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Measurements and calculations of solid–liquid equilibria in the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K

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ARTICLE INFO

Article history:

Received 11 March 2016

Received in revised form

24 June 2016

Accepted 25 June 2016

Available online 17 July 2016

Keywords:

Underground brine

Thermodynamic solid–liquid equilibrium

Solubility

Phase diagram

Pitzer approach

ABSTRACT

Solid–liquid equilibria in the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K were measured by isothermal solution saturation method. The equilibrium solid phase and solubilities of salts in the system were determined. The experimental data are used to plot the solubility diagram and water content diagram of the quaternary system. It was found that quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K contains the double salt Na₂SO₄·3K₂SO₄ (Gla), and its solubility diagram has four invariant points, nine univariant curves, and six crystallization fields. The solids are NaBr·2H₂O, Na₂SO₄, Na₂SO₄·10H₂O, K₂SO₄, KBr and Na₂SO₄·3K₂SO₄ (Gla). The values of binary and mixing interaction parameters, the Debye–Hückel parameter A^{ϕ} and the standard chemical potentials of the salts in the quaternary system at 298 K were obtained from the literature and adapted to standard temperature. Based on the Pitzer approach, the solubilities in the system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K have been calculated using the parameters. The calculated and measured phase diagram of the quaternary system was plotted. The results show that the calculated solubilities agree well with the experimental data.

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1. Introduction

There are abundant liquid mineral resources in China, especially, in Western Sichuan Basin. These have very good exploitation prospect due to the gradual exhaustion of solid resources. The brines contain high concentration of potassium, borate and bromine. The highest content of potassium is as high as 53.27 g L⁻¹; the borate content is up to 4994.36 mg L⁻¹ and in particular, the bromine content is also up to 2533 mg L⁻¹. It has become the rare liquid potassium boron bromine mineral resources in the world [1]. Generally speaking, phase equilibria and phase diagrams are the theoretical basis of the exploitation and utilization of underground brine resources. According to the compositions, the underground gasfield brines in Sichuan Basin can be considered as Na–K–Cl–Br–SO₄–B₄O₇–H₂O system. The phase equilibria of some subsystems of the underground brine in Western Sichuan basin have been carried out by our group: such as Na₂B₄O₇–Na₂SO₄–NaBr–H₂O at 298 K, 323 K and 348 K [2–4], Na–K–Cl–SO₄–B₄O₇–H₂O at 298 K and 323 K [5,6].

The solubilities data in salt–water system depends principally

on experimental measurement. It is often tedious and the accuracy is strongly influenced by experimental condition. Therefore, many scientists have been trying to search calculated method with high accuracy to supplement and revise experimental measurements at 298 K or selected temperatures. In a series of papers Harvie et al. developed a model, based on Pitzer equations [7,8] to predict solubilities in seawater system Na–K–Mg–Ca–H–Cl–SO₄–OH–HCO₃–CO₃–CO₂–H₂O at 25 °C [9–11]. Then, Kim and Friedrich have provided many single-salt parameters and mixing ion–interaction parameters at 25 °C, it can be applied to make the Pitzer equation to 20 mol kg⁻¹ ionic strength [12,13]. Furthermore, Christov and Moller developed a thermodynamic model for solution behavior and solid–liquid equilibria in the H–Na–K–Ca–OH–Cl–HSO₄–SO₄–H₂O system from zero to high concentration and temperature [14–16]. For bromide systems, Christov and co-workers [17–26] develop a well validated and fully consistent model for Li–Na–K–NH₄–Rb–Cs–Mg–Ca–Cl–Br–H₂O system at standard temperature, and for some ternary subsystems at 0 °C, 50 °C and 75 °C [17,21,23,25]. As a next step, Christov determine osmotic coefficients on the basis of isopiestic measurements for binary bromide sub-systems and solubilities in ternary sub-systems within Na–K–Mg–Ca–Br–SO₄–H₂O system [27–32].

The quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O is one subsystem of the underground gasfield brines in Sichuan Basin. Measurements and calculations of solid–liquid equilibria in this

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quaternary system at 323 K have been published in our previous work [33,34], but there is no research report about the phase equilibria in the system at 298 K, which is the objective of this work. In this paper, the research work includes three parts: (1) Measure the solubilities in the equilibrium solution for the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K by isothermal solution saturation method. (2) Calculate solubilities in the quaternary system at 298 K. And (3) Compare calculated solubilities with experimental data of this system.

2. Experimental

2.1. Reagents and instruments

The deionized water (electrical conductivity less than 1.2×10^{-4} S m⁻¹, pH=6.6) used to prepare the experimental solutions was

obtained from a Millipore water system. All chemicals used in this work, including sodium bromide (NaBr, 99.0 wt%), potassium bromide (KBr, 99.0 wt%), sodium sulfate (Na₂SO₄, 99.0 wt%), and potassium sulfate (K₂SO₄, 99.0 wt%), were of analytical purity grade and obtained from Chengdu Kelong Chemical Reagent Factory, China.

A standard analytical balance of 110 g capacity and 0.0001 g resolution (AL104), manufactured by the Mettler Toledo Instruments, was used. An HZS-H type thermostated vibrator with a precision ± 0.1 K was used for the equilibrium measurements. Its temperature control accuracy is ± 0.1 K after secondary calibration using precise thermometer.

2.2. Experimental method

The experiments for the quaternary system have been done by the method of isothermal solution saturation. According to the

Table 1
Solubilities of solution in the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K.

No.	Composition of liquid phase $w(B) \times 100$				Jänecke index			Equilibrium solids
	$w(\text{Na}^+)$	$w(\text{K}^+)$	$w(\text{Br}^-)$	$w(\text{SO}_4^{2-})$	$J(2\text{Na}^+) + J(2\text{K}^+) = 100 \text{ mol}$			
					$J(2\text{Na}^+)$	$J(\text{SO}_4^{2-})$	$J(\text{H}_2\text{O})$	
F, 1	7.26	2.75	0.00	18.55	81.78	100.00	2053.60	NS10 + Gla
2	7.25	2.67	2.41	16.98	82.22	92.14	2045.20	NS10 + Gla
3	6.91	2.52	5.18	14.41	82.36	82.23	2158.43	NS10 + Gla
4	6.87	2.51	7.41	12.98	82.34	74.45	2146.51	NS10 + Gla
5	6.81	2.44	10.58	10.86	82.60	63.06	2146.24	NS10 + Gla
6	6.27	2.22	14.23	7.28	82.75	45.98	2357.13	NS + Gla
7	6.55	2.33	20.61	4.16	82.69	25.15	2137.39	NS + Gla
E2, 8	8.29	3.54	34.99	0.62	79.92	2.87	1293.65	Gla + NS + KB
D, 9	2.13	4.59	0.00	10.08	44.09	100.00	4401.26	KS + Gla
10	2.09	4.53	2.66	8.33	43.96	83.89	4419.97	KS + Gla
11	2.19	4.72	5.15	7.27	44.06	70.15	4150.41	KS + Gla
12	2.06	4.73	8.27	5.14	42.58	50.82	4205.39	KS + Gla
13	2.08	4.83	10.30	4.09	42.30	39.80	4079.53	KS + Gla
14	2.15	6.05	16.15	2.21	37.63	18.57	3283.18	KS + Gla
E1, 15	2.58	9.51	27.26	0.69	31.60	4.02	1872.38	KS + Gla + KB
B, 16	9.80	2.40	38.96	0.00	87.43	0.00	1111.45	NB + KB
17	9.65	2.61	38.70	0.09	86.26	0.40	1116.80	NB + KB
18	9.64	2.76	38.98	0.11	85.59	0.47	1098.45	NB + KB
19	9.62	2.67	38.67	0.12	85.98	0.51	1116.21	NB + KB
20	9.78	2.71	39.23	0.18	86.00	0.75	1078.95	NB + KB
21	9.65	2.70	38.67	0.22	85.88	0.95	1107.57	NB + KB
E3, 22	9.57	2.81	38.59	0.25	85.26	1.08	1108.71	NS + KB + NB
A, 23	0.00	13.77	27.38	0.46	0.00	2.71	1839.64	KS + KB
24	0.64	12.80	27.53	0.51	7.85	3.00	1828.71	KS + KB
25	1.21	12.10	27.92	0.60	14.52	3.43	1784.19	KS + KB
26	1.55	11.64	28.10	0.65	18.47	3.70	1764.66	KS + KB
27	2.34	10.57	28.57	0.70	27.32	3.90	1724.33	KS + KB
28	3.82	8.70	29.83	0.73	42.76	3.91	1625.70	Gla + KB
29	4.96	7.29	30.92	0.74	53.65	3.81	1547.46	Gla + KB
30	7.06	5.05	33.65	0.74	70.39	3.53	1360.14	Gla + KB
31	8.12	4.27	35.75	0.73	76.36	3.27	1226.98	Gla + KB
C, 32	11.03	0.00	37.70	0.38	100.00	1.66	1176.95	NS + NB
33	10.88	0.30	37.82	0.35	98.41	1.53	1169.25	NS + NB
34	10.72	0.62	37.93	0.34	96.72	1.49	1160.46	NS + NB
35	10.45	0.98	37.74	0.34	94.79	1.47	1169.43	NS + NB
36	10.28	1.43	38.12	0.32	92.44	1.37	1143.94	NS + NB
37	9.80	2.56	38.82	0.29	86.68	1.25	1094.61	NS + NB
38	9.66	2.81	38.87	0.26	85.41	1.08	1092.65	NS + NB
G, 39	8.78	0.00	16.90	8.19	100.00	44.63	1920.55	S10 + NS
40	8.82	0.41	17.16	8.60	97.35	45.46	1831.67	S10 + NS
41	8.34	0.84	16.51	8.54	94.39	46.27	1898.18	S10 + NS
42	8.15	1.13	16.26	8.64	92.45	46.91	1905.12	S10 + NS
43	8.03	1.67	16.53	8.88	89.10	47.21	1838.27	S10 + NS
44	7.49	2.13	15.89	8.70	85.66	47.67	1921.08	S10 + NS
E4, 45	7.55	2.54	16.25	9.13	83.47	48.32	1819.32	S10 + NS + Gla

Note: NB=NaBr · 2H₂O, NS=NaSO₄, KB=KBr, KS=K₂SO₄, Gla=Na₂SO₄ · 3K₂SO₄, S10=NaSO₄ · 10H₂O. Standard uncertainties u are $u(T)=0.1$ K, $u(\text{Na}^+)=0.005$, $u(\text{K}^+)=0.003$, $u(\text{Br}^-)=0.003$, $u(\text{SO}_4^{2-})=0.003$.

equilibrium composition of invariant points for its ternary sub-systems, salts were prepared proportionally. The appropriate calculated quantity of salts was dissolved in distilled water. The mixtures were put into sealed glass bottles for the solubility experiments.

Then, sealed glass bottles were placed in the thermostated vibrator (HZS-H), and the temperature was maintained at (298 ± 0.1) K. The solutions were taken out periodically to analyze the concentration of the solution. When the concentration was unchanged, the sign of equilibrium reached. This process took about 15 days. The clarification of the solutions needs about five days. After equilibrium, the liquid phases were taken out and diluted to volumetric flask for the quantitative analysis of the composition.

2.3. Analytical methods

Potassium ion (K^+) concentration was determined using sodium tetraphenyl borate–hexadecyl trimethyl ammonium bromide titration (with a precision of 0.5 wt%). Bromide ion (Br^-) concentrations were determined by Mohr's method using a silver nitrate standard solution (with a precision of 0.3 wt%). Sulfate ion (SO_4^{2-}) concentration was measured by a method of alizarin red S volumetry (precision: 0.5 wt%). Sodium ion (Na^+) concentration was evaluated according to the ion charge balance.

3. Results and discussion

The experimental results of solubilities and equilibrium solids of the equilibrated solution in the quaternary system $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ at 298 K are shown in Table 1. The solubilities of salts in the equilibrium solution are expressed as weight percentages $w(B)$. The solubility diagram of the quaternary system is expressed with Jänecke dry-salt indices, where $J(2Na^+)$, $J(2K^+)$, $J(2Br^-)$, $J(SO_4^{2-})$ and $J(H_2O)$ are the Jänecke indices of their corresponding salts and water, respectively, with $J(2Na^+) + J(2K^+) = J(2Br^-) + J(SO_4^{2-}) = 100$ mol. On the basis of Jänecke index values, the phase diagram was constructed, and was shown in Fig. 1 with solid lines.

The quaternary system $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ at 298 K is interactive saturation systems. It consists of four ternary sub-systems: (1) $Na_2SO_4-K_2SO_4-H_2O$, (2) $NaBr-KBr-H_2O$ (3) $NaBr-Na_2SO_4-H_2O$ and (4) $KBr-K_2SO_4-H_2O$. The ternary system $Na_2SO_4-K_2SO_4-H_2O$ is a classical Salt-water system. For this ternary system, a lot of solubility data have been reported at a wide temperature range and the experimental and calculated data is accurate and reliable through long-term validation. In this system, the double salt $Na_2SO_4 \cdot 3K_2SO_4$ was found. It consist of three univariant curves, three crystallization fields (Na_2SO_4 , K_2SO_4 and $Na_2SO_4 \cdot 3K_2SO_4$), and has two invariant points. The Br-bearing ternary systems $NaBr-KBr-H_2O$, $NaBr-Na_2SO_4-H_2O$ and $KBr-K_2SO_4-H_2O$ at 298 K are all simple co-saturation type. The systems $NaBr-KBr-H_2O$ and $KBr-K_2SO_4-H_2O$ consist of only one invariant point, two univariant curves and two crystallization regions. The $NaBr-Na_2SO_4-H_2O$ system has two invariant points, three univariant curves, and three crystallization fields corresponding to $NaBr \cdot 2H_2O$, Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$.

The phase diagram of the quaternary system in Fig. 1 consists of six crystallization fields, nine univariant curves, and four invariant points (points E1, E2, E3 and E4). The six crystallization fields correspond to five single salts, $NaBr \cdot 2H_2O$, Na_2SO_4 , $Na_2SO_4 \cdot 10H_2O$, K_2SO_4 and KBr , and one double salt, $Na_2SO_4 \cdot 3K_2SO_4$ (Gla). The crystallized area of apthitalite is the largest whereas that of sodium bromide dihydrate is the smallest because of its high solubility. No solid solution has been found in

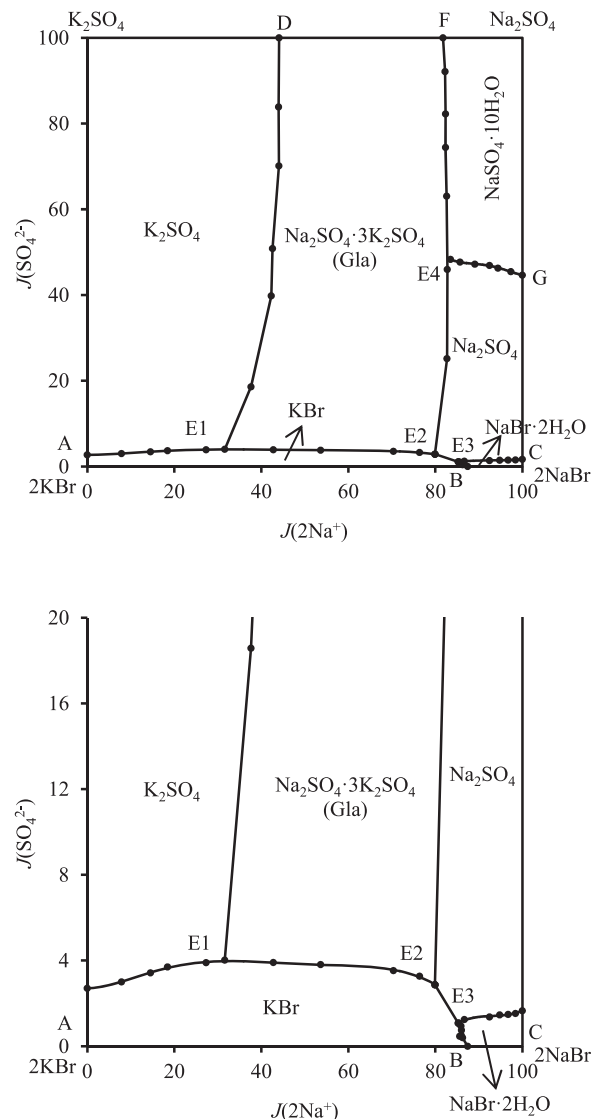


Fig. 1. Equilibrium phase diagram and partial enlarged diagram of the quaternary system $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ at 298 K.

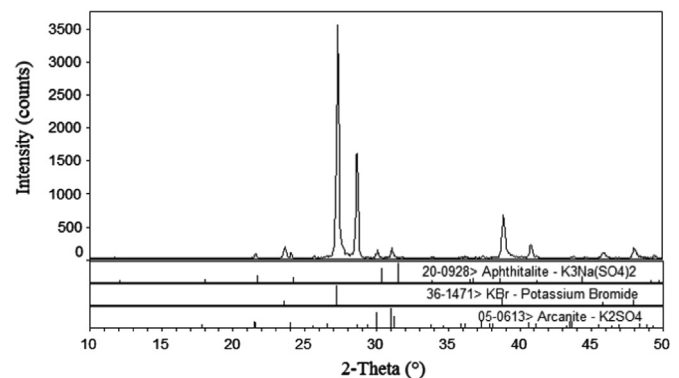


Fig. 2. X-ray diffraction photograph of the invariant point E1 of the quaternary system $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ at 298 K [$Na_2SO_4 \cdot 3K_2SO_4 + KBr + K_2SO_4$].

quaternary system $NaBr-KBr-Na_2SO_4-K_2SO_4-H_2O$ at 298 K. The nine univariant curves, namely, curves AE1, BE3, CE3, DE1, FE4, GE4, E1E2, E2E3 and E2E4, are cosaturated with two salts, respectively. The X-ray diffraction photographs of the invariant

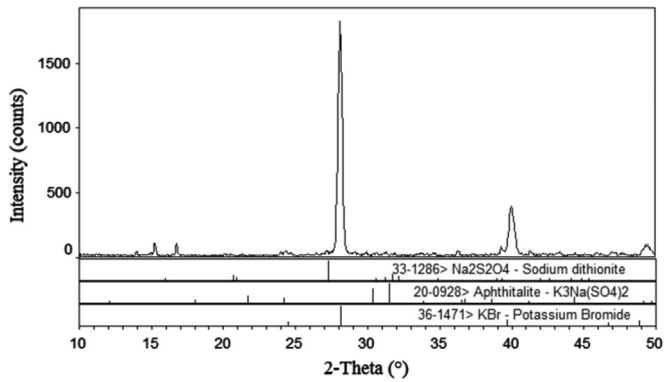


Fig. 3. X-ray diffraction photograph of the invariant point E2 of the quaternary system NaBr-KBr-Na₂SO₄-K₂SO₄-H₂O at 298 K [Na₂SO₄·3K₂SO₄+KBr+Na₂SO₄].

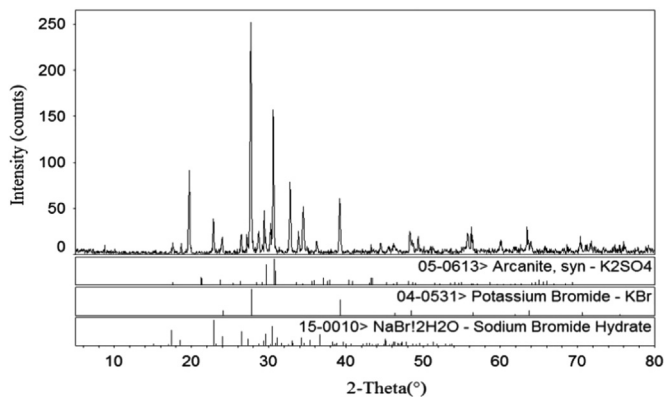


Fig. 4. X-ray diffraction photograph of the invariant point E3 of the quaternary system NaBr-KBr-Na₂SO₄-K₂SO₄-H₂O at 298 K [Na₂SO₄+KBr+NaBr·2H₂O].

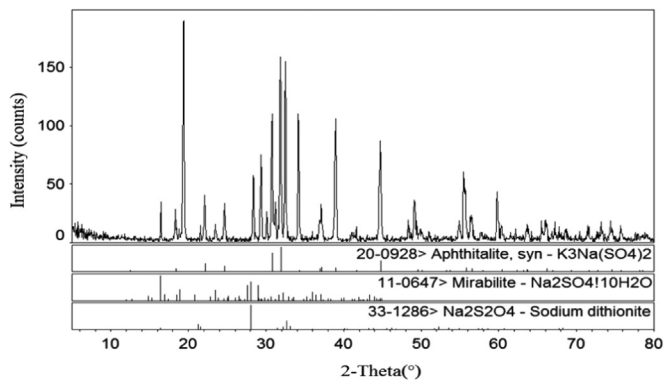


Fig. 5. X-ray diffraction photograph of the invariant point E4 of the quaternary system NaBr-KBr-Na₂SO₄-K₂SO₄-H₂O at 298 K [Na₂SO₄·3K₂SO₄+Na₂SO₄·10H₂O+Na₂SO₄].

points E1, E2, E3 and E4 in the quaternary system are given in Figs. 2–5. The saturated salts and the mass fraction composition for the four invariant points are listed below.

Invariant point E1, saturated with salts K₂SO₄+KBr+Na₂SO₄·3K₂SO₄ (Gla). The mass fraction composition of the corresponding liquid phase is $w(\text{Na}^+)=0.0258$, $w(\text{K}^+)=0.0951$, $w(\text{Br}^-)=0.2726$ and $w(\text{SO}_4^{2-})=0.0069$.

Invariant point E2, saturated with salts Na₂SO₄+KBr+Na₂SO₄·3K₂SO₄ (Gla). The mass fraction composition of the corresponding liquid phase is $w(\text{Na}^+)=0.0829$, $w(\text{K}^+)=0.0354$, $w(\text{Br}^-)=0.3499$ and $w(\text{SO}_4^{2-})=0.0062$.

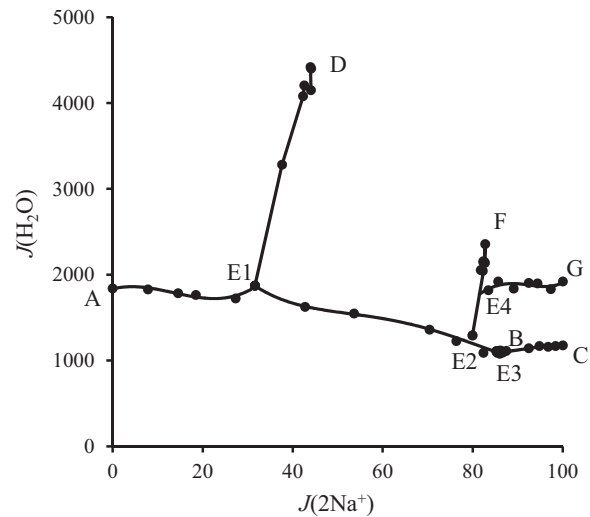


Fig. 6. Water contents of saturated solutions in quaternary system NaBr-KBr-Na₂SO₄-K₂SO₄-H₂O at 298 K.

Table 2

Single-salt parameters and mixing ion-interaction parameters in the solution of the quaternary system NaBr-KBr-Na₂SO₄-K₂SO₄-H₂O at 298 K.

Salt	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	Reference source
Na ₂ SO ₄	0.018693	1.099405	0.006298	[15]
K ₂ SO ₄	0.055536	0.796385	-0.0188	[15]
NaBr	0.1209144	0.0614751	-0.00282	[27]
KBr	0.0518449	0.2767664	-0.000868	[27]

Invariant point E3, saturated with salts NaBr·2H₂O+KBr+Na₂SO₄. The mass fraction composition of the corresponding liquid phase is $w(\text{Na}^+)=0.0957$, $w(\text{K}^+)=0.0281$, $w(\text{Br}^-)=0.3859$ and $w(\text{SO}_4^{2-})=0.0025$.

Invariant point E4, saturated with salts Na₂SO₄·10H₂O+Na₂SO₄+Na₂SO₄·3K₂SO₄ (Gla). The mass fraction composition of the corresponding liquid phase is $w(\text{Na}^+)=0.0755$, $w(\text{K}^+)=0.0254$, $w(\text{Br}^-)=0.1625$ and $w(\text{SO}_4^{2-})=0.0913$.

Fig. 6 is the relevant water diagram of the quaternary system NaBr-KBr-Na₂SO₄-K₂SO₄-H₂O at 298 K. Fig. 6 shows that the Jänecke index values of water $J(\text{H}_2\text{O})$ change with the Jänecke index values of Na⁺ and decrease at the univariant curves DE1, FE4 and E4E2.

Compared with the two phase diagrams of quaternary system Na⁺,K⁺//Br⁻,SO₄²⁻-H₂O at 298 K and 323 K [33,34], the result shows that the double salt all forms in the phase diagrams at two different temperatures. But the numbers of invariant points, crystallization fields, and univariant curves are different. The crystallization fields of solid solution Na₂SO₄·10H₂O has disappeared at 323 K. The phase diagram at 323 K includes three invariant points, seven univariant curves, and five crystallization regions corresponding to NaBr, Na₂SO₄, K₂SO₄, KBr and Na₂SO₄·3K₂SO₄(Gla). And the shape of the each crystallization region is nearly identical. The solubility of NaBr·2H₂O (298 K) or NaBr (323 K) is highest among the salts in this quaternary system at two temperatures. In comparison with the quaternary systems Na⁺,K⁺//Cl⁻,SO₄²⁻-H₂O [15] and Na⁺,K⁺//Br⁻,SO₄²⁻-H₂O at 298 K, the two phase diagrams have very similar shapes, each of them having four invariant points, nine univariant curves, and six crystallization fields. The crystallization field of the salt NaBr is apparently smaller than that of NaCl. It is also found that halide has the salting-out effect on sulfates.

Table 3Values of Debye–Hückel constant (A^ϕ) and mixing ion-interaction parameters in the solution of the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K.

Parameter	$\theta_{\text{Na,K}}$	$\theta_{\text{Br,SO}_4}$	$\Psi_{\text{Na,K,SO}_4}$	$\Psi_{\text{Na,K,Br}}$	$\Psi_{\text{Na,Br,SO}_4}$	$\Psi_{\text{K,Br,SO}_4}$	A^ϕ
Value	–0.003203	0.03	0.007253	–0.002586	–0.012	–0.0115	0.3914752
Ref.	[15]	[32]	[15]	[27]	[32]	[32]	[15]

Table 4Stable solubility constants of salts of the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K.

Parameter	ln Ka	Reference
Na ₂ SO ₄ · 10H ₂ O	–2.80577	[15]
Na ₂ SO ₄	–0.586385	[15]
K ₂ SO ₄	–4.125243	[15]
NaBr · 2H ₂ O	4.643336	[27]
KBr	2.6271912	[27]
Na ₂ SO ₄ · 3K ₂ SO ₄ (Gla)	–17.059879	[15]

4. Prediction of solubility

Pitzer published a series of papers about electrolyte solution, and came up with a set of semi-empirical theory of statistical mechanics [7,8]. Using this theory, a set of expressions for the osmotic coefficients of the solution and mean activity coefficient of electrolytes in the solution has been deduced. A number of theoretical studies on salt minerals and brine system have been carried out in recent decades. Aiming at the seawater system, Harvie et al. carried out a series of research and extended the Pitzer ion-interaction model to Harvie–Weare (H–W) model, and have been

Table 5Calculated value of solution solubilities in the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K.

No.	Composition of liquid phase				Jänecke index		Equilibrium solids
					$J(2\text{Na}^+) + J(2\text{K}^+) = 100 \text{ mol}$		
	M(Na ⁺)	M(K ⁺)	M(Br [–])	M(SO ₄ ^{2–})	$J(2\text{Na}^+)$	$J(\text{SO}_4^{2-})$	
A', 1	0.00	5.99	5.70	0.14	0.00	4.83	KS + KB
2	0.51	5.63	5.82	0.16	8.24	5.24	KS + KB
3	1.01	5.29	5.94	0.18	16.05	5.74	KS + KB
4	1.52	4.96	6.07	0.21	23.41	6.36	KS + KB
E1', 5	2.02	4.66	6.20	0.24	30.28	7.12	KS + KB + Gla
6	1.70	3.33	4.43	0.30	33.78	11.84	KS + Gla
7	1.52	2.75	3.55	0.36	35.60	16.97	KS + Gla
8	1.34	2.25	2.66	0.47	37.35	26.04	KS + Gla
9	1.19	1.87	1.77	0.64	38.92	41.96	KS + Gla
10	1.09	1.62	0.89	0.91	40.29	67.30	KS + Gla
11	1.07	1.53	0.30	1.16	41.19	88.66	KS + Gla
D', 12	1.08	1.51	0.00	1.29	41.67	100.00	KS + Gla
13	2.56	4.28	6.37	0.23	37.43	6.80	KB + Gla
14	3.15	3.90	6.58	0.24	44.67	6.73	KB + Gla
15	3.80	3.52	6.82	0.25	51.90	6.90	KB + Gla
16	4.53	3.14	7.11	0.28	59.05	7.35	KB + Gla
17	5.39	2.77	7.49	0.33	66.08	8.21	KB + Gla
18	6.45	2.39	7.97	0.43	72.99	9.82	KB + Gla
E2', 19	7.98	2.01	8.69	0.65	79.88	13.07	KB + Gla + NS
B', 20	8.77	1.26	10.03	0.00	87.40	0.00	KB + NB
21	8.78	1.27	10.03	0.01	87.40	0.18	KB + NB
22	8.80	1.27	10.03	0.02	87.39	0.35	KB + NB
23	8.81	1.27	10.03	0.03	87.38	0.53	KB + NB
E3', 24	8.83	1.27	10.03	0.04	87.38	0.71	KB + NB + NS
25	8.93	0.95	9.81	0.03	90.38	0.69	NB + NS
26	9.03	0.63	9.60	0.03	93.44	0.66	NB + NS
27	9.13	0.32	9.39	0.03	96.65	0.63	NB + NS
C', 28	9.23	0.00	9.18	0.03	100.00	0.60	NB + NS
29	9.04	1.32	10.01	0.18	87.28	3.41	KB + NS
30	9.11	1.46	9.76	0.40	86.20	7.63	KB + NS
31	8.45	1.73	9.14	0.52	82.97	10.20	KB + NS
32	7.18	1.50	6.93	0.87	82.77	20.12	Gla + NS
33	6.85	1.28	5.95	1.09	84.23	26.88	Gla + NS
34	6.69	1.16	5.23	1.31	85.17	33.45	Gla + NS
35	6.62	1.09	4.64	1.53	85.87	39.81	Gla + NS
F', 36	4.44	1.00	0.00	2.72	81.55	100.00	Gla + S10
37	4.71	0.99	0.73	2.49	82.60	87.21	Gla + S10
38	5.12	0.98	1.46	2.32	83.93	76.08	Gla + S10
39	5.25	0.97	1.92	2.15	84.40	69.16	Gla + S10
E4', 40	5.73	0.96	3.19	1.75	85.60	52.38	Gla + S10 + NS
41	5.95	0.67	3.22	1.70	89.88	51.39	NS + S10
42	6.41	0.24	3.30	1.67	96.46	50.28	NS + S10
G', 43	6.65	0.00	3.35	1.65	100.00	49.59	NS + S10

Note: NB=NaBr · 2H₂O, NS=NaSO₄, KB=KBr, KS=K₂SO₄, Gla=Na₂SO₄ · 3K₂SO₄, S10=NaSO₄ · 10H₂O

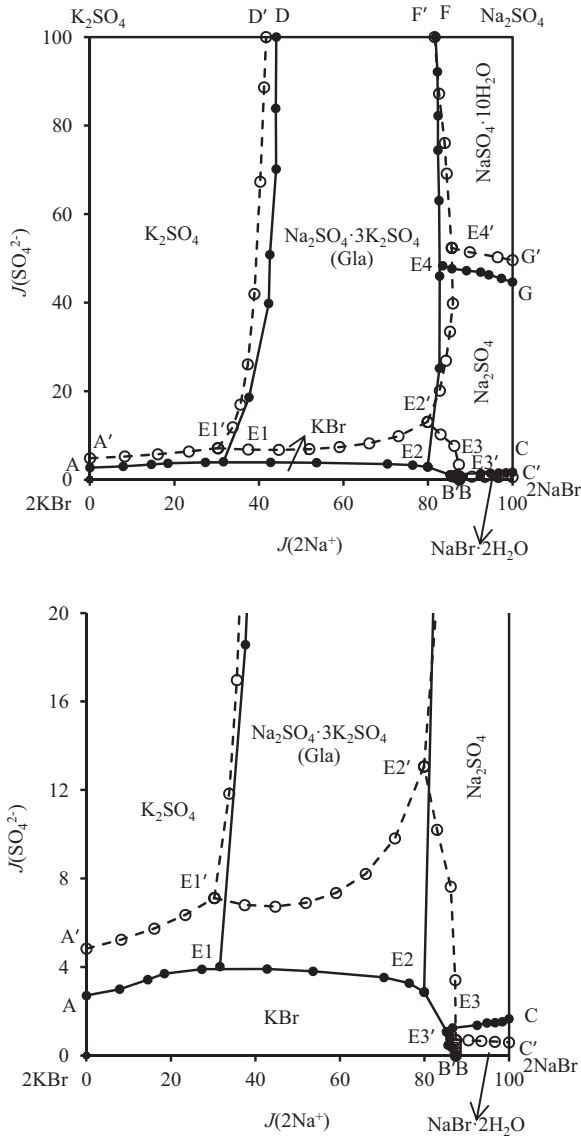


Fig. 7. The experimental and calculated phase diagram and partial enlarged diagram of the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K. —, experimental isotherm curve; ····, calculated isotherm curve; ●, experimental data; ○, calculated data.

successfully used in calculating thermodynamic properties and the solubilities of electrolytes. The H–W equations are as follows [9–11]:

$$\begin{aligned} \phi - 1 = & \frac{1}{\sum_i m_i} \left\{ 2 \left[\frac{-A^{\phi/2}}{1 + 1.212} + \sum_{i_c=1}^{N_C} \sum_{i_A=1}^{N_A} m_C m_A (B_{CA}^{\phi} + ZC_{CA}) + \right. \right. \\ & \sum_{i_c=1}^{N_C-1} \sum_{j_c=i_c+1}^{N_C} m_C m_{C'} \left(\Phi_{CC'}^{\phi} + \sum_{i_A=1}^{N_A} m_A \psi_{ACC'} \right) \\ & + \sum_{i_A=1}^{N_A-1} \sum_{j_A=i_A+1}^{N_A} m_A m_{A'} \left(\Phi_{AA'}^{\phi} + \sum_{i_c=1}^{N_C} m_C \psi_{AA'C} \right) \\ & \left. \left. + \sum_{i_N=1}^{N_N} \sum_{i_A=1}^{N_A} m_N m_A \lambda_{NA} + \sum_{i_N=1}^{N_N} \sum_{i_C=1}^{N_C} m_N m_C \lambda_{NC} \right] \right\} \quad (1) \end{aligned}$$

$$\begin{aligned} \ln \gamma_M = & Z_M^2 F + \sum_{i_A=1}^{N_A} m_A (2B_{MA} + ZC_{CX}) \\ & + \sum_{i_c=1}^{N_C} m_C \left(2\Phi_{MC} + \sum_{i_A=1}^{N_A} m_A \psi_{MCA} \right) \\ & + \sum_{i_A=1}^{N_A-1} \sum_{j_A=i_A+1}^{N_A} m_A m_{A'} \psi_{AA'M} + |Z_M| \sum_{i_c=1}^{N_C} \sum_{i_A=1}^{N_A} m_A m_C C_{CA} \\ & + \sum_{i_N=1}^{N_N} m_N (2\lambda_{NM}) \quad (2) \end{aligned}$$

$$\begin{aligned} \ln \gamma_X = & Z_X^2 + \sum_{i_c=1}^{N_C} m_C (2B_{CX} + ZC_{CX}) \\ & + \sum_{i_A=1}^{N_A} m_A \left(2\Phi_{XA} + \sum_{i_c=1}^{N_C} m_C \psi_{XAC} \right) + \sum_{i_c=1}^{N_C-1} \sum_{j_c=i_c+1}^{N_C} m_C m_{C'} \psi_{CC'X} \\ & + |Z_X| \sum_{i_c=1}^{N_C} \sum_{i_A=1}^{N_A} m_C m_A C_{CA} + \sum_{i_N=1}^{N_N} m_N (2\lambda_{NM}) \quad (3) \end{aligned}$$

$$\ln \gamma_N = \sum_{i_c=1}^{N_C} m_C (2\lambda_{AC}) + \sum_{i_A=1}^{N_A} m_A (2\lambda_{NA}) \quad (4)$$

In the above (Eqs. (1)–4), M, C and C' are referred to cations; X, A and A' are referred to anions; N_C, N_A and N_N refer to cations, anions and neutral molecules respectively.

Christov develop temperature variable fully parameterized solid–liquid equilibria model for two bromide quinary systems: Na–K–Mg–Ca–Br–H₂O [27–31] and Na–K–Ca–Br–SO₄–H₂O [32]. The model for binary subsystems is valid from 0 to 250 °C, and for mixed systems from 0 to 100 °C. It can provide the needed single-salt parameters $\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ} for NaBr and KBr, Pitzer mixing ion-interaction parameters $\psi_{Na,K,Br}$, θ_{Br,SO_4} , ψ_{Na,Br,SO_4} , and ψ_{K,Br,SO_4} , and stable solubility constants $\ln K$ of salts NaBr·2H₂O, KBr for the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K.

Moreover, the other needed Pitzer single-salt parameters $\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ} for Na₂SO₄, K₂SO₄, Pitzer mixing ion-interaction parameters $\theta_{Na,K}$, ψ_{Na,K,SO_4} , Debye–Hückel parameter A^{ϕ} , $\ln K_w(\mu^{\circ}/RT)$ H₂O(aq) and stable solubility constants $\ln K$ of salts Na₂SO₄, Na₂SO₄·10H₂O, K₂SO₄ at 298 K are available using this T -function given in T -variation model by Greenberg and Moller [15]. All of the parameters used in the calculation are presented in Tables 2–4, respectively.

Based on the solubility approach of Harvie et al. for aqueous electrolyte solutions, the solubilities for phase equilibria conditions in the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K were calculated with corresponding parameters and are listed in Table 5. On the Basis of the experimental and calculated solubilities, the phase diagram of the quaternary system was plotted and given in Fig. 7. The calculations data and experiments data were compared, and the results were shown in Table 6. It showed that the calculated values have a good agreement with the experimental data. And it also means that reasonable parameters can be used in aqueous salt system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K.

5. Conclusions

The phase equilibrium of the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O was studied at 298 K by isothermal solution saturation method. It was found that the quaternary system contains the double salt Na₂SO₄·3K₂SO₄ (Gla). The phase diagram of

Table 6Calculated and partly experimental solubilities in the quaternary system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O system at 298 K.

No.	Composition of liquid phase				Jänecke index		Equilibrium solids
	100 · w(B)				J(2Na ⁺)+J(2K ⁺)=100 mol		
	w(Na ⁺)	w(K ⁺)	w(Br ⁻)	w(SO ₄ ²⁻)	J(2Na ⁺)	J(SO ₄ ²⁻)	
Experimental A	0.00	13.77	27.38	0.46	0.00	2.71	KS+KB
Calculated A'	0.00	13.75	26.74	0.82	0.00	4.83	
Experimental B	9.80	2.40	38.96	0.00	87.43	0.00	KB+NB
Calculated B'	9.82	2.41	39.06	0.00	87.40	0.00	
Experimental C	11.03	0.00	37.70	0.38	100.00	1.66	NB+NS
Calculated C'	10.90	0.00	37.64	0.14	100.00	0.60	
Experimental D	2.13	4.59	0.00	10.08	44.09	100.00	KS+Gla
Calculated D'	2.05	4.89	0.00	10.29	41.67	100.00	
Experimental F	7.26	2.75	0.00	18.55	81.78	100.00	Gla+S10
Calculated F'	7.28	2.80	0.00	18.64	81.55	100.00	
Experimental G	8.78	0.00	16.90	8.19	100.00	44.63	NS+S10
Calculated G'	8.84	0.00	17.16	8.16	100.00	49.59	
Experimental E1	2.58	9.51	27.26	0.69	31.60	4.02	KS+KB+Gla
Calculated E1'	2.66	10.42	28.37	1.31	30.28	7.12	
Experimental E2	8.29	3.54	34.99	0.62	79.92	2.87	KB+Gla+NS
Calculated E2'	5.38	7.15	30.97	1.41	79.88	13.07	
Experimental E3	9.57	2.81	38.59	0.25	85.26	1.08	KB+NB+NS
Calculated E3'	9.83	2.41	39.02	0.05	87.38	0.71	
Experimental E4	7.55	2.54	16.25	9.13	83.47	48.32	Gla+NS+S10
Calculated E4'	9.31	2.23	14.14	13.69	85.60	52.38	

Note: NB=NaBr · 2H₂O, NS=NaSO₄, KB=KBr, KS=K₂SO₄, Gla=Na₂SO₄ · 3K₂SO₄, S10=NaSO₄ · 10H₂O.

the system consists of four invariant points, nine univariant curves, and six crystallization fields: NaBr · 2H₂O, Na₂SO₄, Na₂SO₄ · 10H₂O, K₂SO₄ and KBr, and Na₂SO₄ · 3K₂SO₄ (Gla). A model, based on the Pitzer approach for quaternary system under study has been developed. The model, with binary and mixing interaction parameters taken from the literature and adapted to standard temperature, has been used to calculate the solubilities in the system NaBr–KBr–Na₂SO₄–K₂SO₄–H₂O at 298 K. The calculated values are basically in agreement with experiment data.

Acknowledgment

This project was supported by open the National Natural Science Foundation of China (Grant no. 41373062, U1407108), the Specialized Research Fund (20125122110015) for the Doctoral Program of Higher Education of China, scientific research and innovation team in Universities of Sichuan Provincial Department of Education (15TD0009) and the youth science and technology innovation team of Sichuan Province, China (2013TD0005).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.calphad.2016.06.005>.

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