Solid−Liquid Phase Equilibrium in the Quaternary System KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O at 298.15 K

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Abstract—Solubilities, densities and refractive indices for the quaternary system KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O at 298.15 K were determined using the isothermal dissolution equilibrium method. According to the experimental data, the diagrams of solubilities, densities, and refractive indices were plotted, respectively. The phase diagram consist of one invariant point, three isothermal dissolution curves, and three crystallization regions corresponding to potassium chloride (KCl), potassium metaborate hydrate (KBO$_2$·1.33H$_2$O), and potassium sulfate (K$_2$SO$_4$), respectively. The size of crystallization areas of salt is in the order K$_2$SO$_4$ > KCl > KBO$_2$·1.33H$_2$O, which indicates K$_2$SO$_4$ could be more easily separated from the system. The diagrams of solution density and refractive index changed regularly with changing concentration of KCl at 298.15 K.

INTRODUCTION

Potassium and boron are important chemical raw materials, as they are widely used in fertilizer, pigment, pharmaceutical, paper, detergent, glass, and ceramics industries [1]. As the available amounts of solid ores are decreasing, the development of liquid potassium and boron mineral resources has become an inevitable tendency in future. Liquid potassium and boron mineral resources are mainly distributed in salt lake brine, seawater, geothermal water, and oil-field water. There are abundant salt lake brine resources in the Qaidam Basin, China with high contents of lithium, potassium, boron, the valuable brine mostly belong to the MgSO$_4$ subtype brine as a seven-component system (Li$^+$ + Na$^+$ + K$^+$ + Mg^{2+} + Cl$^-$ + SO$_4^{2-}$ + borate + H$_2$O), which is of great exploitation potential and strategic importance [2, 3].

It is well-known that phase diagrams and phase equilibria play an important role in guiding the comprehensive utilization of the valuable brine. To take full advantage of the brine resources, the phase equilibria of some subsystems containing potassium borate have been researched, such as (KBO$_2$ + H$_2$O) [4], (KBO$_2$ + KOH + H$_2$O) [4, 5], (LiBO$_2$ + NaBO$_2$/KBO$_2$ + H$_2$O) [6], (KCl/K$_2$SO$_4$ + KB$_5$O$_8$ + H$_2$O) [7], (LiB$_5$O$_8$/NaB$_5$O$_8$ + KB$_5$O$_8$ + H$_2$O) [8], (K$_2$O + CaO + B$_2$O$_3$ + H$_2$O) [9]. Although the phase equilibrium and phase diagrams of potassium borate-containing systems over a wide temperature range have been previously reported, research has mainly focused on ternary systems, the solubility data of more complex systems is seriously insufficient. The quarternary system (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) is actually part of (K$_2$O + B$_2$O$_3$ + K$_2$SO$_4$ + KCl + H$_2$O) with fixed K$_2$O/B$_2$O$_3$ ratio, which has significant value for separating and purifying potassium and boron salts from the brines. In this paper, the solubilities, densities, and refractive indices of the quaternary systerm (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) at 298.15 K are presented.

EXPERIMENTAL

Apparatus and Reagents

A thermostat with magnetic stirring (XHC-500-6, Beijing Fortunejoy Sci. Technol. Co. Ltd.) was used to maintain the temperature with a precision of 0.01 K in the equilibrium experiments. The refractive index (n_D) was measured using an Abbe refractometer (Abbemat 550, Anton Paar Co. Ltd., Austria) with an uncertainty within ±0.0001. Density (ρ) was determined using Anton Paar Digital vibrating-tube densimeter (DMA 4500, Anton Paar Co. Ltd., Austria) with an uncertainty of less than ±0.15 mg cm^{-3}.

The reagents used in this study were of analytical grade and obtained from the Sinopharm Chemical Reagent Co. Ltd.: KCl (mass fraction >99.0) and K_2SO_4 (mass fraction >99.0). The potassium metaborate were synthesized in the lab [10], and the purity is 99.0 in mass fraction. Doubly deionized water (DDW, $k < 1 \times 10^{-4}$ S m^{-1}, pH 6.60) were employed to prepare the series of samples and for chemical analysis.

Method

The isothermal dissolution equilibrium method was adopted in this work [11, 12]. On the basis of the phase equilibrium composition, salts and water of appropriate quantity were mixed together and loaded into a series of equilibrium bottles, and then placed in the magnetic stirring thermostatic bath and the temperature was set at set at 298.15 ± 0.1 K with 150 rpm to accelerate the achievement of equilibrium. At intervals, a 5.0 mL sample of the clarified solution was taken out for chemical analysis. When the difference between the concentrations of the two samples taken from the same sample was within ±0.3% in mass fraction, it indicated that the equilibrium had been achieved. Generally, it took approximately 14 days to reach the equilibrium state for the two systems. Then, liquid supernatant was taken out for quantitative chemical analysis, and the solid phases were also sampled and identified by X-ray diffractometry.

The BO_2^- ion concentration was measured in triplicate by alkali titration method with sodium hydroxide standard solution in the presence of mannitol and double indicator of methyl red and phenolphthalein and the relative standard uncertainty of the analytical results is no more than ±0.003. The Cl$^-$ ion was determined by volumetric titration with AgNO$_3$ standard solution in the presence of potassium chromate as indicator with relative standard uncertainty of no more than ±0.003. The K$^+$ ion concentration was determined in triplicate by the gravimetric method with sodium tetraphenylborate. The SO_4^{2-} ion was determined via gravimetric method with barium chloride; the relative standard uncertainty for the analytical results in triplicate was within ±0.005 in mass fraction [13].

RESULTS AND DISCUSSION

Phase Equilibrium of Quaternary System at 298.15 K

The experimental data on the solubilities, densities, and refractive indices of the quaternary system (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) at 298.15 K are presented in Table 1. There are three boundary subternary systems in this quaternary system, which are (KCl + KBO$_2$ + H$_2$O), (KBO$_2$ + K$_2$SO$_4$ + H$_2$O), and (KCl + K$_2$SO$_4$ + H$_2$O). A series of studies have been carried out on the stable phase equilibrium of these three ternary subsys-

tems at different temperatures and relevant experimental data and phase diagrams have been obtained [7, 14, 15]. Solubilities of the invariant points for the three subternary systems are shown in Table 2. Among them, the ternary systems (KCl + KBO$_2$ + H$_2$O) and (KBO$_2$ + K$_2$SO$_4$ + H$_2$O) have not solubility data at 298.15 K in the literature; therefore, the solubilities of ternary system containing $K_2B_4O_7$ and KB_5O_8 were listed for comparison in Table 2. The solid phases of potassium borate were showed $K_2B_4O_7·4H_2O$ and $KB_5O_8·4H_2O$, and the solubility of $K_2B_4O_7$ and KB_5O_8 is much less than KBO$_2$ [7, 14]. For the (KCl + K$_2$SO$_4$ + H$_2$O) system, the solid phases and solubilities in the invariant point obtained in this work are in accordance with the literature [15].

In Table 1, w is the mass fraction, $J(b)$ is the Jänecke index values of the component b, with $J(KCl) + J(K_2SO_4) + J(KBO_2) = 100$. The calculating formula for $J(b)$ is

$$J(b) = \frac{w(b)}{w(KCl) + w(K_2SO_4) + w(KBO_2)} \times 100. \quad (1)$$

The calculating formula for water concentration is

$$J(H_2O) = \frac{w(H_2O)}{w(KCl) + w(K_2SO_4) + w(KBO_2)} \times 100. \quad (2)$$

According to the experimental data of the Jänecke index $J(b)$, the dry-salt phase diagram of this system at 298.15 K were plotted with solid line in Fig. 1. In Fig. 1, the stable phase diagram of the quaternary system at 298.15 K consists of one invariant points, three isothermal dissolution equilibrium curves and three crystalline fields corresponding to potassium chloride (KCl), potassium metaborate hydrate (KBO$_2$·1.33H$_2$O), potassium sulfate (K$_2$SO$_4$). The crystallization field decreases in order of K$_2$SO$_4$ > KCl > KBO$_2$·1.33H$_2$O, and the solubility of the corresponding salt increases sequentially. The five isothermal dissolution equilibrium curves correspond to AE (KBO$_2$·1.33H$_2$O + KCl), BE (K$_2$SO$_4$ + KCl), and CE (KBO$_2$·1.33H$_2$O + K$_2$SO$_4$), respectively. The invariant point E is composed of liquid + KCl + K$_2$SO$_4$ + KBO$_2$·1.33H$_2$O, with $w(KCl) = 5.00$, $w(K_2SO_4) = 0.11$, $w(KBO_2) = 39.03$.

In order to fully reflect the existence of a certain point in the system, the diagram of the water-content vs composition was plotted in Fig. 2 according to its dry salt composition. It can be seen that the water content of quaternary system (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) changes regularly with the change of KCl concentration at 298.15 K, and the water content maximizes at point E. Regarding isothermal dissolution equilibrium curve CE, the value of $J(H_2O)$ decreases from 140.27 to 126.55 with the increase of $J(KCl)$, and increases gradually on the curve EB.

Table 1. Solubilities of the quaternary system $KCl + KBO_2 + K_2SO_4 + H_2O$ at 298.15 K and 0.1 MPa

No.	Composition of liquid phase (100w)				$J(b)$, g/100 g salt			ρ, g cm^{-3}	n_D	Solid phase
	KCl	K_2SO_4	KBO_2	H_2O	KCl	K_2SO_4	H_2O			
1, B	25.54	1.05	0	73.41	96.05	3.95	276.10	1.18244	1.3691	K_2SO_4 + KCl
2	24.64	0.99	1.47	72.90	90.92	3.65	268.96	1.19288	1.3709	K_2SO_4 + KCl
3	24.26	0.98	2.41	72.35	87.74	3.53	261.58	1.20089	1.3722	K_2SO_4 + KCl
4	21.29	0.83	6.79	71.09	73.64	2.87	245.94	1.23155	1.3781	K_2SO_4 + KCl
5	18.21	0.66	12.38	68.75	58.27	2.11	220.00	1.27937	1.3856	K_2SO_4 + KCl
6	15.34	0.51	17.27	66.88	46.32	1.54	201.93	1.32099	1.3924	K_2SO_4 + KCl
7	12.94	0.41	21.29	65.36	37.36	1.18	188.68	1.35819	1.3982	K_2SO_4 + KCl
8	10.86	0.35	25.01	63.78	29.98	0.97	176.09	1.39575	1.4040	K_2SO_4 + KCl
9	8.47	0.22	30.16	61.15	21.80	0.57	157.40	1.43959	1.4109	K_2SO_4 + KCl
10, E	5.00	0.11	39.03	55.86	11.33	0.24	126.55	1.55085	1.4264	K_2SO_4 + KCl + $KBO_2 \cdot 1.33H_2O$
11	4.66	0.05	38.16	57.13	10.87	0.12	133.26	1.54629	1.4262	KCl + $KBO_2 \cdot 1.33H_2O$
12, A	4.85	0	41.41	53.74	10.48	0	116.17	1.54463	1.4263	KCl + $KBO_2 \cdot 1.33H_2O$
13	4.59	0.11	38.30	57.00	10.67	0.26	132.56	1.54270	1.4261	K_2SO_4 + $KBO_2 \cdot 1.33H_2O$
14	2.26	0.12	39.66	57.96	5.38	0.29	137.87	1.54463	1.4258	K_2SO_4 + $KBO_2 \cdot 1.33H_2O$
15	1.17	0.14	40.55	58.14	2.80	0.33	138.89	1.53486	1.4246	K_2SO_4 + $KBO_2 \cdot 1.33H_2O$
16, C	0	0.13	41.49	58.38	0	0.31	140.27	1.52868	1.4237	K_2SO_4 + $KBO_2 \cdot 1.33H_2O$

Standard uncertainties u are $u(T)$ = 0.01 K, $u(P)$ = 0.005 MPa, $u(\rho)$ = 0.15 mg cm^{-3}, $u(n_D)$ = 0.0001, $u_r(x)$ for KCl, K_2SO_4, and KBO_2 are 0.003, 0.005, and 0.003, respectively; w is fraction, ρ is density, $J(b)$ is Jänecke index.

Table 2. Comparison of the solubility data in this work and the literature at the invariant points of the boundary subternary systems at 298.15 K

Subternary system	Composition of the solution 100w			Solid phase	Ref.
	KCl	K_2SO_4	K-borate		
$KCl + K_2SO_4 + H_2O$	25.8	1.1	0	KCl + K_2SO_4	[15]
	25.5	1.05	0	KCl + K_2SO_4	[15]
	25.54	1.05	0	KCl + K_2SO_4	This work
$KCl + K_2B_4O_7 + H_2O$	21.27	0	4.09	KCl + $K_2B_4O_7 \cdot 4H_2O$	[14]
$KCl + KB_5O_8 + H_2O$	25.93	0	1.57	KCl + $KB_5O_8 \cdot 4H_2O$	[7]
$KCl + KBO_2 + H_2O$	4.85	0	41.41	KCl + $KBO_2 \cdot 1.33H_2O$	This work
$K_2SO_4 + K_2B_4O_7 + H_2O$	0	7.01	11.21	K_2SO_4 + $K_2B_4O_7 \cdot 4H_2O$	[14]
$K_2SO_4 + KB_5O_8 + H_2O$	0	10.65	2.40	K_2SO_4 + $KB_5O_8 \cdot 4H_2O$	[7]
$K_2SO_4 + KBO_2 + H_2O$	0	0.13	41.49	K_2SO_4 + $KBO_2 \cdot 1.33H_2O$	This work

Standard uncertainties u are $u(T)$ = 0.01 K, $u(P)$ = 0.005 MPa, $u_r(x)$ for KCl, K_2SO_4, and KBO_2 are 0.003, 0.005, and 0.003, respectively; w is mass fraction.
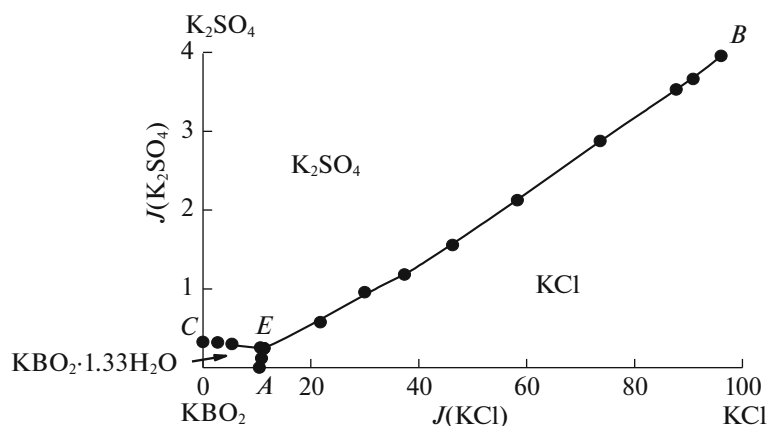
Fig. 1. Phase diagram of the quaternary system KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O at 298.15 K and 0.1 MPa; (points) liquid phase; (lines) isotherm curve; E, invariant point; A, co-saturated point of (KCl + KBO$_2$ + H$_2$O); B, co-saturated point of (KCl + K$_2$SO$_4$ + H$_2$O); C, co-saturated point of (KBO$_2$ + K$_2$SO$_4$ + H$_2$O).
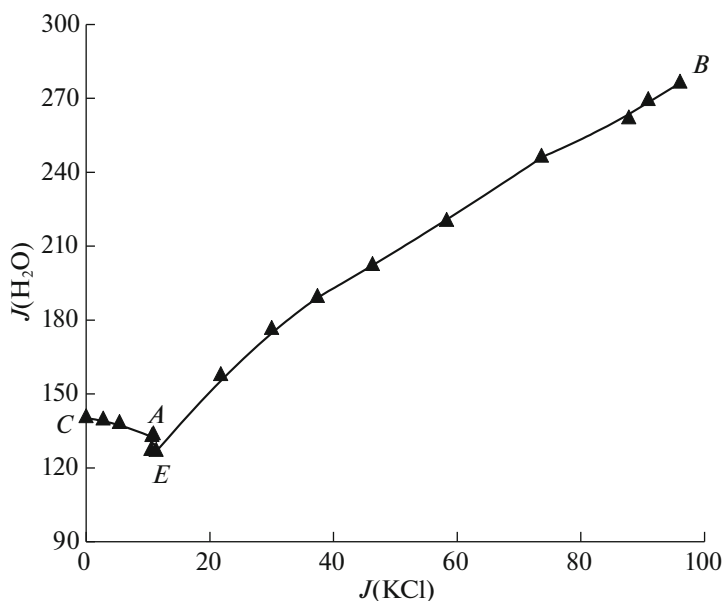
Fig. 2. Water-phase diagram of the quaternary system KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O at 298.15 K and 0.1 MPa; (points) liquid phase; (lines) isotherm curve; E, invariant point; A, co-saturated point of (KCl + KBO$_2$ + H$_2$O); B, co-saturated point of (KCl + K$_2$SO$_4$ + H$_2$O); C, co-saturated point of (KBO$_2$ + K$_2$SO$_4$ + H$_2$O).

The solid phase was identified by X-ray diffraction (XRD) as shown in Fig. 3. The obtained X-ray diffraction pattern matches well with the standard diffraction pattern. It shows that salts KBO$_2$·1.33H$_2$O, K$_2$SO$_4$, and KCl coexist in this quaternary systern (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) at 298.15 K.

The solid phase of potassium borate in (KCl + K$_2$B$_4$O$_7$ + H$_2$O) and (K$_2$SO$_4$ + K$_2$B$_4$O$_7$ + H$_2$O) systems was showed K$_2$B$_4$O$_7$·4H$_2$O, and the solubility of K$_2$B$_4$O$_7$ is much less than KBO$_2$.

The phase equilibria of the quaternary system (KCl + K$_2$B$_4$O$_7$ + K$_2$SO$_4$ + H$_2$O) at 298.15 K has been

reported [14]. For comparison purposes, it is shown in Fig. 4 along with data of (KCl + K$_2$SO$_4$ + KBO$_2$ + H$_2$O) system measured at 298.15 K. The diagrams show that there are remarkable differences in the reported phase field sizes and solid phase types. (1) There are three crystallization phase region present in (KCl + K$_2$B$_4$O$_7$ + K$_2$SO$_4$ + H$_2$O) system: KCl, K$_2$SO$_4$·H$_2$O, and K$_2$B$_4$O$_7$·4H$_2$O; (2) potassium borate of the formula K$_2$B$_4$O$_7$·4H$_2$O is formed in (KCl + K$_2$SO$_4$ + K$_2$B$_4$O$_7$ + H$_2$O) system, while KBO$_2$·1.33H$_2$O generated in (KCl + K$_2$SO$_4$ + KBO$_2$ + H$_2$O) system, and the solubility of K$_2$B$_4$O$_7$ is much less than KBO$_2$; (3) the area of crystallization region of
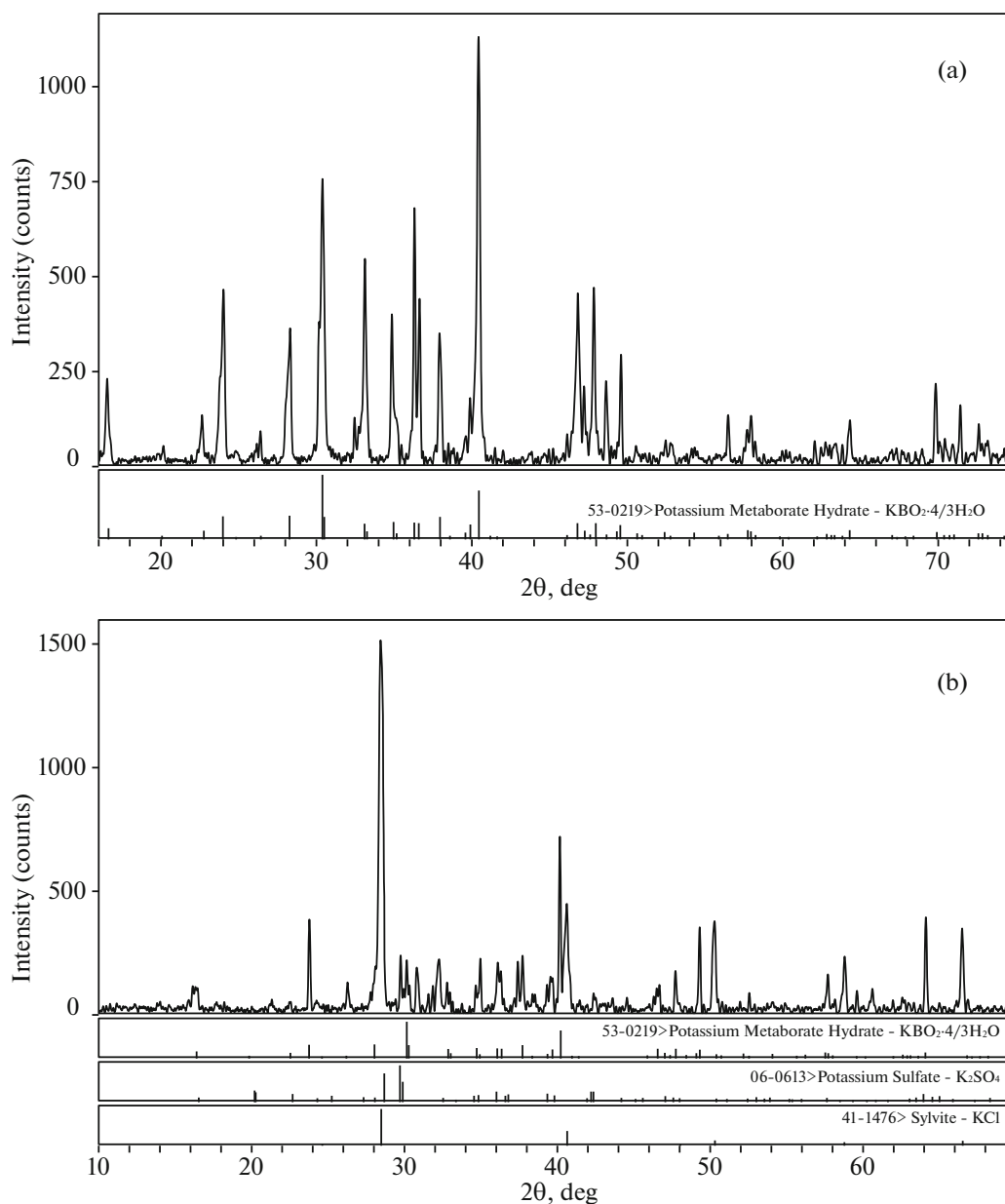
Fig. 3. X-ray diffractive diagram of the solid phase in (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) system; XRD diagram of (a) KBO$_2$·1.33H$_2$O; (b) KBO$_2$·1.33H$_2$O + K$_2$SO$_4$ + KCl.

KCl and K$_2$SO$_4$·H$_2$O decreased, while the K$_2$B$_4$O$_7$·4H$_2$O increased obviously in (KCl + K$_2$SO$_4$ + K$_2$B$_4$O$_7$ + H$_2$O) system.

Based on the experimental data in Table 1, the diagrams for solution densities and refractive indices versus composition in the quaternary system (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) at 298.15 K were drawn and are shown in Fig. 5. It was found that the solution densities and refractive indices changed regularly with the increasing of KCl concentration, which first increased slightly with the increasing concentration of KCl in the solubility isotherm curves of *AE* and *CE*, and

reached the maximum value of 1.55085 g cm^{-3} and 1.4264 at the invariant point *E*, and then decreased sharply with the increasing concentration of KCl in the solubility isotherm curve of *EB*.

CONCLUSIONS

Solid–liquid phase equilibria for the quaternary system of (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) at 298.15 K were studied using the isothermal dissolution equilibrium method, and the solubilities, densities, refractive indices were obtained for the first time. There are one invariant point, three univariant solubility curves and
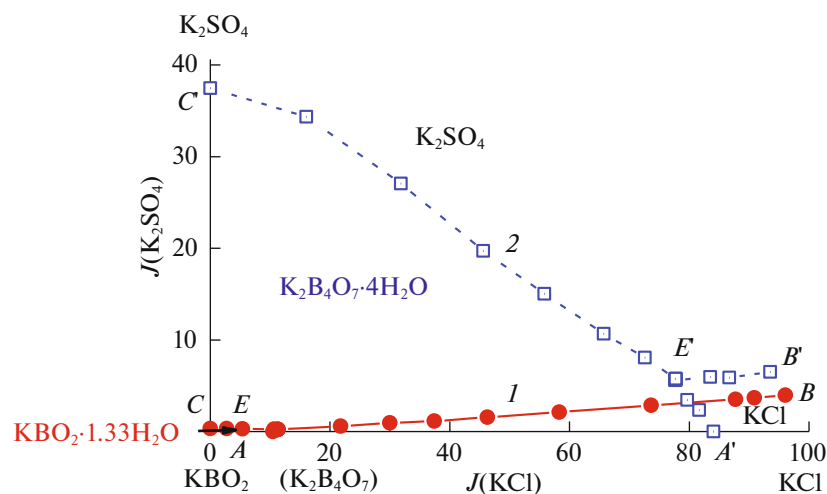
Fig. 4. A comparison of phase diagram for the quaternary system: (*1*) (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) with (*2*) (KCl + K$_2$SO$_4$ + K$_2$B$_4$O$_7$ + H$_2$O) at 298.15 K [14].
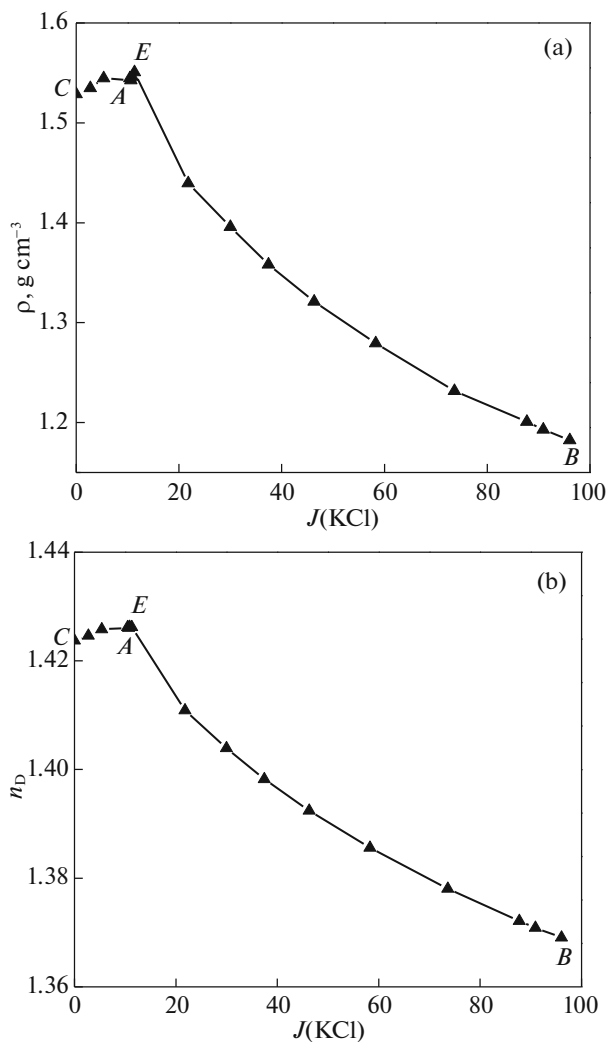

Fig. 5. Diagram of solution densities and refractive indices in the ternary system (KCl + KBO$_2$ + K$_2$SO$_4$ + H$_2$O) at 298.15 K; (a) density vs. composition; (b) refractive index vs. composition.

three crystallization regions corresponding to KCl, KBO$_2$·1.33H$_2$O, K$_2$SO$_4$, respectively. The size of crystallization areas of salt is in the order K$_2$SO$_4$ > KCl > KBO$_2$·1.33H$_2$O, which indicates K$_2$SO$_4$ could be more easily separated from the system. There are remarkable differences in the reported phase field sizes and solid phase types in comparison with the (KCl + K$_2$B$_4$O$_7$ + K$_2$SO$_4$ + H$_2$O) system, and the solubility of K$_2$B$_4$O$_7$ is much less than KBO$_2$. This phase diagram can be used to guide the separating process of KBO$_2$, KCl, K$_2$SO$_4$ from the high concentration potassium-containing salt lake brine.

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