $\text{LiBr} + \text{H}_2\text{O}$ ) and ( $\text{SrBr}_2 + \text{H}_2\text{O}$ ), the water activity for the ternary systems ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) at 288.15 K was measured by the isopiestic apparatus described above. The stock solutions with different series of  $Y_B$  ( $Y_B = m_{\text{LiBr}} / (m_{\text{LiBr}} + m_{\text{SrBr}_2})$ ) were prepared by accurately weighted amounts of the mixing purely dried salts for LiBr and  $\text{SrBr}_2$  using an analytical balance (Mettler Toledo, Swiss) with the precision of 0.1 mg, and then dissolved by DDW. Before each measurement, the experimental and reference solution were prepared by appropriate weighted amounts the stock solution and the DDW in the sample cups using the analytical balance above, then all the sample cups should be immediately transferred to the isopiestic chamber and close the cap of the chamber, in order to reduce the time for reaching isopiestic equilibrium, the air in the chamber should be slowly removed using a vacuum pump, and the equilibrium time were 8-15 days. After reaching isopiestic equilibrium, the sample cups were closed with the caps using the screwing capping device, and remove from the thermostatic

bath system to a desiccator waited for 40 min for weighting. Finally, the isopiestic equilibrium molalities for the refrigeration system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) and its subsystem at 288.15 K were obtained by the initial molalities for the experimental solution and the amount of mass variation.

The solubilities for the ternary system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) at 288.15 K were measured by the isothermal dissolution equilibrium method described in our previous work [13]. On the basis of the solubility of  $\text{LiBr}$  and  $\text{SrBr}_2$ , a series of artificial synthesized complexes were prepared by gradually adding the other salt to the binary aqueous solution in the glass bottles, and they were transferred to the thermostatic bath with the temperature  $(288.15 \pm 0.01)$  K. After stirring for a certain period, the apparatus would stop for 3 h to make the liquid and solid phase stratified, and take the supernatant for chemical analysis when the analytical result of composition reached a constant, the equilibrium would be achieved. It usually took 15 days to reach the equilibrium.

The concentration of  $\text{Br}^-$  were analyzed by the gravimetric method with the precipitant of  $\text{AgNO}_3$  solution [14], the concentration of  $\text{Sr}^{2+}$  was also determined by the gravimetric method with  $\text{K}_2\text{CO}_3$  solution [15], and all the uncertainties of ion concentration analysis were within 0.0005 in mass fraction. But in the phase equilibrium experiment, due to the solubility product constant of  $\text{Li}_2\text{CO}_3$ , the existence of  $\text{Li}^+$  in the liquid may influence the analytical results of  $\text{Sr}^{2+}$ , but after verification, the concentration of  $\text{Li}^+$  in our experiment had no disturbance of the analysis results for  $\text{Sr}^{2+}$ . The  $\text{Li}^+$  concentration was evaluated using an ion balance, and combined with analytical verification using an inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leman Corporation, America. Precision:  $\pm 1.0\%$ ). And the solid phase compositions were identified combining with wet residue method (Schreinemakers technique) [16] and the X-ray diffractometer.

### 3. Results and discussion

#### 3.1. Isopiestic investigation

The  $\text{NaCl(aq)}$  and  $\text{CaCl}_2\text{(aq)}$  were used as reference solution in the isopiestic experiment. The osmotic coefficient  $\phi$  of reference solutions at different molalities  $m$  were obtained from the literature [17,18] and the relationship was fitted by the function as Eq. (1).

$$\phi = A + B(m / \text{mol} \cdot \text{kg}^{-1})^{0.5} + C(m / \text{mol} \cdot \text{kg}^{-1}) + D(m / \text{mol} \cdot \text{kg}^{-1})^{1.5} + E(m / \text{mol} \cdot \text{kg}^{-1})^2 + F(m / \text{mol} \cdot \text{kg}^{-1})^{2.5} + G(m / \text{mol} \cdot \text{kg}^{-1})^3 + H(m / \text{mol} \cdot \text{kg}^{-1})^{3.5} \quad (1)$$

where  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ ,  $F$ ,  $G$  and  $H$  are the empirical parameters, and all the parameters for NaCl(aq) and CaCl<sub>2</sub>(aq) reference solution were listed in Table 2.

**Table 2**

Fitted parameters in Eq. (1) for NaCl and CaCl<sub>2</sub> reference solution

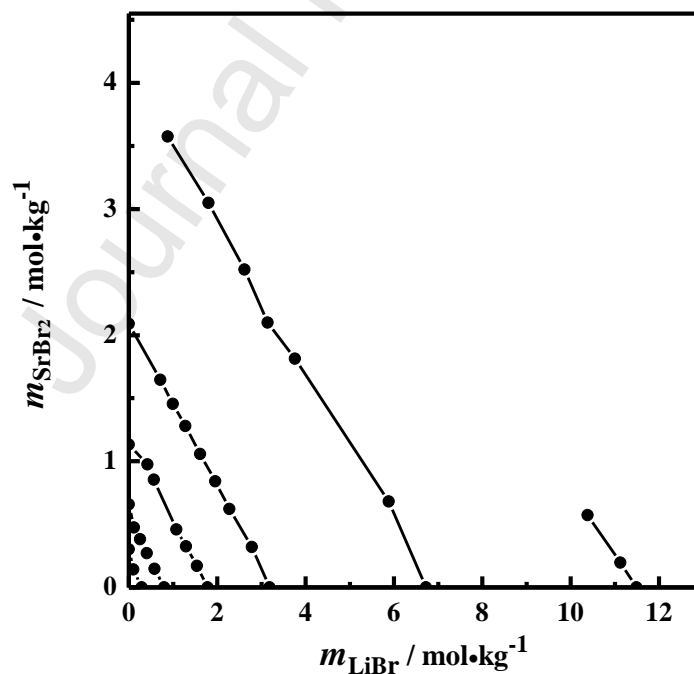
Parameters	NaCl <sup>a</sup>	CaCl <sub>2</sub> <sup>b</sup>
$A$	0.99833	0.99959
$B$	-0.32220	-1.14140
$C$	0.33377	3.27220
$D$	0.22755	-4.51102
$E$	-0.71539	3.80504
$F$	0.59240	-1.76428
$G$	-0.20982	0.43816
$H$	0.02746	0.04649
$r^c$	0.99920	0.99810
SD <sup>c</sup>	0.00003	0.00351

<sup>a</sup> Fitted parameter of NaCl with the data in the literature [17].

<sup>b</sup> Fitted parameter of CaCl<sub>2</sub> with the data in the literature [18].

<sup>c</sup> The correlation coefficients ( $r$ ) and standard deviations.

The isopiestic equilibrium molalities for the ternary system (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) with different  $Y_B$  and reference solution at 288.15 K were listed in Table 3 and plotted in Fig. 2.



**Fig. 2.** Measured isopiestic equilibrium molalities and water iso-activity lines for the ternary system (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K.

The composition points with the same water activity basically formed straight lines, which could be roughly considered to obey Zdanovskii's rule. In each isopiestic measurement, the largest



difference of equilibrium molalities for the duplicated samples was  $0.0003 \text{ mol}\cdot\text{kg}^{-1}$ , which could be considered the errors of weighting, the equilibrium time and impurity of chemicals.

**Table 3**

Isopiestic molalities and water activities for the ternary system (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K and 0.1 MPa <sup>a</sup>.

$Y_B$	$m_{\text{LiBr}}$	$m_{\text{SrBr}_2}$	$m_{\text{ref}}^*$	$\phi_{\text{ref}}^*$	$\alpha_w$
0.0	0	0.3005	0.3047 (NaCl)	0.9189	0.9900
0.8	0.1001	0.1410			
1.0	0.2890	0			
0.0	0	0.7137	0.8764 (NaCl)	0.9285	0.9711
0.2	0.1191	0.4749			
0.4	0.2581	0.3822			
0.6	0.4092	0.2717			
0.8	0.5836	0.1466			
1.0	0.7987	0			
0.0	0	1.1323	2.0686 (NaCl)	0.9794	0.9296
0.3	0.4193	0.9749			
0.4	0.5663	0.8534			
0.5	0.7277	0.7275			
0.7	1.0775	0.4601			
0.8	1.2946	0.3247			
0.9	1.5421	0.1707			
1.0	1.7840	0			
0.0	0	2.0895	3.8781 (NaCl)	1.0984	0.8577
0.3	0.7088	1.6428			
0.4	0.9988	1.4537			
0.5	1.2784	1.2768			
0.6	1.6072	1.0550			
0.7	1.9356	0.8325			
0.8	2.2663	0.6189			
0.9	2.7168	0.3119			
1.0	3.1810	0			
0.2	0.8828	3.5760	3.5263 (CaCl <sub>2</sub> )	2.0264	0.6797
0.4	1.8000	3.0478			
0.5	2.6163	2.5207			
0.6	3.1415	2.0984			
0.7	3.7596	1.8135			
0.9	5.8810	0.6802			
1.0	6.7278	0			
0.7	10.3814	0.5730	5.3558 (CaCl <sub>2</sub> )	2.7825	0.4470
0.9	11.1238	0.1967			
1.0	11.4844	0			

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1 \text{ K}$ ,  $u(p) = 0.005 \text{ MPa}$ ,  $u(m)$  for each duplicated samples is  $0.0003 \text{ mol}\cdot\text{kg}^{-1}$ .

And the water activity  $\alpha_w$  of reference solutions could be calculated by the following equation, Eq. (2):

$$\ln \alpha_w = -\nu m M_w \phi_{\text{ref}} / 1000 \quad (2)$$

Where  $\nu$  is the number of ions stoichiometric dissociation for one molecule of reference solutions, as for NaCl and CaCl<sub>2</sub>,  $\nu = 2$  and 3, respectively,  $M_w$  is the molar mass of H<sub>2</sub>O (g·mol<sup>-1</sup>),  $m$  is the isopiestic equilibrium molalities for the experimental solution,  $\phi_{\text{ref}}$  is the osmotic coefficient of reference solutions, and the calculated results of water activity  $\alpha_w$  were listed in Table 3.

### 3.2. Measured solubilities

The solubilities, wet residue composition and corresponding physicochemical properties including refractive index and density for the ternary system (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K were listed in Table 4.

**Table 4**

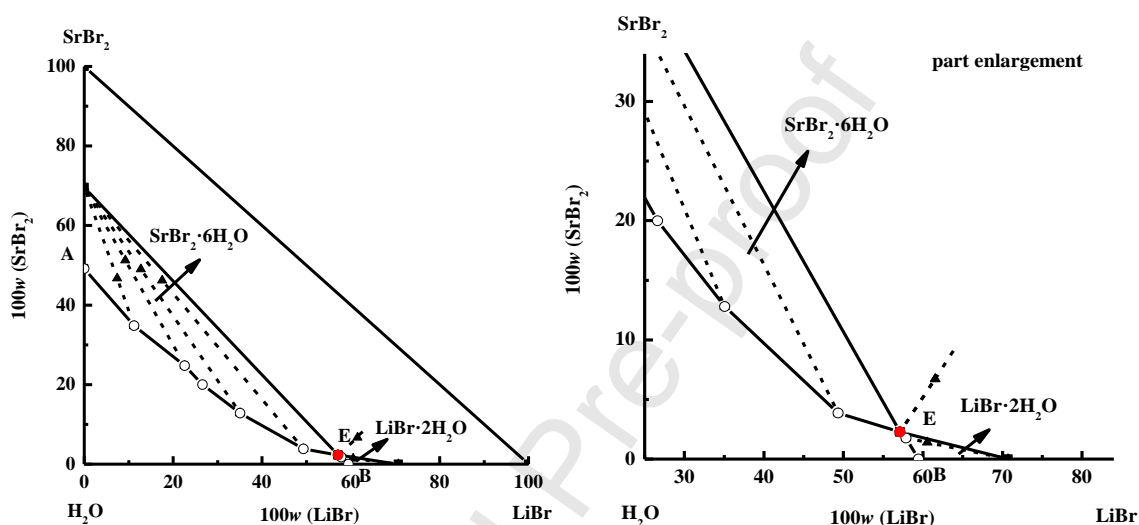
Measured solubilities, density and refractive index for the (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) system at 288.15 K and 0.1 MPa<sup>a</sup>.

No.	Liquid phase, 100w <sup>b</sup>		Wet residue, 100w		Density	Refractive index	Equilibrium solid phase
	LiBr	SrBr <sub>2</sub>	LiBr	SrBr <sub>2</sub>	$\rho$ , g·cm <sup>-3</sup>	$n_D$	
1, A	0	49.27	— <sup>c</sup>	—	1.67482	1.4425	SrBr <sub>2</sub> ·6H <sub>2</sub> O
2	11.24	34.83	7.39	46.74	1.59704	1.4349	SrBr <sub>2</sub> ·6H <sub>2</sub> O
3	22.63	24.75	9.24	51.29	1.54084	1.4299	SrBr <sub>2</sub> ·6H <sub>2</sub> O
4	26.62	19.99	—	—	1.51346	1.4281	SrBr <sub>2</sub> ·6H <sub>2</sub> O
5	35.08	12.79	12.72	49.05	1.49633	1.4283	SrBr <sub>2</sub> ·6H <sub>2</sub> O
6	49.33	3.85	17.57	46.19	1.63460	1.4600	SrBr <sub>2</sub> ·6H <sub>2</sub> O
7, E	57.11	2.28	61.54	6.72	1.73255	1.4772	LiBr·2H <sub>2</sub> O + SrBr <sub>2</sub> ·6H <sub>2</sub> O
8	57.86	1.76	60.54	1.39	1.72755	1.4767	LiBr·2H <sub>2</sub> O
9, B	59.29	0.00	—	—	1.71374	1.4749	LiBr·2H <sub>2</sub> O

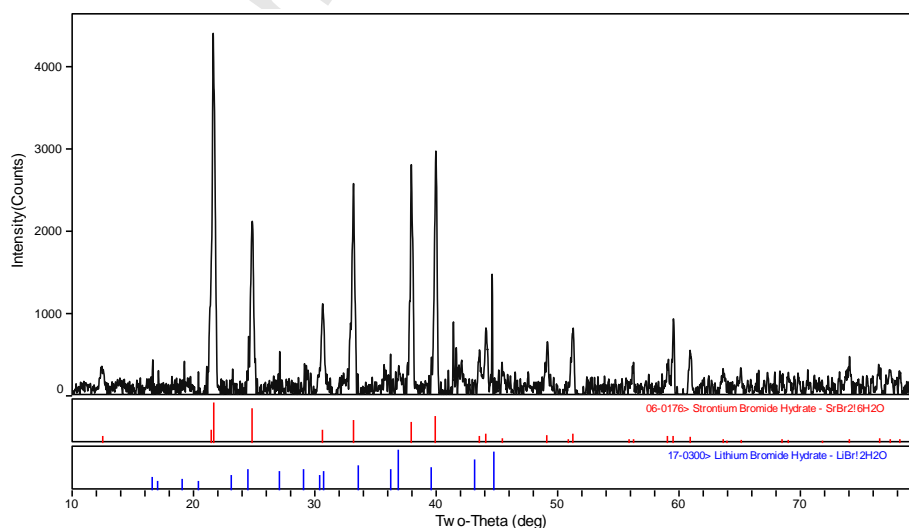
<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 0.005$  MPa,  $u(w(\text{SrBr}_2)) = 0.0009$ ,  $u(w(\text{LiBr})) = 0.0048$ ,  $u(\rho) = 0.15$  mg·cm<sup>-3</sup> and  $u(n_D) = 0.0001$ .

On the basis of the measured solubility data, the phase diagram for this ternary system was plotted in Fig. 3, which have one invariant point E with LiBr·2H<sub>2</sub>O and SrBr<sub>2</sub>·6H<sub>2</sub>O, two isothermal dissolution curves AE and BE, two crystallization regions corresponding to LiBr·2H<sub>2</sub>O and SrBr<sub>2</sub>·6H<sub>2</sub>O, and the crystallization region of SrBr<sub>2</sub>·6H<sub>2</sub>O is much larger than LiBr·2H<sub>2</sub>O. In addition, as the increasing of lithium bromide concentration, the concentration of strontium

bromide was sharply decreased, which indicated that the existed for the of LiBr has a strong salting-out effect of  $\text{SrBr}_2$ . The points A and B represented the solubilities for the binary systems ( $\text{LiBr} + \text{H}_2\text{O}$ ) and ( $\text{SrBr}_2 + \text{H}_2\text{O}$ ) at 288.15 K, respectively. And the phase diagram with Schreinemakers lines of the ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) system at 288.15 K is also shown in Fig. 3. This system belong to the simple eutectic type, and neither double salt nor solid solution was found in this system. The X-ray diffraction pattern of solid phase ( $\text{LiBr} \cdot 2\text{H}_2\text{O} + \text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ ) for the invariant point in the ternary system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) at 288.15 K was shown in Fig. 4.



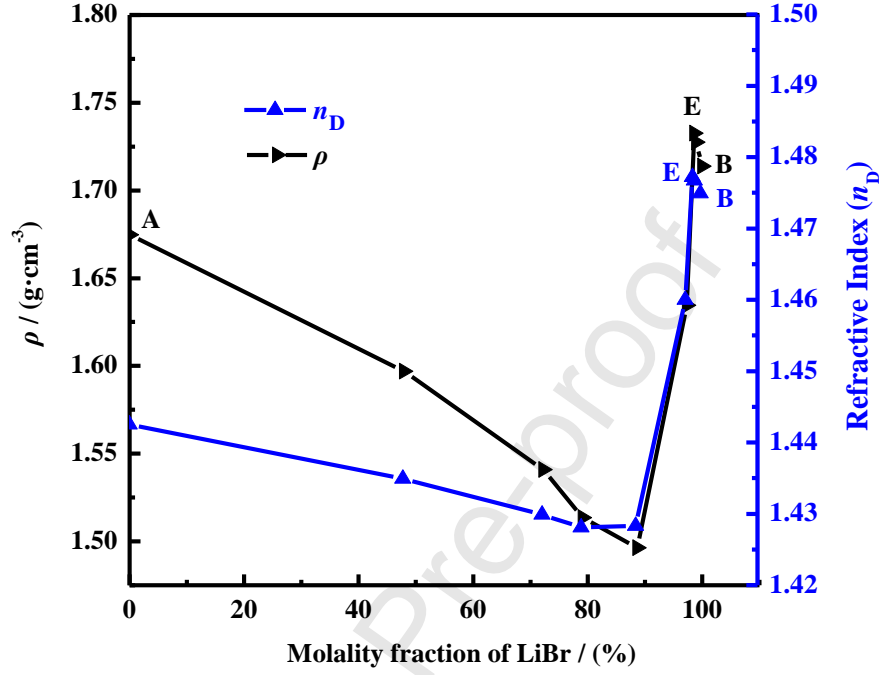
**Fig. 3.** Phase diagram for the ternary system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) at 288.15 K.  $\circ$ , solubility data in this work; A and B, invariant points for the binary systems ( $\text{SrBr}_2 + \text{H}_2\text{O}$ ) and ( $\text{LiBr} + \text{H}_2\text{O}$ ), respectively; E, invariant point for this ternary system; —, isothermal solubility curve; ..., wet residue curve.



**Fig. 4.** X-ray diffraction pattern of solid phase for the invariant point in the ternary system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) at 288.15 K.

The measured refractive indices and density with different composition of LiBr for the

ternary system (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K were plotted in Fig. 5, respectively. It can be clearly seen that the refractive index and density changed regularly with the increasing of the composition of LiBr (first decrease, then increase), after reaching the maximum value at the invariant point E with a sharply decrease.



**Fig. 5.** Refractive index (a) and density (b) at different molality fraction of LiBr for the ternary system (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K.

#### 4. Solubility calculation

##### 4.1. Model construction

Pitzer ion-interaction theory was widely used to evaluate the thermodynamic properties of the electrolyte aqueous solution [19, 20]. On the basis of the semi-empirical equations employed by Pitzer, Harvie and Weare developed a simple and accurate model to describe the thermodynamic properties of high concentration aqueous solution according to the osmotic coefficient and activity coefficient [21,22], and the calculated equations are shown as following:

$$(\phi - 1) = (2/\sum_i m_i) [-A^\phi I^{3/2}/(1 + bI^{1/2}) + m_{Li}m_{Cl}(B_{Li,Cl}^\phi + ZC_{Li,Cl}^\phi) + m_{Sr}m_{Cl}(B_{Sr,Cl}^\phi + ZC_{Sr,Cl}^\phi) + m_{Li}m_{Sr}(\Phi_{Li,Sr}^\phi + m_{Cl}\Psi_{Li,Sr,Cl})] \quad (3)$$

$$\Phi_{Li,Sr}^\phi = \theta_{Li,Sr} + E\theta_{Li,Sr} + I^E\theta'_{Li,Sr} \quad (4)$$

$$B_{M,X}^\phi = B_{M,X}^{(0)} + B_{M,X}^{(1)}\exp(-\alpha I^{0.5}) \quad (5)$$

Where  $M$  represent cations (Li<sup>+</sup> and Sr<sup>2+</sup>), and  $X$  represent anions (Cl<sup>-</sup>),  $b = 1.2 \text{ kg}^{0.5}\cdot\text{mol}^{-0.5}$ ,  $\alpha =$

$2.0 \text{ kg}^{0.5} \cdot \text{mol}^{-0.5}$ ,  $A^\phi$  is Debye–Hückel parameter,  $Z$  and  $m_i$  are the valence state and molality ( $\text{mol} \cdot \text{kg}^{-1}$ ) of each ion, respectively,  $\phi$  is osmotic coefficient of the solution,  $B^{(0)}$ ,  $B^{(1)}$  and  $C^\phi$  are the Pitzer single salt parameters,  $\theta_{Li,Sr}$  and  $\Psi_{Li,Sr,Cl}$  are the Pitzer mixing ion-interaction parameters, the terms for unsymmetrical mixing  $E\theta_{Li,Sr}$  and  $I^E\theta'_{Li,Sr}$  depend on the charges of the ions  $\text{Li}^+$  and  $\text{Sr}^{2+}$ , and the total ionic strength. And the other symbols in Eqs.(3)–(5) have been described in detail in the references [23].

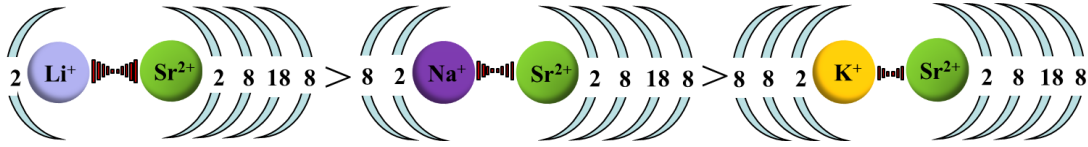
In this work, on the basis of the experimental osmotic coefficients and Pitzer single salt parameter for  $\text{SrBr}_2$  reported in our previous work [12], the Pitzer binary parameters  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C^{(\phi)}$  for  $\text{LiBr}$  and the mixing ion-interaction parameters  $\theta_{Li,Sr}$  and  $\Psi_{Li,Sr,Br}$  for the ternary system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) at 288.15 K were obtained, the Debye–Hückel coefficient ( $A^\phi = 0.376704$  at 288.15 K) using in this work was obtained from the literature [24], and the fitted Pitzer parameters were shown in Table 5.

**Table 5**

Pitzer parameters for the ternary system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) at 288.15 K.

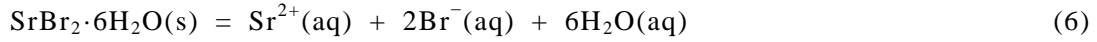
Species	$\beta^{(0)}$	$\beta^{(1)}$	$C^{(\phi)}$	$\theta$	$\Psi$	ref
LiBr	0.158730	0.597187	-0.004789			This work
$\text{SrBr}_2$	0.408961	-3.461831	-0.029171			[12]
$\text{Li}^+, \text{Sr}^{2+}$				0.152011		This work
$\text{Li}^+, \text{Sr}^{2+}, \text{Br}^-$					0.002890	This work

The interaction between the two ions  $\text{Li}^+$  and  $\text{Sr}^{2+}$ , and three ions  $\text{Li}^+$ ,  $\text{Sr}^{2+}$  and  $\text{Br}^-$  in the aqueous solution could be represented by the mixing parameters  $\theta_{Li,Sr}$  and  $\Psi_{Li,Sr,Br}$  obtained by the Pitzer HW model, which are quite strong and can't be omitted on the molecular-level. The comparison of the mixing parameters  $\theta_{Li,Sr} = 0.152011$  (this work),  $\theta_{Na,Sr} = 0.070668$  and  $\theta_{K,Sr} = 0.024708$  at 288.15 K [12] indicated that the ion interaction between  $\text{Sr}^{2+}$  and another alkali metal ion gradually decreased with the increase of atomic mass in the existence of bromide ion, which could be briefly illustrated by Fig. 6, the atomic nucleus of each alkali metal ion was surrounded with electronic shells, and the number of electronic shells increased with the increasing of atomic mass for alkali metal ions, meanwhile, the distance of atomic nucleus between alkali metal ions and  $\text{Sr}^{2+}$  also increased, so the ion-interaction was gradually decreased.



**Fig. 6.** The comparison of ion-interactions between alkali metal ions with strontium ion in the existence of bromide ion in aqueous solutions.

The solubility product constant ( $K_{sp}$ ) for the equilibrium solid phase, such as  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ , could be expressed as Eqs.(6) and (7):

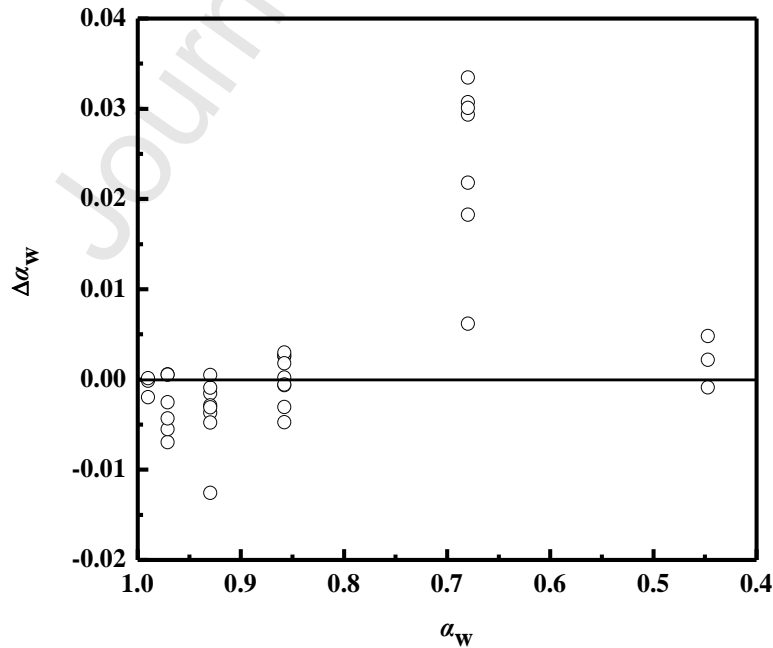


$$\ln K_{sp} = \ln(m_{\text{Sr}}\gamma_{\text{Sr}}) + 2\ln(m_{\text{Br}}\gamma_{\text{Br}}) + 6\ln\alpha_w = \ln m_{\text{Sr}} + 2\ln m_{\text{Br}} + 3\ln\gamma_{\pm} + 6\ln\alpha_w \quad (7)$$

combining the Pitzer parameters fitted in this work and the measured solubilities for LiBr and  $\text{SrBr}_2$ , eventually, the solubility product constant ( $K_{sp}$ ) for  $\text{LiBr} \cdot 2\text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  were obtained, and the calculated results for  $\ln K_{sp}$  were 7.5504 and 2.0871, respectively.

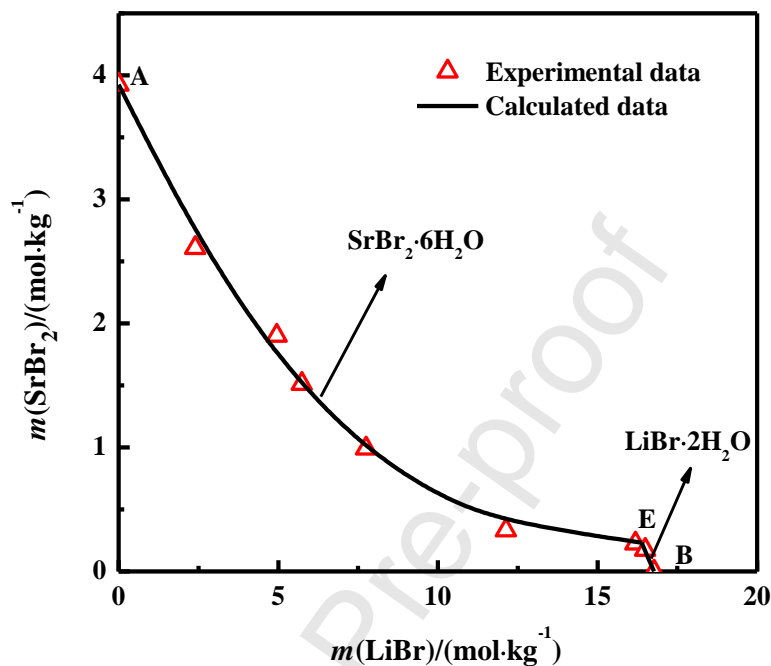
#### 4.2. Solubility calculation

The Pitzer and HW model was used to predict the solubilities for the ternary system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) at 288.15 K. On the basis of the Pitzer parameters and the solubility product constants ( $K_{sp}$ ) obtained in this work, the water activity for this ternary system was calculated by the Pitzer parameters, and the deviation between the experimental and calculated water activity was shown in Fig. 7.



**Fig. 7.** Deviation of the water activity for the ternary system ( $\text{LiBr} + \text{SrBr}_2 + \text{H}_2\text{O}$ ) calculated by Pitzer model with experimental values at 288.15 K,  $\Delta\alpha_w = \alpha_w(\text{exp}) - \alpha_w(\text{cal})$ .

Then the solubilities of saturated component were calculated with the unsaturated solute fixed at continuous molalities. The calculated solubilities were in good agreement with the experimental data, and the comparison of experimental and predicted phase diagram for the ternary (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K was shown in Fig. 8.



**Fig. 8.** Experimental and calculated phase diagram for the ternary system (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K.  $\Delta$ , experimental solubility data; —, calculated data with binary and mixing parameters obtained in this work.

In this ternary system, the salt-out effect could be explained using the Pitzer and HW model on the molecular-level. The process could be illustrated using the following Eq.(8), when added LiBr·2H<sub>2</sub>O into aqueous solutions saturated with SrBr<sub>2</sub>·6H<sub>2</sub>O, the concentration of Br<sup>-</sup> would increase as the dissolving of LiBr·2H<sub>2</sub>O, and the activity coefficients ( $\gamma_{\text{Sr}}$  and  $\gamma_{\text{Br}}$ ) and water activity could be considered as a stable value in a very short period of time, due to the  $K_{\text{sp}}$  of SrBr<sub>2</sub>·6H<sub>2</sub>O is a constant at a certain temperature and pressure, so the concentration of Sr<sup>2+</sup> would gradually decrease. And  $dm$  in Eq.(8) represented the small change of the concentration  $m$  for relative ions.

$$K_{\text{sp}}(\text{SrBr}_2 \cdot 6\text{H}_2\text{O}) = m_{\text{Sr}}\gamma_{\text{Sr}} \times (m_{\text{Br}}\gamma_{\text{Br}})^2 + \alpha_{\text{w}}^6 = (m_{\text{Sr}} - dm_{\text{Sr}})\gamma_{\text{Sr}} \times (m_{\text{Br}} + dm_{\text{Sr}})^2\gamma_{\text{Br}}^2 + \alpha_{\text{w}}^6 \quad (8)$$

## 5. Conclusion

Water activities, solubilities, refractive index and densities for the ternary system (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) and its binary subsystems at 288.15 K were measured for the first time in this work. The phase diagram was consisted of one invariant point, two isothermal dissolution curves, and

two crystallization regions, and this ternary system belong to the simple eutectic type. The refractive index and density changed regularly with the composition of LiBr. On the basis of the Pitzer and HW model, the binary and mixing Pitzer parameters and solubility product constant ( $K_{sp}$ ) for  $\text{LiBr} \cdot 2\text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  at 288.15 K were obtained. Then, the solubilities for this ternary system was successfully predicted, and the predicted solubilities were in good agreement with experimental data, which indicated the model constructed in this work was reliable. Eventually, the ion-interactions between alkali ions with  $\text{Sr}^{2+}$  and salt-out effect were illustrated on the molecular level.

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Financial supports from the National Natural Science Foundation of China (21773170, U1607123 and U1507112), the Key Projects of Natural Science Foundation of Tianjin (18JCZDJC10040) and the Yangtze Scholars and Innovative Research Team in Chinese University (IRT-17R81) are acknowledged.

### References

- [1] A. Cammarata, V. Verda, A. Sciacovelli, Y. Ding, Hybrid strontium bromide natural graphite composites for low to medium temperature thermochemical energy storage: Formulation, fabrication and performance investigation, *Energ. Convers. Manag.* 166 (2018) 233-240.
- [2] Y.G. Ma, X.W. Zhang, M. Liu, J.J. Yan, J.P. Liu, Proposal and assessment of a novel supercritical  $\text{CO}_2$  Brayton cycle integrated with LiBr absorption chiller for concentrated solar power applications, *Energy* 148 (2018) 839-854.
- [3] B. Pandya, N. Modi, R. Upadhyai, J. Patel, Thermodynamic performance and comparison of solar-assisted double effect absorption cooling system with  $(\text{LiCl} + \text{H}_2\text{O})$  and  $(\text{LiBr} + \text{H}_2\text{O})$  working fluid, *Build. Simul.* 12 (2019) 1063-1075.
- [4] R. Palacios-Bereche, R. Gonzales, S.A. Nebra, Exergy calculation of lithium bromide–water solution and its application in the energetic evaluation of absorption refrigeration systems  $(\text{LiBr} + \text{H}_2\text{O})$ , *Int. J. Energy Res.* 36 (2012) 166-181.
- [5] P. D'Ans, E. Courbon, M. Frere, G. Descy, T. Segato, M. Degrez, Severe corrosion of steel and copper by strontium bromide in thermochemical heat storage reactors, *Corrosion Sci.* 138 (2018) 275-283.



- [6] H.T. Wen, A.G. Wu, Z.C. Liu, Y.J. Shang, A state-space model for dynamic simulation of a single-effect LiBr/H<sub>2</sub>O absorption chiller, *IEEE Access* 7 (2019) 57251-57258.
- [7] M. Królikowska, M. Zawadzki, M. Skonieczny, The influence of bromide-based ionic liquids on solubility of {LiBr (1) + water (2)} system. Experimental (solid + liquid) phase equilibrium data. Part 2, *J. Mol. Liq.* 265 (2018) 316-326.
- [8] M. Donate, L. Rodriguez, A. De Lucas, J.F. Rodriguez, Thermodynamic evaluation of new absorbent mixtures of lithium bromide and organic salts for absorption refrigeration machines, *Int. J. Refrigeration* 29 (2006) 30-35.
- [9] L. Dong, D.X. Zheng, N. Nie, Y. Li, Performance prediction of absorption refrigeration cycle based on the measurements of vapor pressure and heat capacity of H<sub>2</sub>O + [DMIM]DMP system, *Appl. Energy* 98 (2012) 326-332.
- [10] L.Z. Meng, M.S. Gruszkiewicz, T.L. Deng, Y.F. Guo, D. Li, Isopiestic measurements of thermodynamic properties for the aqueous system (LiBr + CaBr<sub>2</sub> + H<sub>2</sub>O) at 373.15 K, *J. Chem. Thermodyn.* 129 (2019) 83-91.
- [11] D. Li, S.S. Li, L.Z. Meng, T.L. Deng, Y.F. Guo, Solid-liquid phase equilibria of ternary systems (LiCl + LiBr + H<sub>2</sub>O) and (CaCl<sub>2</sub> + CaBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K, *J. Chem. Eng. Data* 62 (2017) 833-838.
- [12] D. Li, L.Z. Meng, T.L. Deng, Y.F. Guo, Y. Pan, Experimental and thermodynamic modeling study of solid-liquid equilibrium in ternary systems (NaBr + SrBr<sub>2</sub> + H<sub>2</sub>O) and (KBr + SrBr<sub>2</sub> + H<sub>2</sub>O) at 288.15 K and 0.1 MPa, *J. Mol. Liq.* 252 (2018) 362-367.
- [13] L.Z. Meng, T.L. Deng, Y.F. Guo, D. Li, L. Yang, Measurement and thermodynamic model study on solid + liquid equilibria and physicochemical properties of the ternary system (MgBr<sub>2</sub> + MgSO<sub>4</sub> + H<sub>2</sub>O) at 323.15 K, *Fluid Phase Equilib.* 342 (2013) 88-94.
- [14] M. Kolthoff, E.B. Sandell, E.J. Meehan, Quantitative chemical analysis, New York, Macmillan, 1969.
- [15] X. Ji, H.J. Han, D.D. Li, L.J. Guo, D.W. Zeng, Gravimetric analysis of calcium and strontium in calcium and strontium chloride system, *Metal. Anal.* 36 (2016) 26-30.
- [16] P.S. Song, The application of wet residue method in the study of water-salt system, *J. Salt Lake Res.* 1 (1991) 15-23.

- [17] E.C. Clarke, D.N. Glew, Evaluation of the thermodynamic functions for aqueous sodium chloride from equilibrium and calorimetric below 427 K, *J. Phys. Chem. Ref. Data*, 14 (1985) 489-610.
- [18] J. Ananthaswamy, G. Atkinson, Thermodynamics of concentrated electrolyte mixtures 5. A review of the thermodynamics properties of aqueous calcium chloride in the temperature 273.15-373.15 K, *J. Chem. Eng. Data*, 30 (1985) 120-128.
- [19] K.S. Pitzer, Ion interaction approach: Theory and data correlation, Activity coefficients in electrolyte solutions, Boca Raton, CRC Press, 1991.
- [20] K.S. Pitzer, J.J. Kim, Thermodynamics of electrolytes.: IV. Activity and osmotic coefficients for mixed electrolytes, *J. Am. Chem. Soc.* 96 (1974) 5701-5707.
- [21] A.R. Felmy, J.H. Weare, The prediction of borate mineral equilibria in natural water: Application to Searles lake, California, *Geochim. Cosmochim. Acta* 50 (1986) 2771-2783.
- [22] C.E. Harvie, N. Møller, J.H. Weare, The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-H<sub>2</sub>O system to high ionic strengths at 25 °C, *Geochim. Cosmochim. Acta* 48 (1984) 723-751.
- [23] C.E. Harvie, J.H. Weare, The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system from zero to high concentration at 25 °C, *Geochim. Cosmochim. Acta* 44 (1980) 981-997.
- [24] R.J. Spencer, N. Møller, J.H. Weare, The prediction of mineral solubilities in natural water: A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO<sub>4</sub>-H<sub>2</sub>O system at temperature below 25 °C, *Geochim. Cosmochim. Acta* 54 (1990) 575-590.

## Author Statement

The individual contributions of all authors were outlined as following:

**Kaiyu Zhao:** Formal analysis, Investigation, Writing-original draft. **Yafei Guo:** Project administration, Visualization, Supervision. **Dan Li:** Resources, Software. **Lingzong Meng:** Software, Methodology, Data Curation. **Tianlong Deng:** Conceptualization, Methodology, Funding acquisition, Writing-Review & Editing.

**Conflict of Interest**

Authors declare that there is no conflict of interest.

Journal Pre-proof

**Highlights**

Water activities and solubilities of absorption refrigerants were firstly studied.

Water activity of (LiBr + SrBr<sub>2</sub> + H<sub>2</sub>O) system was measured by isopiestic method.

Thermodynamic properties were evaluated by the Pitzer ion-interaction model.

Ion-interactions between alkali metal ions and Sr<sup>2+</sup> were compared.

Salt-out effect in phase equilibrium process was illustrated on molecular level.