Study of the Phase Equilibrium and Solution Properties of the Quinary System $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 298.15$ K

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The phase equilibria of the quinary system $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ was studied at $T = 298.15$ K by the isothermal dissolution equilibrium method. The solubility and physicochemical properties (density, viscosity, refractive index, conductivity, and pH value) of the equilibrium solutions were determined. A phase diagram and physicochemical properties−composition diagrams were plotted on the basis of the solubility data. The isothermal solubility diagram of the quinary system (saturated with KCl) consists of 14 univariant curves, 7 invariant points, and 8 crystallization regions corresponding to NaCl, $Na_2B_4O_7{\cdot}10H_2O$, $K_2B_4O_7{\cdot}4H_2O$, $Na_2CO_3{\cdot}10H_2O$, $Na_2CO_3{\cdot}7H_2O$, $Na_2CO_3{\cdot}H_2O$, $NaKCO_3{\cdot}6H_2O$, and $K_2CO_3{\cdot}1.5H_2O$, respectively. Pitzer's theory was adapted for theoretically describing relations of the high-concentration multicomponent systems in the study. Using Harvie's chemical equations, which are based on Pitzer's theory, the solubility of the quinary system at $T = 298.15$ K was calculated. The calculated values agree with the measured ones, with a deviation of less than 9.59%.

1. Introduction

The Zabuye Saline Lake, Tibet, PRC, is unrivaled in the world for its high concentration of chloride, sulfate, carbonate, and borate of lithium, sodium, and potassium, especially for the very high concentration of lithium, potassium, and boron.[1] The main components of its brines can be described with the $Li^+ + Na^+ + K^+ + Cl^- + SO_4^{2-} + CO_3^{2-}$ + borate + H_2O system.

In aqueous solutions containing boron, the dissolving behavior of boron is very complicated. The various species of boron in aqueous solution depend on the pH value, the total concentration of boron and salts, and the kinds of coexistent salts, in which the total boron concentration is the most important.

Until now, the existing research has demonstrated that boron exists in aqueous solution in the forms of planar monomeric boric acid $B(OH)_3$, the tetrahedral orthoborate ion $B(OH)_4^-$,[2,3] and several different polyborate species.[2,4,5] However, at high pH and total boron concentration, the main species of borate in aqueous solutions are polytriborate $B_3O_3(OH)_4^-$ and polytetraborate $B_4O_5(OH)_4^{2-}$.[6,7] Until now, there has been no good experimental method to determine the accurate concentration distribution among polyborate species except for theoretical calculation;[6] therefore, $B_4O_7^{2-}$ is often used to denote the traditional stoichiometric expression for various boric species in solution. In this way, the system mentioned above can be approximately simplified to the $Li^+ + Na^+ + K^+ + Cl^- + SO_4^{2-} + CO_3^{2-} + B_4O_7^{2-} + H_2O$ system.

In this paper, the phase equilibrium of the quinary subsystem $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ of this complex system was studied at $T = 298.15$ K by the isothermal dissolution equilibrium method. The solubility and physicochemical properties (density, viscosity, refractive index, conductivity, and pH value) of the equilibrium solutions were determined at $T = 298.15$ K. Also, a study on the prediction of the solubility was done.

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2. Experiments

2.1. Reagents. Deionized water (pH ~6.6, conductivity less than 1.5×10^{-4} $S{\cdot}m^{-1}$) and reagents NaCl, KCl, Na_2CO_3, K_2CO_3, $Na_2B_4O_7{\cdot}10H_2O$, and $K_2B_4O_7{\cdot}5H_2O$ were used. All reagents were analytical reagent grade. More attention should be given to sodium and potassium carbonate; sodium and potassium bicarbonate should be removed from them at about $T = 470$ K before being used.

2.2. Experimental Method. The isothermal dissolution equilibria method was used. The composition of the invariant points of the quaternary subsystems (saturated with three kinds salts) is taken as the composition of the initial samples. The desired samples were obtained by adding the fourth salt of different quantities to the initial samples. Then, all of the samples were transferred into sealed hard-plastic bottles, which were put into a water bath constant-temperature oscillator (±0.1 K, model HZS-H, made by Haerbin Donglian Electronic Technology Corporation, China) kept at a constant temperature of $T = (298 \pm 0.1)$ K and a constant oscillation frequency (130 rpm) to accelerate equilibration. The liquid phase of each sample was analyzed periodically, usually within (2 to 3) days after 1 month. When the composition of the liquid phase remained constant for a long period of time, the system was assumed to be at equilibrium. Generally, it took about (45 to 50) days to reach equilibrium. The equilibrium solid phase was identified by X-ray diffraction and micropolariscopy.

2.3. Analytical Method.[8] The concentration of Cl^- ions was measured by $AgNO_3$ precipitation titration. The concentration of CO_3^{2-} ions was measured by acid−base titration. The concentration of $B_4O_7^{2-}$ ions was measured by basic titration with the existence of mannitol. The concentration of K^+ ions was measured by sodium tetra-

10.1021/je049934j CCC: $27.50
Published on Web 09/10/2004

Table 1. Experimental Solubility Values of the Quinary System $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at T = 298.15 K (Saturated with KCl)[a]

	composition of liquid phase, (w(B) × 10^2)						Janecke index, n(B)			
no.	$w(Na_2^{2+})$	$w(K_2^{2+})$	$w(Cl_2^{2-})$	$w(CO_3^{2-})$	$w(B_4O_7^{2-})$	$w(H_2O)$	$n(Na_2^{2+})$	$n(CO_3^{2-})$	$n(B_4O_7^{2-})$	equilibrium solid phase
A	10.3	4.18	9.77	16.7	0.00	59.1	61.6	38.4	0.00	$KCl + NaCl + Na_2CO_3{\cdot}7H_2O$
B	8.54	7.05	4.04	26.3	0.00	54.1	45.9	54.1	0.00	$KCl + Na_2CO_3{\cdot}7H_2O + Na_2CO_3{\cdot}H_2O$
C	6.71	10.7	2.04	30.5	0.00	50.0	36.5	63.5	0.00	$KCl + Na_2CO_3{\cdot}H_2O + NaKCO_3{\cdot}6H_2O$
D	1.59	22.4	0.320	37.9	0.00	37.8	9.84	90.2	0.00	$KCl + NaKCO_3{\cdot}6H_2O + K_2CO_3{\cdot}1.5H_2O$
E	0.00	30.9	2.02	21.6	1.15	44.4	0.00	98.0	2.01	$KCl + K_2B_4O_7{\cdot}4H_2O + K_2CO_3{\cdot}1.5H_2O$
F	5.71	9.62	17.6	0.00	1.52	66.6	96.2	0.00	3.80	$KCl + NaCl + Na_2B_4O_7{\cdot}10H_2O$
G	4.71	9.60	14.4	0.00	3.17	68.0	83.4	0.00	16.6	$KCl + Na_2B_4O_7{\cdot}10H_2O + K_2B_4O_7{\cdot}4H_2O$
1	6.23	3.28	8.58	2.50	2.29	77.1	70.6	21.7	7.69	$KCl + NaCl + Na_2B_4O_7{\cdot}10H_2O$
2	8.99	4.96	12.2	3.89	3.35	66.6	69.4	23.0	7.65	$KCl + NaCl + Na_2B_4O_7{\cdot}10H_2O$
3	9.95	1.33	10.6	4.25	2.11	71.8	71.9	23.5	4.52	$KCl + NaCl + Na_2B_4O_7{\cdot}10H_2O$
4	10.5	2.84	11.9	5.03	2.18	67.5	70.0	25.7	4.30	$KCl + NaCl + Na_2B_4O_7{\cdot}10H_2O$
E_1	9.85	4.52	12.4	4.97	2.34	66.0	68.6	26.5	4.83	$KCl + NaCl + Na_2B_4O_7{\cdot}10H_2O + Na_2CO_3{\cdot}10H_2O$
5	9.20	3.34	10.9	4.66	1.77	70.1	69.2	26.9	3.94	$KCl + NaCl + Na_2CO_3{\cdot}10H_2O$
6	9.73	3.15	11.4	4.86	1.57	69.3	69.9	26.8	3.34	$KCl + NaCl + Na_2CO_3{\cdot}10H_2O$
7	10.9	3.01	12.2	5.80	1.25	66.8	69.4	28.2	2.35	$KCl + NaCl + Na_2CO_3{\cdot}10H_2O$
E_2	10.8	4.89	11.7	7.10	2.28	63.3	63.9	32.2	3.99	$KCl + NaCl + Na_2CO_3{\cdot}10H_2O + Na_2CO_3{\cdot}7H_2O$
8	8.52	5.44	11.7	4.51	2.32	67.5	67.3	27.3	5.43	$KCl + Na_2CO_3{\cdot}10H_2O + Na_2B_4O_7{\cdot}10H_2O$
E_3	7.41	5.19	9.38	4.72	2.57	70.7	62.9	30.7	6.46	$KCl + Na_2CO_3{\cdot}10H_2O + Na_2B_4O_7{\cdot}10H_2O + Na_2CO_3{\cdot}7H_2O$
9	5.55	10.5	7.61	7.86	2.51	66.0	45.1	48.9	6.04	$KCl + Na_2B_4O_7{\cdot}10H_2O + Na_2CO_3{\cdot}H_2O$
10	5.72	10.5	7.96	7.84	2.51	65.5	45.9	48.2	5.96	$KCl + Na_2B_4O_7{\cdot}10H_2O + Na_2CO_3{\cdot}H_2O$
E_4	3.66	23.0	0.770	4.75	1.03	66.8	48.1	47.9	4.01	$KCl + Na_2B_4O_7{\cdot}10H_2O + Na_2CO_3{\cdot}H_2O + Na_2CO_3{\cdot}7H_2O$
11	1.78	9.58	8.05	1.13	4.48	75.0	44.8	21.8	33.4	$KCl + Na_2B_4O_7{\cdot}10H_2O + K_2B_4O_7{\cdot}4H_2O$
E_5	5.13	11.2	7.84	7.61	2.66	65.6	43.6	49.6	6.71	$KCl + Na_2B_4O_7{\cdot}10H_2O + K_2B_4O_7{\cdot}4H_2O + Na_2CO_3{\cdot}7H_2O$
12	5.45	7.69	4.13	8.46	2.75	71.5	42.8	50.9	6.39	$KCl + K_2B_4O_7{\cdot}4H_2O + Na_2CO_3{\cdot}H_2O$
13	5.21	10.8	6.81	8.45	2.25	66.5	42.2	52.4	5.40	$KCl + K_2B_4O_7{\cdot}4H_2O + Na_2CO_3{\cdot}H_2O$
14	5.95	13.8	4.63	13.3	2.30	77.9	35.4	60.6	4.05	$KCl + K_2B_4O_7{\cdot}4H_2O + Na_2CO_3{\cdot}H_2O$
E_6	3.33	16.7	0.710	16.1	1.08	62.1	20.8	77.2	2.00	$KCl + K_2B_4O_7{\cdot}4H_2O + Na_2CO_3{\cdot}H_2O + NaKCO_3{\cdot}6H_2O$
15	3.54	21.8	1.14	19.8	1.41	52.3	18.5	79.3	2.18	$KCl + K_2B_4O_7{\cdot}4H_2O + NaKCO_3{\cdot}6H_2O$
16	2.80	21.5	0.950	18.9	1.37	54.5	15.9	81.8	2.30	$KCl + K_2B_4O_7{\cdot}4H_2O + NaKCO_3{\cdot}6H_2O$
17	2.42	21.5	0.910	18.3	1.53	55.3	14.3	83.0	2.68	$KCl + K_2B_4O_7{\cdot}4H_2O + NaKCO_3{\cdot}6H_2O$
18	2.91	25.9	0.670	22.8	0.760	47.0	14.1	84.8	1.09	$KCl + K_2B_4O_7{\cdot}4H_2O + NaKCO_3{\cdot}6H_2O$
19	1.51	24.6	0.650	19.9	1.10	52.2	8.84	89.3	1.91	$KCl + K_2B_4O_7{\cdot}4H_2O + NaKCO_3{\cdot}6H_2O$
20	1.40	26.0	0.920	20.8	0.680	50.2	7.99	90.9	1.15	$KCl + K_2B_4O_7{\cdot}4H_2O + NaKCO_3{\cdot}6H_2O$
E_7	1.05	26.1	0.720	16.5	0.510	55.2	7.60	91.3	1.09	$KCl + K_2B_4O_7{\cdot}4H_2O + NaKCO_3{\cdot}6H_2O + K_2CO_3{\cdot}1.5H_2O$
21	1.09	26.3	0.710	20.8	0.700	50.4	6.34	92.5	1.21	$KCl + NaKCO_3{\cdot}6H_2O + K_2CO_3{\cdot}1.5H_2O$
22	0.190	23.6	1.10	19.2	1.05	54.8	1.25	96.7	2.04	$KCl + NaKCO_3{\cdot}6H_2O + K_2CO_3{\cdot}1.5H_2O$
23	0.180	26.2	0.950	19.5	1.03	51.7	1.17	96.9	1.98	$KCl + NaKCO_3{\cdot}6H_2O + K_2CO_3{\cdot}1.5H_2O$

[a] Note: w(B) = mass fraction; $n(Na_2^{2+}) + n(CO_3^{2-}) + n(B_4O_7^{2-})$ = 100 mol.

phenylborated-hexadecyltrimethylammonium bromide titration. The concentration of Na^+ ions was measured by atomic absorption spectroscopy (AAS) and evaluated according to ion balance. The accuracy of the measurement was better than 1%.

2.4. Determination Methods of Physicochemical Properties. The densities of the equilibrium solution were measured by a specific gravity bottle method with a correction for the floating force of air. The measured values are accurate to ±0.0001 g·cm^{-1}. Viscosities were measured

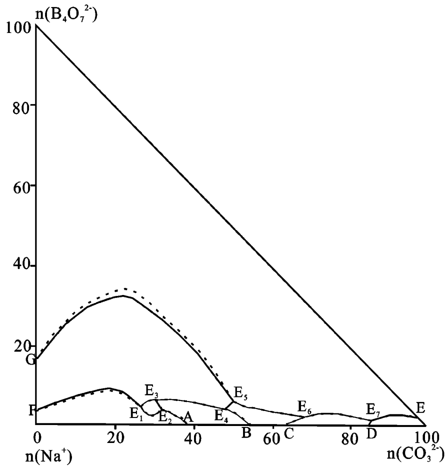

Figure 1. Isothermal diagram of the $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ quinary system at 298.15 K. Solid line, experimental values; dotted line, calculated values (saturated with KCl).

using a capillary viscosimeter (size 75, supplied by Shanghai Grass Instrument Factory). The measured viscosity values are accurate to ±0.0001 mPa·s. Refractive indices were measured using a thermostatically controlled Abbe refractometer (supplied by Beijing Science Instrument Factory). A minimum of three independent readings were taken for each composition, and their average value is used in all of the calculations. The measured values are accurate to ±0.0001 units. Conductivities were measured to an accuracy of ±0.015 $S \cdot m^{-1}$ using a DDS-11A conductometer (supplied by the Second Analytical Instrument Factory, China). The pH values were measured using a numerical acidometer (PHS-3C, supplied by Jiangshu Electronic-Analytical Instrument Factory, China). The results of pH values are accurate to ±0.01 units.

3. Experimental Results

The experimental solubility data of equilibrium solutions of the quinary system $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 298.15$ K are listed in Table 1, in which w(B) is the mass fration of B; n(B) is Janëcke index values of B, with $n(Na_2^{2+}) + n(CO_3^{2-}) + n(B_4O_7^{2-}) = 100$ mol.

According to the Janëcke index of ions, the experimented phase diagram (saturated with KCl) was plotted and is shown with solid lines in Figure 1. The isothermal solubility diagram of the quinary system consists of 14 univariant curves, 7 invariant points, and 8 crystallization phase regions corresponding to salts NaCl, $Na_2B_4O_7 \cdot 10H_2O$, $K_2B_4O_7 \cdot 4H_2O$, $Na_2CO_3 \cdot 10H_2O$, $Na_2CO_3 \cdot 7H_2O$, $Na_2CO_3 \cdot H_2O$, $NaKCO_3 \cdot 6H_2O$, and $K_2CO_3 \cdot 1.5H_2O$, respectively. Among the eight crystallization fields, the crystallization field of $K_2B_4O_7 \cdot 4H_2O$ is the largest. This feature is very important for extracting potassium borate from the salt lake brine.

The seven invariant points are marked as follows:

E_1, saturated with salts KCl + NaCl + $Na_2B_4O_7 \cdot 10H_2O$ + $Na_2CO_3 \cdot 10H_2O$;

E_2, saturated with salts KCl + NaCl + $Na_2CO_3 \cdot 10H_2O$ + $Na_2CO_3 \cdot 7H_2O$;

E_3, saturated with salts KCl + $Na_2CO_3 \cdot 10H_2O$ + $Na_2CO_3 \cdot 7H_2O$ + $Na_2B_4O_7 \cdot 10H_2O$;

E_4, saturated with salts KCl + $Na_2B_4O_7 \cdot 10H_2O$ + $Na_2CO_3 \cdot H_2O$ + $Na_2CO_3 \cdot 7H_2O$;

E_5, saturated with salts KCl + $Na_2B_4O_7 \cdot 10H_2O$ + $K_2B_4O_7 \cdot 4H_2O$ + $Na_2CO_3 \cdot H_2O$;

E_6, saturated with salts KCl + $K_2B_4O_7 \cdot 4H_2O$ + $Na_2CO_3 \cdot H_2O$ + $NaKCO_3 \cdot 6H_2O$; and

Table 2. Density ρ, Viscosity η, Refractive Index n_D, Conductivity κ, and pH Values for the Quinary System $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 298.15$ K (Saturated with KCl)[a]

no.	$\rho/(g \cdot cm^{-3})$	$10^{-3}\eta/(Pa \cdot s)$	n_D	$\kappa/(S \cdot m^{-1})$	pH value
1	1.2669	4.6275	1.3877	6.08	10.55
2	1.3057	4.2445	1.3962	6.38	10.00
3	1.2678	4.3308	1.3895	5.38	10.30
4	1.2932	3.7184	1.3909	6.42	10.45
E_1	1.3040	7.5303	1.3968	5.08	10.58
5	1.2661	3.5990	1.3893	5.65	10.21
6	1.2583	3.4561	1.3849	5.10	10.00
7	1.2952	4.7026	1.3929	5.42	10.50
E_2	1.3109	4.9937	1.3934	6.09	10.75
8	1.2966	3.8930	1.3920	6.32	10.40
E_3	1.3077	4.0689	1.3952	6.02	10.60
9	1.2976	3.1645	1.3896	7.11	10.19
10	1.3053	3.4153	1.3918	6.71	10.60
E_4	1.5557	13.816	1.4202	4.66	12.85
11	1.1913	1.4354	1.3712	7.07	9.28
E_5	1.3092	3.6319	1.3916	6.20	10.60
12	1.2574	3.2998	1.3821	6.26	10.51
13	1.3006	3.3365	1.3900	7.28	10.20
14	1.3958	7.2884	1.3998	6.45	11.40
E_6	1.8579	16.915	1.4126	4.79	12.25
15	1.4897	9.6283	1.4112	5.84	12.25
16	1.4850	9.3228	1.4127	4.24	12.08
17	1.4850	9.3228	1.4094	5.22	12.08
18	1.5471	13.529	1.4193	4.41	13.03
19	1.5622	12.263	1.4188	6.11	12.60
20	1.5433	13.410	1.4193	4.88	13.00
E_7	1.5400	13.716	1.4180	4.81	13.02
21	1.5491	13.272	1.4162	4.75	13.10
22	1.5046	8.6087	1.4142	6.00	12.40
23	1.5151	9.5988	1.4150	5.11	13.35

[a] Note: Numbers in Table 2 corresponding to Table 1.

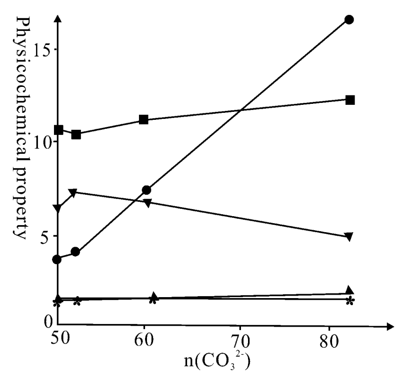

Figure 2. Physicochemical properties−Jenneck index of CO_3^{2-} diagrams of the quinary system $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at 298.15 K: ●, viscosity; ■, pH value; ▼, conductivity; ▲, density; ★, refractive index (saturated with KCl).

Table 3. Pitzer Single Salt Parameters for the Quinary System $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 298.15$ K

	NaCl	KCl	Na_2CO_3	K_2CO_3	$Na_2B_4O_7$	$K_2B_4O_7$
$\beta^{(0)}$	0.07722	0.04835	0.0399	0.1488	−0.11	−0.1129
$\beta^{(1)}$	0.25183	0.2122	1.389	1.43	−0.40	0.3370
C^{Φ}	0.00106	−0.00084	0.0044	−0.0015	0.00	−0.1030
source	[11]	[11]	[9]	[9]	[6]	this work

E_7, saturated with salts KCl + $K_2B_4O_7 \cdot 4H_2O$ + $NaKCO_3 \cdot 6H_2O$ + $K_2CO_3 \cdot 1.5H_2O$.

In this system, the double salt $NaKCO_3 \cdot 6H_2O$ was found. Such a double salt for sodium and potassium carbonate also emerged in Teeple's studies on Searles Lake.[9]

Table 2 shows the physicochemical properties (density, viscosity, refractive indice, conductivity, and pH values) of the equilibrium solutions of the quinary system $Na^+ + K^+$

Table 4. Pitzer Mixing Ion-Interaction Parameters for the Quinary System $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 298.15$ K[a]

parameter	$\theta_{Na,K}$	$\theta_{Cl,B}$	$\theta_{Cl,C}$	$\theta_{C,B}$	$\Psi_{Na,K,Cl}$	$\Psi_{Na,K,C}$	$\Psi_{Na,K,B}$	$\Psi_{Na,Cl,C}$	$\Psi_{Na,Cl,B}$	$\Psi_{Na,C,B}$	$\Psi_{K,Cl,C}$	$\Psi_{K,Cl,B}$	$\Psi_{K,C,B}$
value	−0.012	0.074	−0.02	−2.0630	−0.0018	0.003	0.05381	0.0085	0.025	0.3062	0.004	0.01852	0.07432
source	[9]	[6]	[9]	this work	[9]	[9]	this work	[9]	[6]	this work	[9]	this work	this work

[a] Note: C-CO_3^{2-}, B-$[B_4O_5(OH)_4]^{2-}$.

$+ Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 298.15$ K. Combined with the composition of equilibrium solutions in Table 1, the diagrams of the physicochemical properties−Janecke index of CO_3^{2-} of one univariant curve (which was saturated with salts $KCl + K_2B_4O_7{\cdot}4H_2O + Na_2CO_3{\cdot}H_2O$) were plotted; these were depicted in Figure 2. The results show that the physicochemical properties of the equilibrium solutions present normal changes with solution composition and reach the maximum or minimum value at the invariant points.

4. Prediction of Solubility

4.1. Theory for Calculations. In this study, we adapted the chemical model of Harvie et al.,[10] which is based upon the semiempirical equation of Pitzer[11] and co-workers, to calculate the solubility of the quinary system $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ at $T = 298.15$ K. Using the activity coefficient and the solubility product of the equilibrium solid phase, the coexisting phases and their compositions at equilibrium were identified. The necessary model parameters for the activity coefficient expressions were fit from binary or ternary subsystems' solubility data by a multiple linear regression method.

4.2. Model Parameters. The molecular formulas of the equilibrium solid phases adapted in this work are NaCl, $Na_2[B_4O_5(OH)_4]{\cdot}8H_2O$, $K_2[B_4O_5(OH)_4]{\cdot}2H_2O$, $Na_2CO_3{\cdot}10H_2O$, $Na_2CO_3{\cdot}7H_2O$, $Na_2CO_3{\cdot}H_2O$, $NaKCO_3{\cdot}6H_2O$, and $K_2CO_3{\cdot}1.5H_2O$. The used parameters and their sources are given in Tables 3 and 4. The values for the Pitzer single salt parameters for $K_2B_4O_7$, $\theta_{C,B}$ and $\Psi_{K,C,B}$, were fit from the solubility data in the system $K_2CO_3-K_2B_4O_7-H_2O$.[13] The values for $\Psi_{Na,K,B}$, $\Psi_{K,Cl,B}$, and $\Psi_{Na,C,B}$ were fit from the solubility data of $Na_2B_4O_7-K_2B_4O_7-H_2O$,[14] $KCl-K_2B_4O_7-H_2O$,[14] and $Na_2CO_3-Na_2B_4O_7-H_2O$,[15] respectively.

4.3. Calculated Solubilities. Using the parameters above, the solubilities of the quinary system at 298.15 K were calculated. According to the calculated values, the calculated phase diagram (saturated with KCl) was plotted and is shown with dotted lines in Figure 1. From Figure 1, we can see from most of the univariant curves that the calculated values of the quinary system $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ agree with determined ones, with a deviation of less than 2%. But deviation still exist in measured and calculated values, especially on the univariant curves E_5G, which contain borate. The maximum deviation is up to 9.59%.

5. Conclusions

The quinary system $Na^+ + K^+ + Cl^- + CO_3^{2-} + B_4O_7^{2-} + H_2O$ is one of the most important subsystems of brines for Zabuye Lake. The phase relationships among the coexisting salts of this system are very complex, with crystallization regions of different hydrated salts of sodium carbonate and the double salt $NaKCO_3{\cdot}6H_2O$.

The chemical equilibrium model of Harvie, based on Pitzer's semiempirical equation, was applied to predict the solubility of this complex system. The agreement between the calculated and experimental solubility data is good. This demonstrated that the parameters obtained in this work are reliable and the model is valid for the multicomponent, high-ionic-strength, high-concentration natural water in the Zabuye Lake.

Finally, it should be pointed out that borate in aqueous solution can exist in several different species. However, because no other species except for the polymeric species $[B_4O_5(OH)_4]^{2-}$ is involved in the calculation, the prediction for the solubility curves containing borate has some inaccuracy. This needs further study.

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Received for review February 10, 2004. Accepted August 2, 2004. This work was supported by the National Natural Science Foundation of China (49773200) and the Key Discipline Growing Point Foundation of the National Land and Resources Ministry of China (H.Y.).

JE049934J