Journal of chemical & engineering data

Article

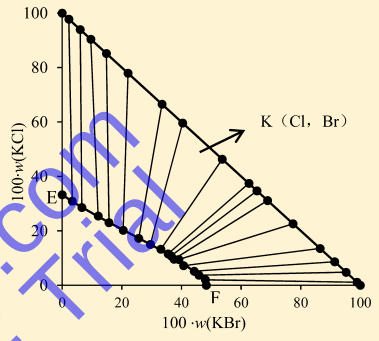
pubs.acs.org/jced

Solid–Liquid Equilibria in the Ternary System KCl–KBr–H_2O at 348 K

Yong-Xia Hu,[†,‡] Shi-Hua Sang,*[,†,‡] Rui-Zhi Cui,[†,‡] and Si-Yao Zhong[†,‡]

[†]College of Materials Chemistry & Chemical Engineering and [‡]Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu University of Technology, Chengdu 610059, Sichuan, P. R. China

ABSTRACT: Phase equilibria in the ternary system KCl–KBr–H_2O at 348 K were studied by the isothermal solution dissolution equilibrium method. The solubilities of salts and densities of saturated solutions in the ternary system were determined experimentally. The equilibrium solid phases were also determined by chemical analysis and X-ray powder diffraction. Using the experimental data, the phase diagram of the ternary system was obtained, which comprises one univariant curve and one stationary phase in the crystallization field of K(Cl,Br). The ternary system was a solid solution type. The density transformation rules were discussed simply, and the relationship equations of equilibrium liquid phase and the solid phase composition data were fitted with a cubic equation.



Equilibrium phase diagram of the ternary system KCl–KBr–H_2O at 348 K.

1. INTRODUCTION

There is mounting concern about high-salinity liquid mineral resources because of the gradual consumption of solid resources. In particular, China has very abundant liquid mineral resources, which are mainly concentrated in Qinghai, Tibet, Xinjiang, Inner Mongolia, and the Sichuan Basin. Especially, the brine resources in the west of Sichuan Basin of China are very rare liquid mineral resources in the world. The underground brine is mainly composed of Na^+, K^+, Cl^-, Br^-, SO_4^{2-}, $B_4O_7^{2-}$, H_2O, etc.[1] The potassium, boron, and bromine contents in the hydrochemistry of brines are far beyond the lower grades of the comprehensive industrial utilization. The highest content of potassium (K^+) in the brines is up to 53.27 g·L^{-1}, much higher than those in the Searles salt lake brine (USA) (23.1 g·L^{-1}), the Zabuye salt lake brine in Tibet, China (27.0 g·L^{-1}), and the Qarhan salt lake brine in Qinghai (12.1 g·L^{-1}).[2,3] These rare liquid mineral resources have very good exploitation prospects. Generally speaking, phase equilibria and phase diagrams are the theoretical basis of the exploitation and utilization of the underground brine resources. A number of experimental and theoretical studies have been carried out in recent decades on K-bearing phase equilibria such as in the ternary system K–Li–B_4O_7–H_2O at 288 K, K–SO_4–B_4O_7–H_2O at 348 K, the quaternary system Na–K–Ca–Cl–H_2O at 288.15 K,[4−6] the quinary system Na–K–Cl–SO_4–B_4O_7–H_2O at 298 K and 323 K, and Ca–Sr–K–Na–Cl–H_2O at 316 K to 412 K;[7−9] as well, the measurements and calculation of the solid–liquid equilibria of the quaternary system Na–K–Br–SO_4–H_2O at 323 K have also been studied by our group.[10]

Recently, study on phase equilibria with Br-bearing systems has been attracted more and more attention. Christov has made a series of research work in predicting the solubilities of bromides and solution behavior in solid–liquid equilibrium systems, and the thermodynamic modeling was made with Pitzer equations, having comparatively high calculating precision and good practicability.[11−16] In addition, the Br-bearing phase equilibria of some ternary, quaternary, and quinary subsystems of the underground brine in the Western Sichuan basin have been carried out in a systematic research program by our group: K–B_4O_7–Br–H_2O at 298 K,[17] K–Cl–Br–H_2O at 373 K,[18] Na–K–Br–SO_4–H_2O at 323 K,[10] Na–Cl–Br–SO_4–H_2O at 323 K and 348 K,[19,20] K–Cl–Br–SO_4–H_2O at 323 K, 348 K and 373 K,[21−23] Na–Cl–Br–B_4O_7–H_2O at 348 K, and K–Cl–Br–B_4O_7–H_2O at 373 K.[23,24] Furthermore, we will make further calculations on the basis of experiments in the near future. In terms of these Br-bearing systems, we have found that they can form solid solutions while containing Cl^- and Br^-.

The solid phases in salt-water systems are usually pure salts, complex salts, or salt hydrates, but solid solutions are rarely met.[25] Since chlorine and bromine have similar ion radii, their chemical properties as salts are closely related. When the coexistence of Cl^- and Br^- precipitates a concentrated salt solution, the bromine does not form an independent mineral, and most of it cannot remain in the mother liquor; only a small number replace the chlorine ion in the form of isomorphism, entering the lattice of salt and other chloride.[26] Data on structural arrangement, crystal imperfection, and thermodynamic stability of natural and synthesized crystals of variable compositions, obtained in complex experimental and theoretical researches, formed a solid basis for a fundamental theory, though interpretations of some phenomena still remain ambiguous. The equilibrium data of the KCl–KBr–H_2O system are numerous, as presented by the authors.[27−29] However, the solubility data involving solid solutions have not been reported very frequently especially at superoptimal temperatures. Hence, it is very necessary to conduct more in-depth study.

Received: October 24, 2013
Accepted: February 10, 2014
Published: February 20, 2014

   dx.doi.org/10.1021/je400931p | J. Chem. Eng. Data 2014, 59, 802–806

By now, a series of efforts describing solid solutions containing Cl^- and Br^- have been reported for such ternary systems as K−Cl−Br−H_2O at 298 K, 313 K, 323 K and 333 K and Na−Cl−Br−H_2O at 313 K and 333 K.[30−32] In early studies, corresponding solid phase composition data had been seldom reported; however, aiming at those solid solution phase systems, we concluded that there is a correlation between the solid solution composition and the liquid phase composition. For this reason, our research work focuses on the ternary system KCl−KBr−H_2O at 348 K, which is one subsystem of the underground brines. So far, the ternary system at 373 K has been reported by us,[18] but there is no research report about the phase equilibrium of the ternary subsystem at 348 K, which is just the object of this work. It is important to note that the relationship equation of equilibrium liquid phase and the solid phase composition data were presented by a cubic equation.

Consequently, the research work reported in this article includes three parts: (1) Measure the densities and solubilities in the equilibrium solution for the ternary system at 348 K. (2) Identify the equilibrium solid phases and give the experimental phase diagram of the ternary system. (3) Construct the relationship equation of equilibrium liquid phase and the solid phase composition data with a cubic equation.

2. EXPERIMENTS

2.1. Reagents and Instruments. Deionized water, with conductivity less than $1.2\cdot10^{-4}$ $S\cdot m^{-1}$ and pH = 6.6 at 298.15 K, was used to prepare synthesized brines and for chemical analysis. The reagents used were of analytical purity grade (Chengdu KeLong Chemical Reagent Factory, China): KCl (99.5 wt %), and KBr (≥ 99.0 wt %).

An SHA-GW type thermostatted vibrator (Jintan Guowang Instrument Factory) with a precision ± 0.1 K was used for the equilibrium measurements.

A standard analytical balance of 110 g capacity and 0.0001 g resolution (AL104, the Mettler Toledo Instruments Co., Ltd.) was used to determine the solution densities.

2.2. Experimental Methods. The solid−liquid equilibria in this work were studied by the method of isothermal solution saturation. The system points of the ternary system were prepared by adding the other salt component gradually on the basis of the binary invariant points at 348 K. Then the samples were poured into 50 mL of water in a sealed glass bottle and placed in the oil-bath vibrator (SHA-GW). The sealed glass bottles were kept in the vibrator, which was controlled at 348 ± 0.1 K. The solid−liquid systems in sealed tubes were stirred for over a week. The clarification of the solutions needs about 5 days. The solutions were taken out periodically for chemical analysis. When the composition of a solution does not change any more, the system should have reached the thermodynamic equilibrium state. After equilibrium, the pure solid phases were obtained by taking out the wet crystals from the sealed glass bottles, filtering the liquid phase, and washing the crystals first with an alcohol−water mixture and finally with pure alcohol, followed by air drying. The compositions of the solutions were determined by chemical analysis, and the solid phases were analyzed by X-ray diffraction (XRD; Siemens D500 X-ray diffractometer) and observed under SEM at 20.0 KV (SEM; Hitachi-S-3000N Japan) after drying. The densities of saturated solutions were measured using a density bottle with an uncertainty of 0.0002 $g\cdot cm^{-3}$.

2.3. Analytical Methods. The K^+ concentration was evaluated from an ion charge balance and assisted by sodium tetraphenylborate−hexadecyl trimethyl ammonium bromide titration (precision: ± 0.5 %). The concentration of Br^- was determined by iodometry with a sodium thiosulfate standard solution (uncertainty: ± 0.5 %). The total concentration of Cl^- and Br^- was determined by Mohr's method using a silver nitrate standard solution (uncertainty: ± 0.3 %). The concentration of Br^- was determined by iodometry with a sodium thiosulfate standard solution (uncertainty: ± 0.5 %). The concentration of Cl^- was determined from the total concentration of Cl^- and Br^- minus Br^- concentration.

3. RESULTS AND DISCUSSION

3.1. Results. The stable equilibrium experimental data of the solubilities, densities and equilibrium solids of the ternary system KCl−KBr−H_2O at 348 K are given in Table 1. The

Table 1. Experimental Composition of Salts and Densities of Solution in the Ternary System KCl−KBr−H_2O at 348 K[a]

	Composition of liquid phase		Composition of solid phase			
	$100\cdot w(B)^b$		$100\cdot w(B)^c$			Solution density ρ
no. (point)	KBr	KCl	KBr	KCl	equilibrium solid phases	($g\cdot cm^{-3}$)
1(E)	0.00	33.26	0.00	100	KCl	1.2498
2	3.38	30.90	2.23	97.77	K(Cl,Br)	1.2825
3	6.59	28.55	6.04	93.96	K(Cl,Br)	1.3224
4(C)	12.07	25.43	9.59	90.41	K(Cl,Br)	1.3365
5	15.71	23.01	14.81	85.19	K(Cl,Br)	1.3490
6	20.46	20.22	22.08	77.92	K(Cl,Br)	1.3739
7	25.65	17.22	33.49	66.51	K(Cl,Br)	1.4097
8	29.58	15.03	40.40	59.60	K(Cl,Br)	1.4343
9(G)	33.10	13.24	53.68	46.32	K(Cl,Br)	1.4472
10	35.51	11.53	62.64	37.46	K(Cl,Br)	1.4261
11	36.52	10.76	65.31	34.69	K(Cl,Br)	1.4299
12	37.47	9.57	68.87	31.13	K(Cl,Br)	1.4456
13	39.12	9.44	77.41	22.59	K(Cl,Br)	1.4425
14	40.69	7.18	86.49	13.51	K(Cl,Br)	1.4486
15(D)	44.27	5.15	91.38	8.62	K(Cl,Br)	1.4602
16	45.85	3.68	95.22	4.78	K(Cl,Br)	1.4682
17	48.04	1.99	98.91	1.09	K(Cl,Br)	1.4753
18(F)	48.35	0.00	100	0.00	KBr	1.4865

[a]Standard uncertainties: $u(T)$ = 0.1 K, $u(\rho)$ = 0.0002 $g\cdot cm^{-3}$, $u(w)$ = 0.005. [b]$w(B)$ is the mass fraction of liquid phase component. [c]$w(B)$ is the mass fraction of solid phase component.

concentrations of all components (salts and water) in solutions are expressed in mass fractions [$w(B)$, where B is a component, i.e., salt or water]. The solution density (ρ) is given in $g\cdot cm^{-3}$. The isothermal solubility diagram is given in Figure 1 and the density−composition diagram of the ternary system KCl−KBr−H_2O at 348 K is given in Figure 2. The X-ray diffraction photograph of point G [w(KCl) = 0.4632, w(KBr) = 0.5368] of this system is presented in Figure 3, which indicate that the ternary system KCl−KBr−H_2O at 348 K has no complex salt, but contains the solid solution, that is, K(Cl,Br).

Figure 1 shows that the ternary system has one crystallization region [solid solution K(Cl,Br)], one univariant curve (EF), but no invariant point. Points E and F are the invariant points of the binary subsystems KCl−H_2O and KBr−H_2O at 348 K, respectively. At point E [w(KCl) = 0.3326], the solution is saturated with KCl. At point F [w(KBr) = 0.4835], the solution is saturated with KBr.

dx.doi.org/10.1021/je400931p | J. Chem. Eng. Data 2014, 59, 802−806

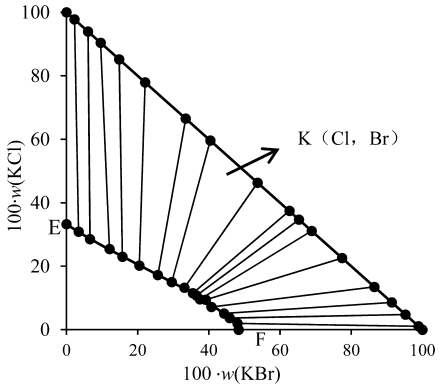


Figure 1. Equilibrium phase diagram of the ternary system KCl−KBr−H_2O at 348 K.

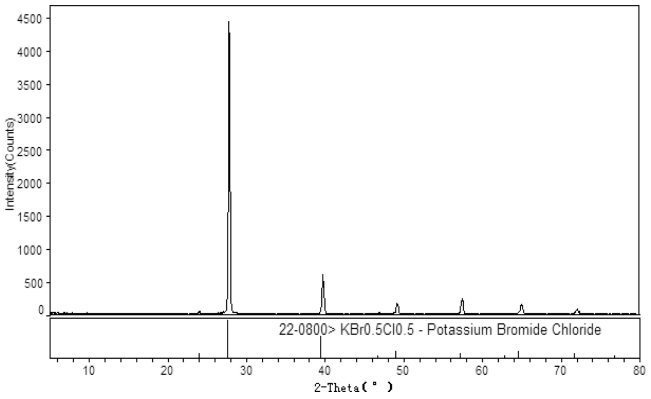


Figure 3. X-ray diffraction photograph of a data point G of the ternary system KCl−KBr−H_2O at 348 K [solid solution, K(Cl,Br)].

According to Figure 2, it can be stated that the solution density changes monotonically with w(KBr), or the Br concentration. In addition, the presence of KBr in the solid phase decreases the chemical potential of KCl in the solid phase, and this must also decrease the solubility of KCl in the aqueous solution liquid phase. Figures 4 and 5 are scanning electron microscopy (SEM) images that show a close-up view at point C and point D of the solid solution after drying in the air. The experimental results indicate that the solid solutions [K(Cl,Br)] are dense and well crystallized, and close to different cuboctahedral geometry shapes.

Compared with previous studies on the ternary systems K−Cl−Br−H_2O at 298 K, 313 K, 323 K, and 333 K,[30,31] the solid−liquid equilibria of KCl−KBr−H_2O at 348 K is a similar type of solid solution, where the crystallization region area is a solid solution K(Cl,Br). Otherwise, the crystallization region gradually reduced with the increasing temperature, which may probably be caused by the changing solubilities of KCl and KBr associated with rising temperature.

3.2. Discussion. The solid phase compositions of the ternary system KCl−KBr−H_2O at 348 K are in the crystallization field of K(Cl,Br). On the basis of the equilibrium data presented in Table 1, the isotherm of solubility and the dependence of the equilibrium solid phase compositions have been described by mathematic equations. Available mathematical software is used to describe the data and determine a regression model among the parameters.

The equation of solubility isotherm:

$$x_1 = 50.20 - 1.22x_2 - 0.01(x_2)^2 \quad (R^2 = 0.9970) \qquad (1)$$

where x_1 is the KBr mass percentage of the solution, x_2 is the KCl mass percentage of the solution, and R^2 is the coefficient of determination.

Equation 2 is applied to describe the relationship equation of the equilibrium liquid phase and the solid phase composition.

$$y = a_0 + a_1x_1 + a_2x_2 + a_3(x_1)^2 + a_4(x_2)^2 + a_5(x_1)^3 + a_6(x_2)^3 \qquad (2)$$

where, y is the KBr mass percentage of the solid phase and a_0, a_1, etc. are regression coefficients. The main concern in this work was with the effects of the KBr (x_1) and KCl (x_2) mass percentage of the liquid phase on the KBr mass percentage of the solid phase. This resulted in a final equation of the form

$$y = 261.4474 - 12.7323x_1 + 1.8700x_2 + 0.2627(x_1)^2 - 0.2599(x_2)^2 - 0.0014(x_1)^3 + 0.0010(x_2)^3 \quad (R^2 = 0.9969) \qquad (3)$$

The regression eq 3, expressing the relationship equation of equilibrium liquid phase and the solid phase composition data, together with the coefficient of determination (R^2) is 0.9969. And the experimental composition of the solid phase and the calculated composition of solid phase are summarized in Table 2. The maximum relative deviation is 4.12 %, and as well, the average relative deviation is 1.43 % in the ternary system KCl−KBr−H_2O at 348 K, indicating that calculated results from the regression of eq 3 are reliable.

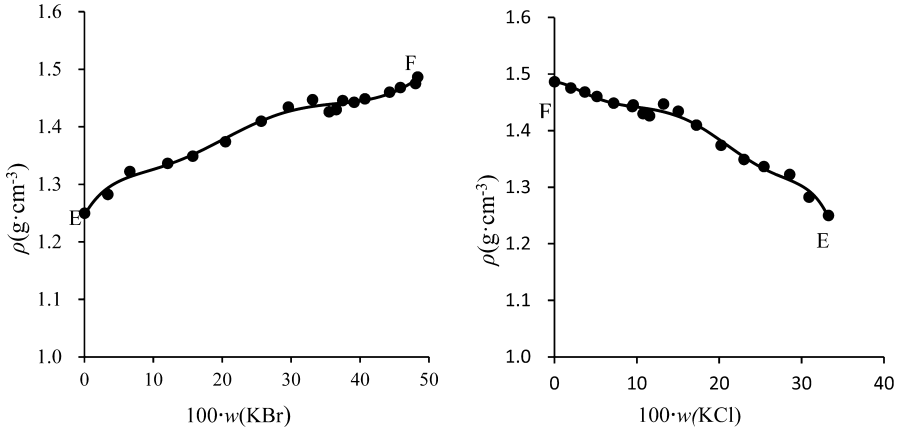


Figure 2. Density−composition diagram of the ternary system KCl−KBr−H_2O at 348 K.

dx.doi.org/10.1021/je400931p | J. Chem. Eng. Data 2014, 59, 802−806

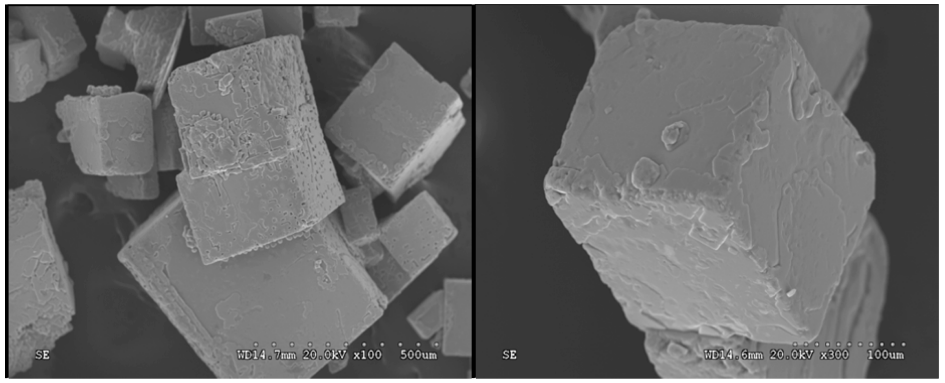


Figure 4. Scanning electron microscopic view of the solid solution particles at point C after drying [solid solution, K(Cl,Br)].

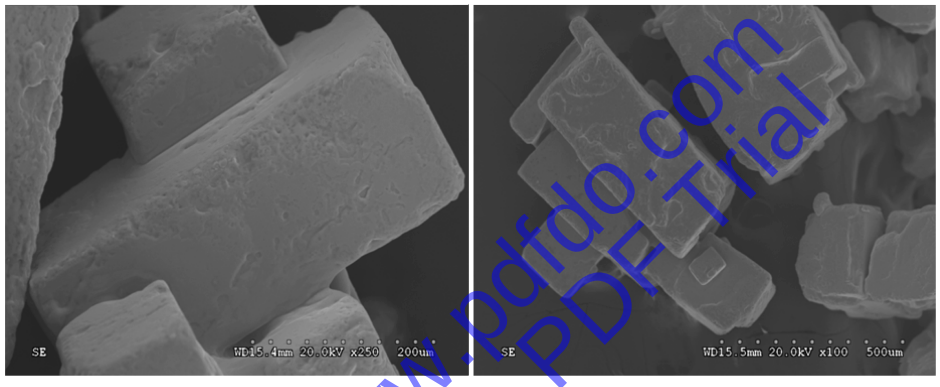


Figure 5. Scanning electron microscopic view of the solid solution particles at point D after drying. [solid solution, K(Cl,Br)].

Table 2. Experimental Composition of Solid Phase and Calculated Composition of Solid Phase in the Ternary System KCl−KBr−H_2O at 348 K[a]

	experimental composition of solid phase		calculated composition of solid phase			
	100·w(B)[b]		100·w(B)[c]			relative deviation
no.(point)	KBr (y_0)	KCl	KBr (y)	KCl	equilibrium solid phases	$\lvert y_0 - y \rvert$
1(E)	0.00	100	0.03	99.97	KCl	0.03
2	2.23	97.77	2.04	97.96	K(Cl,Br)	0.19
3	6.04	93.96	7.29	92.71	K(Cl,Br)	1.25
4(C)	9.59	90.41	6.99	93.01	K(Cl,Br)	2.60
5	14.81	85.19	14.23	85.77	K(Cl,Br)	0.58
6	22.08	77.92	22.24	77.76	K(Cl,Br)	0.16
7	33.49	66.51	33.88	66.12	K(Cl,Br)	0.39
8	40.40	59.60	44.05	55.95	K(Cl,Br)	3.65
9 (G)	53.68	46.32	53.28	46.72	K(Cl,Br)	0.40
10	62.64	37.46	62.53	37.47	K(Cl,Br)	0.11
11	65.31	34.69	66.52	33.48	K(Cl,Br)	1.21
12	68.87	31.13	71.78	28.22	K(Cl,Br)	2.91
13	77.41	22.59	74.10	25.9	K(Cl,Br)	3.31
14	86.49	13.51	82.37	17.63	K(Cl,Br)	4.12
15(D)	91.38	8.62	92.11	7.89	K(Cl,Br)	0.73
16	95.22	4.78	96.43	3.57	K(Cl,Br)	1.21
17	98.91	1.09	101.38	−1.38	K(Cl,Br)	2.47
18(F)	100	0.00	99.54	0.46	KBr	0.46

[a]Standard uncertainties: $u(T)$ = 0.1 K, $u(\rho)$ = 0.0002 g·cm^{-3}, $u(w)$ = 0.005. [b]w(B) is the mass fraction of solid phase component. [c]w(B) is the mass fraction of calculated solid phase component by eq 3.

4. CONCLUSIONS

The solid−liquid equilibria of the ternary KCl−KBr−H_2O system at 348 K were studied by the isothermal solution saturation method. Solubilities, densities, and corresponding equilibrium solids were determined. The results show that the ternary system contains solid solution K(Cl,Br). The ternary diagram has no invariant point, one univariant curve, and one crystallization region. The experimental results show that KBr

dx.doi.org/10.1021/je400931p | J. Chem. Eng. Data 2014, 59, 802−806

has obvious common-ion effects on KCl, and can obviously increase the solution density.

AUTHOR INFORMATION

Corresponding Author

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

Funding

This work was supported by the National Natural Science Foundation of China (41373062, 40973047) and the Specialized Research Fund (20125122110015) for the Doctoral Program of Higher Education of China.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Lin, Y. T. Study on sustainable development of potassium boron iodine and bromine in brine of sichuan basin. *J. Salt Lake Res.* **2001**, *9* (2), 56−60 in Chinese.

(2) Lin, Y. T.; Cao, S. X. Rare gasfield brines rich in potassium and boron was found in the West of Sichuan Basin. *Chin. Geol.* **2001**, *28* (7), 45−47 in Chinese.

(3) Lin, Y. T. Geochemical characteristics and exploitation assessment of the underground water of a gas field in Western Sichuan. *Nat. Gas Ind.* **2000**, *20* (5), 9−14 in Chinese.

(4) Sang, S. H.; Yin, H. A.; Tang, M. L. Solubility investigations in the systems $K_2B_4O_7 + Li_2B_4O_7 + H_2O$ and $Na_2B_4O_7 + Li_2B_4O_7 + H_2O$ at T = 288 K. *J. Chem. Eng. Data* **2004**, *49*, 1586−1589.

(5) Cui, R. Z.; Sang, S. H.; Zhang, K. J.; Li, T. Phase equilibria in the ternary systems K_2SO_4−$K_2B_4O_7$−H_2O and Na_2SO_4−$Na_2B_4O_7$−H_2O at 348 K. *J. Chem. Eng. Data* **2012**, *57*, 3498−3501.

(6) Deng, T. L.; Li, D. C. Solid-liquid metastable equilibria in the quaternary system (NaCl−KCl−$CaCl_2$−H_2O) at 288.15 K. *Fluid Phase Equilib.* **2008**, *269*, 98−103.

(7) Sang, S. H.; Zhang, X.; Zeng, X. X.; Wang, D. Solid−liquid equilibria in the quinary Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$−H_2O system at 298 K. *Chin. J. Chem.* **2011**, *29*, 1285−1289.

(8) Sang, S. H.; Zhang, X.; Zhang, J. J. Solid−liquid equilibria in the quinary Na^+, K^+//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$−H_2O system at 323 K. *J. Chem. Eng. Data* **2012**, *57*, 907−910.

(9) Assarsson, G. O.; Balder, A. Equilibria in the aqueous systems containing Ca^{2+}, Sr^{2+}, K^+, Na^+ and Cl^- between 18 and 114°. *J. Phys. Chem.* **1954**, *58* (3), 253−255.

(10) Zeng, X. X.; Sang, S. H.; Wang, D.; Zhang, J. J. Theoretical calculation of phase equilibria in the reciprocal quaternary system Na^+, K^+//Br^-, SO_4^{2-}−H_2O at 323 K. *Chem. Eng.* **2012**, *40* (5), 32−35 in Chinese.

(11) Christov, C. An isopiestic study of aqueous NaBr and KBr at 50°C: Chemical equilibrium model of solution behavior and solubility in the NaBr-H_2O, KBr−H_2O and Na−K−Br−H_2O systems to high concentration and temperature. *Geochim. Cosmochim. Acta* **2007**, *71*, 3557−3569.

(12) Christov, C. Temperature variable chemical model of bromide−sulfate solution interaction parameters and solid−liquid equilibria in the Na−K−Ca−Br−SO_4−H_2O system. *CALPHAD* **2012**, *36*, 71−81.

(13) Christov, C. Isopiestic investigation of the osmotic coefficients of $MgBr_2$(aq) and study of bromide salts solubility in the (m_1KBr + m_2MgBr_2)(aq) system at T = 323.15 K. Thermodynamic model of solution behaviour and (solid + liquid) equilibria in the $MgBr_2$(aq), and (m_1KBr + m_2MgBr_2)(aq) systems to high concentration and temperature. *J. Chem. Thermodyn.* **2011**, *43*, 344−353.

(14) Christov, C. Study of bromide salts solubility in the (m_1KBr + m_2CaBr_2)(aq) system at T = 323.15 K. Thermodynamic model of solution behaviour and (solid + liquid) equilibria in the ternaries (m_1KBr + m_2CaBr_2)(aq), and (m_1MgBr_2 + m_2CaBr_2)(aq), and in the quinary (Na + K + Mg + Ca + Br + H_2O) systems to high concentration and temperature. *J. Chem. Thermodyn.* **2012**, *55*, 7−22.

(15) Christov, C. Isopiestic investigation of the osmotic coefficients of aqueous $CaBr_2$ and study of bromide salt solubility in the NaBr−$CaBr_2$−H_2O system at 50 °C: Thermodynamic model of solution behavior and solid−liquid equilibria in the $CaBr_2$−H_2O, and NaBr−$CaBr_2$−H_2O systems to high concentration and temperature. *CALPHAD* **2011**, *35*, 42−53.

(16) Christov, C. Study of bromide salts solubility in the (m_1NaBr + m_2MgBr_2)(aq) system at T = 323.15 K, thermodynamic model of solution behavior and solid−liquid equilibria in the (Na + K + Mg + Br + H_2O) system to high concentration and temperature. *J. Chem. Thermodyn.* **2012**, *47*, 335−340.

(17) Sang, S. H.; Yin, H. A.; Ni, S. J.; Zhang, C. J. A study on the equilibrium solubilities of salts and properties of solutions in the ternary system $K_2B_4O_7$−KBr−H_2O at 298 K. *J. Chengdu Univ. Technol.* **2006**, *33*, 414−416 in Chinese.

(18) Hu, Y. X.; Sang, S. H.; Cui, R. Z.; Zhong, S. Y. Phase equilibria in the ternary system KBr−KCl−H_2O at 373 K. *China Sciencepap.* **2013**, *8* (9), 847−851 in Chinese.

(19) Sang, S. H.; Cui, R. Z.; Hu, J. W.; Wang, D. Measurements of the solid−liquid equilibria in the quaternary system NaCl−NaBr−Na_2SO_4−H_2O at 323 K. *J. Solution Chem.* **2013**, *42*, 1633−1640.

(20) Zhang, Y. G.; Sang, S. H.; Zhang, K. J.; Hu, F. M.; Cui, R. Z. Equilibria in the quaternary system NaCl−NaBr−Na_2SO_4−H_2O at 348 K. *J. Salt Chem. Ind.* **2013**, *42* (2), 12−15 in Chinese.

(21) Wang, D.; Sang, S. H.; Zeng, X. X.; Ning, H. Y. The phase equilibria of quaternary system KCl−KBr−K_2SO_4−H_2O at 323 K. *Petrochem. Technol.* **2011**, *40* (3), 285−288 in Chinese.

(22) Zhang, K. J.; Sang, S. H.; Li, T.; Cui, R. Z. Liquid−solid equilibria in the quaternary system KCl−KBr−K_2SO_4−H_2O at 348 K. *J. Chem. Eng. Data* **2013**, *58* (1), 115−117.

(23) Cui, R. Z.; Sang, S. H; Hu, Y. X. Solid−liquid equilibria in the quaternary systems KCl−KBr−$K_2B_4O_7$−H_2O and KCl−KBr−K_2SO_4−H_2O at 373 K. *J. Chem. Eng. Data* **2013**, *58* (2), 477−481.

(24) Li, T.; Sang, S. H; Cui, R. Z.; Zhang, K. J. Phase equilibria of quaternary system NaCl−NaBr−$Na_2B_4O_7$−H_2O at 348 K. *Chem. Res. Chin. Univ.* **2013**, *29* (2), 311−313.

(25) Niu, Z. D.; Cheng, F. Q. *The Phase Diagrams of Salt-Water Systems and Their Applications*; University Press: Tianjin , China, 2002 (in Chinese).

(26) Voloshin, A. E.; Kovalev, S. I.; Rudneva, E. B.; Glikin, A. E. Phenomena and mechanisms of mixed crystal formation in solutions II. Mechanism of interface processes. *J. Cryst. Growth* **2004**, *261*, 105−117.

(27) Dejewska, B. The characteristics of the mixed crystals of the KCl−KBr−H_2O system at 298 K. *Cryst. Res. Technol.* **1999**, *34* (8), 975−979.

(28) Durham, G. S.; Rock, E. J.; Frayn, S. F. Solid solutions of the alkali halides. 1. The systems KBr−KCl−H_2O, RbBr−RbCl−H_2O, RbBr−KBr−H_2O at 25 °C. *J. Am. Chem. Soc.* **1953**, *75*, 5793−5794.

(29) Putnis, C. V.; Mezger, K. A mechanism of mineral replacement: Isotope tracing in the model system KBr−KCl−H_2O. *Geochim. Cosmochim. Acta* **2004**, *68* (13), 2839−2848.

(30) Weng, Y. B.; Wang, Y. F.; Wang, J. K.; Yin, Q. X. Phase diagram of the ternary system K^+, Cl^-, Br^--H_2O at 298 K, 313 K and 333 K. *J. Chem. Eng. Chin. Univ.* **2007**, *21* (4), 695−698 in Chinese.

(31) Zhang, K. J.; Sang, S. H.; Wang, D.; Zhang, J. J. Study on the phase equilibria in the ternary system KCl−KBr−H_2O at 323 K. *J. Salt Chem. Ind.* **2011**, *35* (6), 5−7 in Chinese.

(32) Weng, Y. B.; Wang, J. K.; Yin, Q. X.; Wang, Y. F. Solid−liquid equilibria in the ternary system NaCl−NaBr−H_2O. *Petrochem. Technol.* **2007**, *36* (4), 358−361 in Chinese.

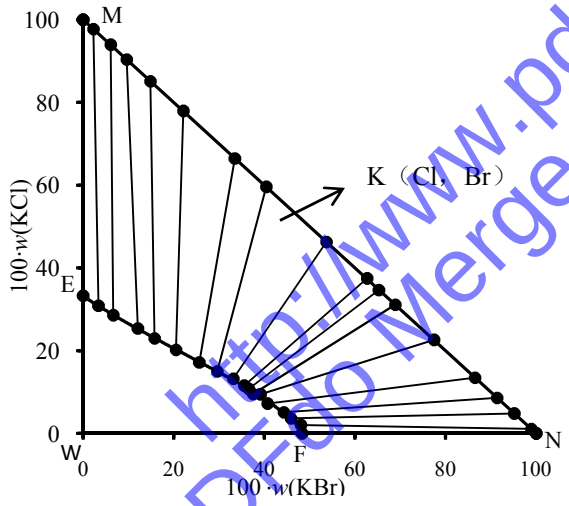
三元体系KCl-KBr－H20在 348K时固液相平衡研究

胡咏霞 [a,b]，桑世华*[a,b]，崔瑞芝 [a,b]，钟丝摇 [a,b]

([a]成都理工大学材料与化学化工学院，四川成都 610059)

([b]矿产资源化学四川省高校重点实验室，四川成都 610059)

摘要：采用等温溶解平衡法研究了三元体系KBr–KCl–H_2O在348K时的相平衡关系，测定了相应温度条件下饱和溶液的溶解度及密度，通过化学分析和X-射线粉晶衍射的方法确定了相应的平衡固相；根据溶解度数据绘制了相应的三元体系平衡相图，研究发现，三元体系KBr–KCl–H_2O在348 K下的等温溶解度图有一条单边度曲线和一个固相结晶区K(Cl,Br)，该三元体系相平衡关系为固溶体类型，讨论了该三元体系平衡溶液密度的变化规律， 建立了固溶体平衡固相组成和液相组成对应的方程。



三元体系 KCl-KBr－H20 在 348K 时相图