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Solid-Liquid Phase Equilibria in the Aqueous System Containing Potassium, Magnesium, and Borate at 308.15 K

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Abstract: Experimental studies on the solubility, density, refractive index, and pH value in the aqueous system containing potassium, magnesium, and borate at 308.15 K were determined with the method of isothermal dissolution equilibrium. Based on the experimental results, the diagrams of solubility, density, refractive index, and pH value in this system were plotted. We found that there were one eutectic point and two crystallization regions corresponding to the large area of inderite ($L + Mg_2B_6O_{11} \cdot 15H_2O$) and the relatively small area of potassium borate tetrahydrate ($L + K_2B_4O_7 \cdot 4H_2O$), respectively. Neither double salt nor solid solution was found in this system. The physicochemical properties (density, refractive index, and pH value) in solution at 308.15 K changed regularly with increasing potassium borate concentration. The calculated values of density and refractive index using empirical equations of the aqueous system were in good agreement with the experimental values.

Key words: Stable phase equilibrium; Phase diagram; Solubility; Physicochemical property

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1 Introduction

Salt lakes are widely distributed in the western China, especially in the area of the Qinghai-Xizang (Tibet) Plateau. Dongtai Lake, Xitai Lake, and Yiliping Lake in Qaidam Basin are examples of magnesium sulfate brines famous for their abundance of lithium, potassium, magnesium, and boron resources[1-3]. The brines mostly belong to the complex seven-component system of (Li + Na + K + Mg + Cl + SO_4 + borate + H_2O). It is well known that solid-liquid phase equilibria data and phase diagrams are essential for process development, design, and control[4]. To utilize the valuable brine resources economically, the phase equilibria and phase diagrams of brine systems containing magnesium and borate at different temperatures are required.

Borate in aqueous solution can exist in several different species, such as metaborate (BO_2^-), diborate ($B_2O_4^{2-}$), triborate ($B_3O_5^-$), and polytetraborate ($B_4O_7^{2-}$, $B_5O_8^-$, $B_6O_{10}^{2-}$), and the dissolving behavior of boron is very complicated. To better un-

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derstand the thermodynamic behaviors of boron-containing brine, our research group has studied phase equilibrium subsystems at different temperatures, such as ($LiBO_2 + Li_2CO_3 + H_2O$) at (288.15 and 298.15) K[5], ($LiBO_2 + CaB_2O_4 + H_2O$) at (288.15 and 298.15) K[6], ($Li_2SO_4 + LiBO_2 + H_2O$) at (288.15, 298.15 and 323.15) K[7-8], ($Li_2B_4O_7 + MgB_4O_7 + H_2O$) and ($Na_2B_4O_7 + MgB_4O_7 + H_2O$) at 288.15 K[9], ($K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K[10], and ($Li_2SO_4 + Li_2CO_3 + LiBO_2 + H_2O$) at (288.15, 298.15, and 308.15) K[11], and ($Li_2B_4O_7 + Na_2B_4O_7 + Mg_2B_6O_{11} + H_2O$) at (298.15 and 308.15) K[12-13]. To better separate and purify the boron-containing mixture salts from salt-lake brine, the isothermal solubility, solution density, and refractive index for the aqueous system containing potassium, magnesium, and borate at 308.15 K were determined by the isothermal dissolution equilibrium method in this paper.

2 Experimental Section

2.1 Apparatus and reagents

A magnetic stirring thermostatic water bath (HXC-500-6A, Beijing Fortunejoy Sci. Technol. Co. Ltd.) with a precision of 0.01 K was used to control the temperature. A digital polarizing microscope (BX51, Olympus Co., Japan) and X-ray powder diffractometer (MSAL XD-3, Beijing Purkinje Instrument Co. Ltd., China) were used to identify the crystal structures of the solid phases.

All chemicals used were obtained from Sinopharm Chemical Reagent Co., Ltd. Potassium tetraborate ($K_2B_4O_7 \cdot 4H_2O$, A. R. grade, purity by mass percentage > 0.995), Hungchaoite ($MgB_4O_7 \cdot 9H_2O$) was synthesized in our laboratory with by mass percentage higher than 0.991[14]. In addition, doubly deionized water (DDW) with conductivity less than 1×10^{-4} $S \cdot m^{-1}$ and pH 6.60 was used to prepare the series of artificially synthesized brines and for chemical analysis.

2.2 Experimental method

The isothermal dissolution method was used in this study; more details of the experimental method are available in our previous works [15-16]. Briefly, the series of artificially synthesized complexes were sealed in hard polyethylene bottles and placed in the magnetic stirring thermostatic bath (HXC-500-6A). The temperatures of the baths were set at 308.15 ± 0.01 K with 150 rpm stirring speed to accelerate the establishment of equilibrium states. After the artificially synthesized complexes were stirred for about 3 to 5 days, it could be found that the equilibrium had been reached when the compositions of the liquid phase were determined and became constant state. Before sampling, the aqueous solution was undisturbed for 1 h to achieve a clear solution. Two samples were taken from the bottles: one was used for determining physicochemical properties of density and refractive index of the liquid phase of the ternary system, and the other was applied to quantitative analysis. In addition, the solid phase minerals were identified by X-ray powder diffraction.

The concentration of boron in the liquid phase was analyzed by the weight method of mannitol with sodium hydroxide standard solution in the presence of the double indicators methyl red and phenolphthalein; the relative error of the analytical results was less than ±0.003 in mass fraction. The K^+ ion concentration was measured in triplicate by the gravimetric method of sodium tetraphenyl borate; the uncertainty was within ±0.003 in mass fraction. The Mg^{2+} concentration was determined by titration with ethylenediamine tetraacetic acid disodium salt standard solution ($NH_3 \cdot H_2O - NH_4Cl$ buffer, pH = 9.5 to 10) using Eriochrome Black-T as the indicator with a precision of ±0.003 in mass fraction[17].

The measurements of the liquid-phase physicochemical properties were corresponding to density and refractive index. The densities (ρ) were measured using a digital vibrating-tube densimeter (DMA

4500, Anton Paar Co. Ltd., Austria) with an uncertainty of ±0.00001 $g \cdot cm^{-3}$. An Abbe refractometer (Abbemat 550, Anton Paar Co. Ltd., Austria) was used to measure the refractive index (n_D) with an accuracy of ±0.000001. All the measurements were maintained at the desired temperature with ±0.01 K through control of the thermostat (K20 – cc – NR, Huber, Germany).

3 Results and Discussion

3.1 Solubilities of the aqueous system ($K_2B_4O_7 + MgB_4O_7 + H_2O$)

The experimental data on the solubility and the relevant physicochemical properties including density, refractive index, and pH value of the aqueous system ($K_2B_4O_7 + MgB_4O_7 + H_2O$) at 308.15 K were determined and are presented in Table 1. The composition of the liquid phase in the aqueous ternary system was expressed in mass fraction. According to the experimental data in Table 1, the stable phase diagram of the ternary system at 308.15 K was plotted, as shown in Fig. 1.

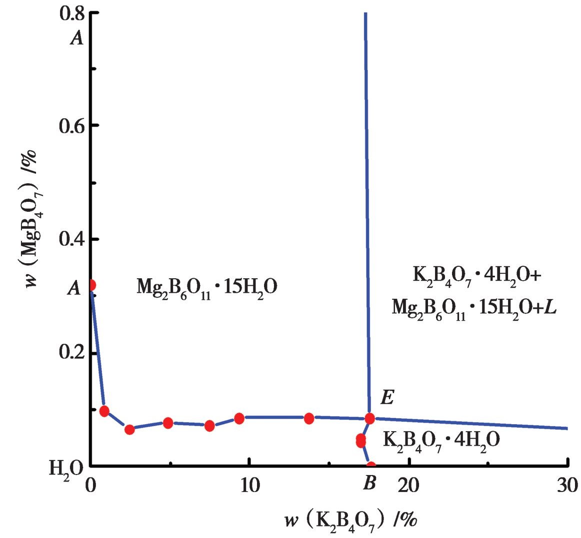

Fig. 1 Phase diagram of the ternary system ($K_2B_4O_7 + MgB_4O_7 + H_2O$) at 308.15 K

Table 1 Solubility, density, and refractive index of the ternary system ($K_2B_4O_7 + Mg_2B_6O_{11} + H_2O$) at 308.15 K

No.	composition of liquid phase $w_i \times 10^2$			density $\rho/(g \cdot cm^{-3})$	n_D	pH	solid phase
	$K_2B_4O_7$	MgB_4O_7	H_2O				
1, A	0.00	0.320	99.68	0.99807	1.332135	9.432	$Mg_2B_6O_{11} \cdot 15H_2O$
2	0.85	0.098	99.052	1.00312	1.333033	9.450	$Mg_2B_6O_{11} \cdot 15H_2O$
3	2.42	0.066	97.514	1.01613	1.335423	9.675	$Mg_2B_6O_{11} \cdot 15H_2O$
4	4.87	0.078	95.052	1.0376	1.339341	9.809	$Mg_2B_6O_{11} \cdot 15H_2O$
5	7.48	0.072	92.448	1.05936	1.343242	9.929	$Mg_2B_6O_{11} \cdot 15H_2O$
6	9.35	0.086	90.564	1.07431	1.346095	9.970	$Mg_2B_6O_{11} \cdot 15H_2O$
7	13.72	0.086	86.194	1.11274	1.35224	9.949	$Mg_2B_6O_{11} \cdot 15H_2O$
8, E	17.53	0.085	82.385	1.14796	1.358519	10.184	$Mg_2B_6O_{11} \cdot 15H_2O + K_2B_4O_7 \cdot 4H_2O$
9	16.93	0.043	83.027	1.14407	1.357886	10.198	$Mg_2B_6O_{11} \cdot 15H_2O$
10	16.96	0.050	82.990	1.14498	1.357861	10.201	$K_2B_4O_7 \cdot 4H_2O$
11, B	17.56	0.00	82.44	1.14573	1.357814	10.230	$K_2B_4O_7 \cdot 4H_2O$

In Fig. 1, the phase diagram consists of two crystallization zones corresponding to potassium borate tetrahydrate ($L + K_2B_4O_7 \cdot 4H_2O$) and inderite ($L + Mg_2B_6O_{11} \cdot 15H_2O$), and two univariant isothermal dissolution curves of AE and BE, indicating the co-saturation of two salts. The size of crystallization areas of salt is in the order $Mg_2B_6O_{11}\cdot 15H_2O > K_2B_4O_7\cdot 4H_2O$, which demonstrates $Mg_2B_6O_{11}\cdot 15H_2O$ can be more easily separated from the solution in this ternary system. Hungchaoite ($MgB_4O_7\cdot 9H_2O$), an incongruently dissolved solid, is a metastable phase, can convert to $Mg_2B_6O_{11}\cdot 15H_2O$ due to changes in density, pH, and the common ions effect. Point E is the eutectic point, which is saturated with ($L + K_2B_4O_7\cdot 4H_2O + Mg_2B_6O_{11}\cdot 15H_2O$). Points A and B are the solubilities of the single salts $Mg_2B_6O_{11}$ and $K_2B_4O_7$ in the liquid phase with mass percent (10^2w) corresponding to 0.320 and 17.56, respectively. Due to the high solubility of potassium borate, there is a strong salting-out effect to magnesium borate. Neither double salts nor solid solution was formed in this aqueous system at 308.15 K.

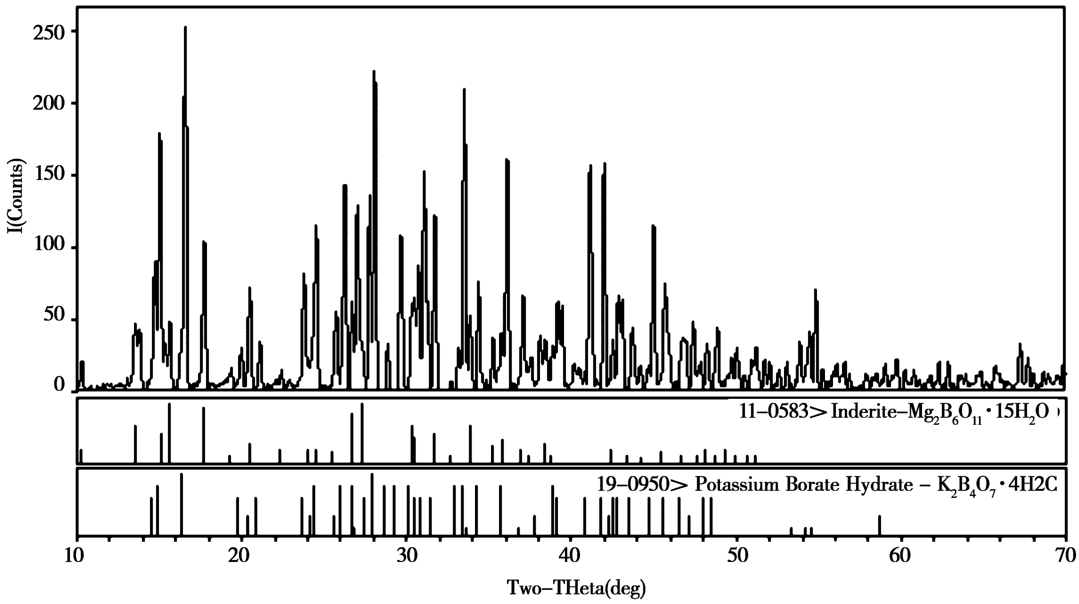

Fig. 2　X-ray diffraction pattern of the eutectic point E($K_2B_4O_7\cdot 4H_2O + Mg_2B_6O_{11}\cdot 15H_2O$)

Fig. 2 shows the X-ray diffraction pattern of the composition at the eutectic point. The abscissa is the 2θ from 10° to 70°; the vertical ordinate is the intensity. The XRD pattern of the eutectic point was well matched to the standard diffraction pattern of $K_2B_4O_7\cdot 4H_2O$ and $Mg_2B_6O_{11}\cdot 15H_2O$ with powder diffraction file (pdf) numbers "19 – 0950" and "11 – 0583", respectively. It shows that salts $K_2B_4O_7\cdot 4H_2O$ and $Mg_2B_6O_{11}\cdot 15H_2O$ coexist at the eutectic point. The compositions of $K_2B_4O_7$ and $Mg_2B_6O_{11}$ at the eutectic point in the liquid phase with mass fraction (10^2w) are 17.53 and 0.085 at 308.15 K, respectively.

The comparison of the solubility data for the ternary system ($K_2B_4O_7 + MgB_4O_7 + H_2O$) at 298.15 K[18] and 308.15 K is shown in Fig. 3. It is

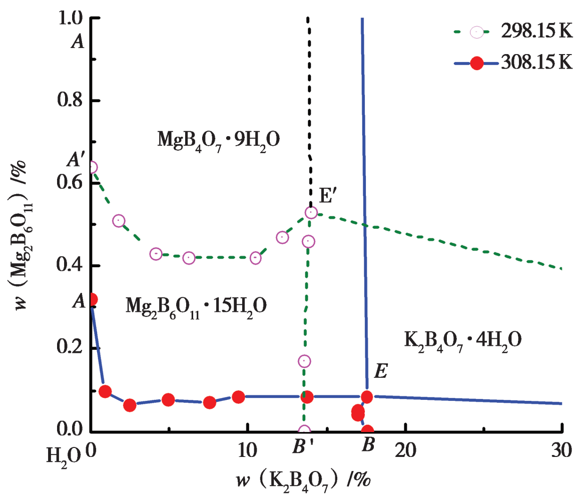

Fig. 3　Comparison of phase diagram of the system K^+, Mg^{2+}//borate – H_2O at 298.15 K[18] and 308.15 K

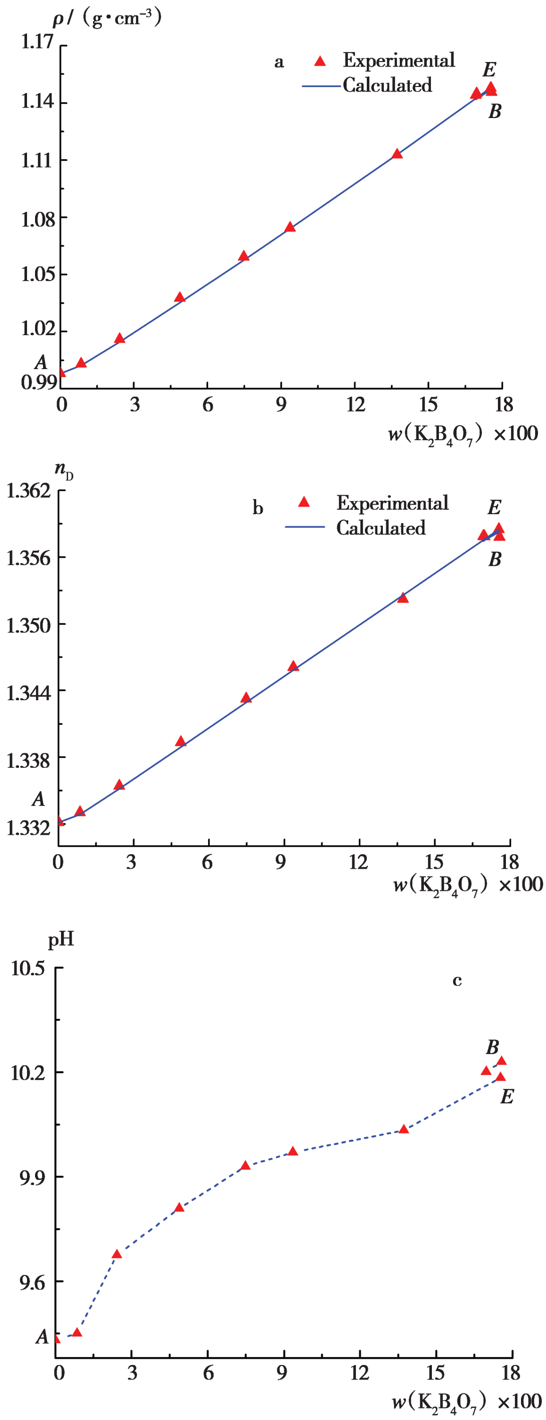

Fig. 4 Physicochemical properties of the solution versus composition diagram of the ternary system ($K_2B_4O_7$ + MgB_4O_7 + H_2O) at 308.15 K; (a) density versus composition; (b) refractive index versus composition; (c) pH versus composition; ▲ , experimental data; —, calculated data

shown that the area of the crystallization region of $K_2B_4O_7 \cdot 4H_2O$ is decreased significantly as the temperature increases, the mineral $MgB_4O_7 \cdot 9H_2O$ is transformed into $Mg_2B_6O_{11} \cdot 15H_2O$, and the area of crystallization region increased obviously as the temperature increases.

3.2 The solution physicochemical properties

On the basis of experimental data in Table 1, the relationship of the solution physicochemical properties including density, refractive index, and pH value versus the concentration of potassium borate was plotted in Fig. 4. It was found that the solution density, refractive index, and pH value in the aqueous system changed regularly with the increasing of potassium borate concentration.

As shown in Fig. 4(a), the density curve of the equilibrium liquid phase increased gradually with increasing concentration of potassium borate at the saturated region of $Mg_2B_6O_{11} \cdot 15H_2O$(curve AE), and reached the maximum value of 1.14796 $g \cdot cm^{-3}$ at the eutectic point E at 308.15 K; the solution density decreased at the saturated region of $K_2B_4O_7 \cdot 4H_2O$ (curve EB).

Fig. 4(b) shows the refractive index value versus composition of $K_2B_4O_7$ in the solution at 308.15 K. Similar to the density in the solution, the refractive index value increased from point A to point E, with a maximum value of 1.3372 at eutectic point E at 308.15 K.

In Fig. 4(c), the solution pH value decreased gradually with increasing $K_2B_4O_7$ concentration, with a singular value of 10.184 at the invariant point of E.

3.3 Empirical equations for density and refractive index

Based on the following empirical equations of the density and refractive index in electrolyte solutions developed in the previous study [19], the density and refractive index of the solution were also calculated.

$$\ln \frac{\rho}{\rho_0} = \sum A_i w_i = A_{K_2B_4O_7} \times w_{K_2B_4O_7} + A_{MgB_4O_7} \times w_{MgB_4O_7} \quad (1)$$

$$\ln \frac{n_D}{n_{D0}} = \sum B_i w_i = B_{K_2B_4O_7} \times w_{K_2B_4O_7} + B_{MgB_4O_7} \times w_{MgB_4O_7} \quad (2)$$

In the above equations, where d and d_0 refer to the density values of the solution and of pure water at the same temperature, the d_0 value of pure water at 308.15 K is 0.99403 g · cm^{-3}. D and D_0 refer to the refractive index values of the solution and of pure water at the same temperature; the D_0 value of pure water at 308.15 K is 1.33131[20]. A_i and B_i are the constants of each possible component i in the system, which were calculated in the present work. w_i is the salt of i in the solution with weight percentage, in mass fraction. Constants A_i of $K_2B_4O_7$ and MgB_4O_7 for the calculation of density in the solution are 0.008159 and 0.012675 at 308.15 K, respectively, and constants B_i of $K_2B_4O_7$ and MgB_4O_7 for the calculation of refractive index in the solution are 0.001143 and 0.001936 at 308.15 K, respectively. The experimental values and calculated data are compared and plotted in Fig. 4, which shows they are in good agreement, with the maximum relative error within 0.30%. This agreement shows that coefficients A_i and B_i obtained in this work are reliable and can be used for more complicated systems containing borate.

4 Conclusions

The solubility and the relevant physicochemical properties including density, refractive index, and pH value of the aqueous system containing potassium, magnesium, and borate at 308.15 K were determined using the isothermal dissolution method. According to experimental data, the equilibrium phase diagram and the diagrams of physicochemical properties versus concentration of potassium borate were constructed. The phase diagram of the ternary system at 308.15 K contains one eutectic point (L + $K_2B_4O_7 \cdot 4H_2O$ + $Mg_2B_6O_{11} \cdot 15H_2O$) and two crystallization regions corresponding to the small area potassium borate tetrahydrate (L + $K_2B_4O_7 \cdot 4H_2O$) and the relatively large area of inderite (L + $Mg_2B_6O_{11} \cdot 15H_2O$). The physicochemical properties including solution density, refractive index, and pH value of the solution in this aqueous system changed regularly with increasing potassium borate concentration in the solution. The calculated values of density and refractive index using empirical equations were in good agreement with the experimental values.

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