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Measurements and calculations of solid–liquid equilibria in the quaternary system $NaBr–KBr–CaBr_2–H_2O$ at 298 K

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ABSTRACT

The solubilities and densities of the quaternary system $NaBr–KBr–CaBr_2–H_2O$ were investigated by the method of isothermal solution saturation at 298 K. On the basis of the experimental data, the phase diagram, water content diagram and the density-composition diagram were plotted, respectively. In the phase diagram of quaternary system $NaBr–KBr–CaBr_2–H_2O$ at 298 K, no complex salt or solid solution was found. There are two invariant points, five univariant curves, and four crystallization fields corresponding to NaBr, $NaBr\cdot 2H_2O$, KBr and $CaBr_2\cdot 6H_2O$. Pitzer's equations based model has been applied to calculate bromide minerals solubilities in the quaternary system $NaBr–KBr–CaBr_2–H_2O$ at 298 K. All binary and mixing ion interaction parameters and solubility products of bromide solids are taken from previously published T-variation model for the system under study, adapted to 298 K. The predicted and experimental solubilities are in a very good agreement up to a very high total concentration of the quaternary system.

1. Introduction

The underground brines in Sichuan Basin (China) are very rare liquid mineral resources in the world. The brine resources are very huge. The contents of these useful mineral components in the brines reach or exceed their corresponding industrial grades, and so many inorganic chemical products can be directly obtained by separating the brines. As the world's largest agriculture country, potassium is always one of the most shortage mineral resources in China. The average content of potassium in the brines is 18.86 g L^{-1}. The highest content of potassium (K^+) is as high as 53.27 g L^{-1}, much higher than those in the Qarhan salt lake brine in Qinghai, China (12.1 g L^{-1}), the Zabuye salt lake brine in Tibet, China (27.0 g L^{-1}), and the Searls salt lake brine (USA) (23.1 g L^{-1}) [1,2]. Bromine is a kind of basic material of chemical industry in the national economy development. In the field of industry, agriculture and military, it is an urgently needed material in the world. At present, the bromine is no independent ore in nature. The underground brine is the important source of bromine. In particular, the bromine content is up to 2533 mg L^{-1} in Sichuan Basin [3]. In addition to high concentrations of potassium and bromine, the brine has calcium, strontium, magnesium, lithium, and many other useful components. These rare liquid mineral resources will have great social and economic value and very good exploitation prospect.

Multi-temperature phase diagrams play an important role for the comprehensive exploitation and utilization of liquid mineral resources. It is very necessary and urgent to obtain the phase equilibria and phase diagrams at different temperatures. By now, our group has carried out a series of research on the phase equilibria of underground brines in Sichuan Basin, such as the ternary system $KBr–K_2B_4O_7–H_2O$ 298 K, 323 K, 348 K, and 373 K [4–7], quaternary system $KCl–KBr–K_2SO_4–H_2O$ at 323 K, 348 K, and 373 K [8–10], and quinary system $Na–K–Cl–SO_4–B_4O_7–H_2O$ at 298 K and 323 K [11,12]. The measurements and calculations of solid–liquid equilibria in the quaternary systems $KCl–K_2SO_4–K_2B_4O_7–H_2O$ at 298 K [13,14] and $NaBr–KBr–Na_2SO_4–K_2SO_4–H_2O$ at 323 K [15,16] has also been done.

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. developed a chemical equilibrium model in the prediction for the $Na–K–Mg–Ca–H–Cl–SO_4–OH–HCO_3–CO_3–CO_2–H_2O$ system at 25 °C [17–19]. Moller [20] and Greenberg and Moller [21] developed a T-variation thermodynamic model for solution behavior and solid–liquid equilibria in $Na–K–Ca–Cl–SO_4–H_2O$ system. Christov and Moller [22,23] extend with concentration $CaCl_2–H_2O$ model of Moller [20] up to saturation and added acid-base ($H–HSO_4–OH$) reactions and solids to the model described Greenberg and Moller. Spencer, Moller and

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Weare predicted mineral solubilities in natural waters Na–K–Ca–Mg–Cl–H_2O system at temperatures below 25 °C [24]; on this basis Marion and Farren investigated the Spencer–Moller–Weare model to predict this system again and improved its accuracy [25]. For the bromide-bearing brine system, Christov [26], Rard and Archer [27] developed an model for NaBr–H_2O system; Balarew et al. [28] developed an model for KBr–H_2O system; Christov [29] developed an model for $CaBr_2$–H_2O system; and Christov summarized for all solid–liquid equilibria bromide models at 298 K [30]. These studies would provide available Pitzer-based solid–liquid equilibrium models for binary bromide systems at 298 K. In recent years, Christov have made a series of research work for bromide-rich brine system Na–K–Mg–Ca–Br–SO_4–H_2O [31–36]. A T-variable ion-interaction model for this system has been developed. The model was based on his own osmotic coefficient data of binary bromide systems from isopiestic experiments, and solubility data of ternary systems, as well as activity and solubility data in the literature.

According to the compositions in brines, the underground gasfield brines in Sichuan Basin can be considered as Na–K–Ca–Mg–Sr–Li–Cl–Br–SO_4–B_4O_7–I–H_2O system. The quaternary system NaBr–KBr–$CaBr_2$–H_2O is one of its subsystems. There is no experimental and modeling study on the solid–liquid equilibria in the quaternary system at 298 K, which is the objective of this work. In this paper, the research work includes four parts: (1) measure the solubilities and densities in the equilibrium solution for the quaternary system NaBr–KBr–$CaBr_2$–H_2O at 298 K. (2) Identify the equilibrium solid phases and give the experimental phase diagram of the quaternary system. (3) Calculate solubilities in quaternary system NaBr–KBr–$CaBr_2$–H_2O at 298 K by using Pitzer's equations and (4) compare calculated solubilities with experimental data.

Table 2
Pitzer pure electrolyte parameters in the quaternary system NaBr–KBr–$CaBr_2$–H_2O at 298 K.

Salt	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Reference source
NaBr	0.1209144	0.0614751	−0.00282	[31]
KBr	0.0518449	0.2767664	−0.000868	[31]
$CaBr_2$	0.3357135	2.9061559	0.0089749	[32]

2. Experimental

2.1. Reagents and instruments

Distilled water with an electrical conductivity less than 1.2×10^{-4} S m^{-1} and pH=6.6 was used to produce the experimental solutions. All chemicals used in this work were of analytical grade. There were NaBr (≥99.0 wt%), KBr (≥99.0 wt%) (Chengdu Kelong Chemical Reagent Manufactory, China.) and $CaBr_2 \cdot 2H_2O$ (≥98.0 wt%) (Tianjin Guangfu Fine Chemical Research Institute, China).

Table 1
Solubilities and densities of solution in the quaternary system NaBr–KBr–$CaBr_2$–H_2O at 298 K.

No.	Composition of liquid phase $100 \cdot w$(B)			Jänecke index J/(g/100 g) J(NaBr)+J(KBr)+J($CaBr_2$)=100 g				Equilibrium solids	Solution density ρ/g cm^{-3}
	w(NaBr)	w(KBr)	w($CaBr_2$)	J(NaBr)	J(KBr)	J($CaBr_2$)	J(H_2O)		
1, A	43.06	7.23	0.00	85.62	14.38	0.00	98.86	NB2+KB	1.6177
2	40.04	6.91	4.12	78.40	13.53	8.07	95.82	NB2+KB	1.6187
3	36.81	6.54	8.29	71.28	12.66	16.06	93.67	NB2+KB	1.6236
4	33.07	5.88	13.14	63.48	11.28	25.23	91.96	NB2+KB	1.6337
5	23.16	4.65	25.53	43.42	8.71	47.86	87.46	NB2+KB	1.6369
6	14.66	3.56	36.11	26.99	6.55	66.47	84.07	NB2+KB	1.6806
7	5.85	2.77	49.94	10.00	4.73	85.27	70.76	NB+KB	1.8107
8, E	0.74	1.50	57.76	1.23	2.50	96.27	66.68	NB+KB+CB6	1.8593
9, B	0.00	1.33	58.24	0.00	2.23	97.77	67.89	CB6+KB	1.8473
10	0.06	1.37	58.20	0.10	2.30	97.60	67.68	CB6+KB	1.8457
11	0.07	1.45	57.86	0.12	2.44	97.44	68.41	CB6+KB	1.8503
12	0.14	1.49	57.74	0.24	2.51	97.25	68.42	CB6+KB	1.8475
13	0.16	1.50	57.80	0.27	2.52	97.22	68.21	CB6+KB	1.8411
14	0.21	1.42	57.59	0.36	2.40	97.24	68.85	CB6+KB	1.8476
15	0.34	1.45	57.65	0.57	2.44	96.99	68.25	CB6+KB	1.8452
16	0.67	1.47	57.63	1.12	2.46	96.41	67.30	CB6+KB	1.8544
17, D	10.32	0.00	42.28	19.61	0.00	80.39	90.13	NB+NB2	1.6602
18	10.32	0.51	41.98	19.55	0.96	79.49	89.34	NB+NB2	1.6898
19	10.26	0.85	41.62	19.46	1.61	78.92	89.65	NB+NB2	1.6713
20	10.22	1.17	41.18	19.45	2.22	78.33	90.20	NB+NB2	1.6501
21	10.50	1.38	41.82	19.55	2.56	77.88	86.26	NB+NB2	1.7011
22	10.44	1.95	41.68	19.30	3.61	77.09	84.96	NB+NB2	1.6650
23	10.68	2.54	41.75	19.44	4.61	75.95	81.92	NB+NB2	1.6750
24, F	10.45	3.05	40.61	19.31	5.64	75.05	84.78	NB+NB2+KB	1.7181
25, C	0.84	0.00	58.97	1.41	0.00	98.59	67.18	NB+CB6	1.7900
26	0.81	0.56	58.26	1.36	0.93	97.70	67.70	NB+CB6	1.8079
27	0.80	0.64	58.17	1.34	1.07	97.59	67.76	NB+CB6	1.8065
28	0.77	0.95	57.81	1.29	1.60	97.11	67.97	NB+CB6	1.8075
29	0.79	1.38	57.51	1.32	2.30	96.37	67.57	NB+CB6	1.8149
30	0.65	1.52	57.54	1.10	2.54	96.36	67.48	NB+CB6	1.8147
31	0.75	1.47	57.41	1.26	2.46	96.28	67.70	NB+CB6	1.8239
32	0.73	1.55	57.05	1.23	2.62	96.16	68.55	NB+CB6	1.8390

w(B) is the mass fraction of component B.
Uncertainties: T, ±0.1 K; w(NaBr): ±0.5%; w(KBr): ±0.5%; w($CaBr_2$): ±0.3%.
Abbreviations: NB=NaBr, NB2=$NaBr \cdot 2H_2O$, KB=KBr, CB6=$CaBr_2 \cdot 6H_2O$.