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Phase Equilibrium for the Aqueous System Containing Lithium, Sodium, Potassium, Chloride, and Borate Ions at 298.15 K

Tianlong Deng*

College of Materials and Bioengineering, Chengdu University of Technology, 610059, People's Republic of China

The solubility of the aqueous system containing lithium, sodium, potassium, chloride, and borate ions and the densities, viscosities, refractive indexes, conductivities, and pH at 298.15 K of the system have been studied. On the basis of the Jãneche index values, the phase diagrams of dry salt, sodium, and water of the system were plotted. The dry-salt phase diagram of the system includes two four-salt cosaturation points, five solubility isotherm curves, and four crystallization zones all saturated with sodium chloride corresponding to potassium chloride, lithium chloride monohydrate, borax, and lithium borate trihydrate. No solid solution and double salts were found. On the basis of Pitzer's semiempirical equation for a mixed aqueous electrolytic solution, the chemical equilibrium model of Harvie was used to fit the single-salt Pitzer parameters of lithium borate, $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} and the triplet mixed parameters $\Psi_{\mathrm{Li,Cl,B4O5(OH)4}}$, $\Psi_{\mathrm{Li,K,B4O5(OH)4}}$, and $\Psi_{\mathrm{Li,Na,B4O5(OH)4}}$ in this system, which are not reported in the literature. The prediction of the solubilities of salts in the five-component system was then demonstrated. The calculated solubilities agree well with the experimental values.

Introduction

Alkaline lakes are widely distributed in the area of the Qinghai-Xizang Plateau and the Inner Mongolia Autonomous Region, China. The Zabuye Salt Lake, located in Tibet, is one of the alkaline lakes famous for its high concentrations of sodium, lithium, potassium, and borate as well as carbonate and sulfate ions.[1] The brines mostly belong to the complex eight-component system of $Li + Na + K + Cl + B_4O_7 + CO_3 + HCO_3 + SO_4 + H_2O$. When the metallic lithium storage capacities in the lakes around the world are compared, that of the Zabuye Salt Lake is in third place, preceded by those of Atacama Lake in Chile and Pastos Grandes Lake in Bolivia.[2] Mounds of crystallized minerals of sodium chloride, potassium chloride, and borax can be found in the salt sediments of the lake. Although these salt lake brine resources are very valuable, nothing has been reported on multipurpose utilization because the relevant phase relations are lacking, although Chen[3] mentioned his results on an isothermal evaporation study of the surface water at 298.15 K. As a part of the complex eight-component system, some four- or five-component subsystems have been measured.[4−7]

Because the solubilities of salts in multicomponent saltwater systems are generally a few molal, it is necessary to use a reliable theory for aqueous solutions of electrolytes in calculating solubilities.[8] On the basis of the semiempirical equations of Pitzer,[9−10] Harvie and co-workers have developed a chemical equilibrium model capable of high ionic strength.[11−12] This model was successfully utilized in the major seawater ions of the $Na + K + Mg + Cl + SO_4 + H_2O$ five-component system[10,12] and the ternary and quaternary subsystems of the $Na + K + Ca + Mg + H + Cl + SO_4 + CO_2 + B(OH)_4 + H_2O$ system in Searles Lake, California.[13] For the Li^+, Na^+, K^+/Cl^-, $B_4O_7^{2-} + H_2O$ system at 298.15 K, there is no report on the Pitzer parameters of single salts of lithium borate and three mixing triplet parameters of $\Psi_{\mathrm{Li,Cl,B4O5(OH)4}}$, $\Psi_{\mathrm{Li,K,B4O5(OH)4}}$, and $\Psi_{\mathrm{Li,Na,B4O5(OH)4}}$.

In this paper, the solubility and physicochemical property data of the five-component system at 298.15 K were measured. On the basis of the subsystems of the ternary and quaternary system,[14−17] the Pitzer single-salt parameters for lithium borate and the three mixing triplet parameters of $\Psi_{\mathrm{Li,Cl,B4O5(OH)4}}$, $\Psi_{\mathrm{Li,K,B4O5(OH)4}}$, and $\Psi_{\mathrm{Li,Na,B4O5(OH)4}}$ were fit, and the calculated solubilities of the quaternary system are presented.

Experimental Section

Apparatus and Reagents. A thermostatic shaker (model HZQ-C) whose temperature could controlled to ±0.1 K was used for the measurement of phase equilibrium. A SIEMENS D500 X-ray diffraction analyzer was used for the X-ray diffraction analysis of the solid phase.

The chemicals used were of analytical grade and were obtained from either the Chengdu Chemical Reagent Manufactory or the Shanghai Chemical Plant: sodium chloride (NaCl, 99.5 mass %), lithium chloride ($LiCl\cdot H_2O$, ≥ 99 mass %), borax ($Na_2B_4O_7\cdot 10H_2O$, 99.8 mass %), potassium borate ($K_2B_4O_7\cdot H_2O$, 99.9 mass %), and lithium borate ($Li_2B_4O_7\cdot 3H_2O$, 99.5 mass %). Doubly deionized water was used to prepare the series of saturated solutions.

Experimental Method. The isothermal dissolution method was used in this study. The series of complexes of the five-component system were loaded into clean polyethylene bottles and capped tightly. The bottles were placed in the thermostatic rotary shaker, whose temperature was controlled to (298.15 ± 0.1) K, and rotated at 120 rpm to accelerate the equilibrium of those complexes. A 5.0-mL sample of the clarified solution was taken from the liquid phase of each polyethylene bottle with a pipet at regular intervals and diluted to 50.0-mL final volume in a volumetric flask filled with doubly distilled water. If the compositions of the liquid phase in the bottle became constant, then equilibrium was achieved. Generally, it takes about 50 days to come to equilibrium.

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* Corresponding author. E-mail: dtl@cdut.edu.cn. Tel: 86-28-89989195. Fax: 86-28-84079074.

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Table 1. Solubility Data of the Li^+, Na^+, K^+/Cl^-, $B_4O_7^{2-}$ + H_2O System at 298.15 K[a]

	composition of liquid phase (mass %)						Jãneck index/[mol/100 mol ($B_4O_7^{2-}$+ $2K^+$ + $2Li^+$)]					equilibrium solid phase
no	$B_4O_7^{2-}$	K^+	Li^+	Cl^-	Na^+	H_2O	$B_4O_7^{2-}$	$2K^+$	$2Li^+$	$2Na^+$	H_2O	
1	0.60	0.00	0.00	15.76	10.40	73.24	100.00	0.00	0.00	849.62	10 5275.7	NaCl + borax
2	0.00	5.84	0.00	17.69	8.03	68.44	0.00	100.00	0.00	233.15	5978.3	NaCl + KCl
3	0.00	0.00	7.45	38.17	0.08	54.15	0.00	0.00	100.00	0.30	559.7	NaCl + S_A
4, D	1.52	9.62	0.00	17.57	6.16	65.16	7.36	92.65	0.00	100.59	2718.0	NaCl + KCl + borax
5	1.08	8.82	0.082	17.25	6.04	66.72	5.52	89.77	7.10	107.42	2942.7	NaCl + KCl + borax
6	1.14	7.86	0.20	17.16	6.17	67.47	5.99	82.20	11.81	109.42	3057.8	NaCl + KCl + borax
7	1.20	7.73	0.23	17.29	6.25	80.26	6.26	80.26	13.48	110.04	3028.0	NaCl + KCl + borax
8	1.14	7.43	0.34	17.69	6.29	67.13	5.77	74.89	19.34	107.50	2931.8	NaCl + KCl + borax
9	1.24	6.43	0.67	18.09	6.08	67.49	5.75	59.35	34.90	95.16	2699.4	NaCl + KCl + borax
10, K	1.21	6.33	0.78	17.88	5.63	68.17	5.36	55.82	38.82	84.18	2694.9	NaCl + KCl + borax + S_B
11	0.93	6.95	1.18	18.40	4.19	68.35	3.32	49.37	47.31	50.47	2139.0	NaCl + KCl + S_B
12	0.52	6.91	1.57	19.18	3.30	68.52	1.63	43.10	55.27	34.90	1851.9	NaCl + KCl + S_B
13	0.66	6.67	2.15	19.71	1.89	68.93	1.73	34.86	63.41	16.74	1560.8	NaCl + KCl + S_B
14	0.71	6.45	2.39	20.02	1.44	68.99	1.76	31.78	66.46	12.03	1473.0	NaCl + borax + S_B
15, H	0.85	6.08	2.91	21.13	0.69	68.34	1.86	26.51	71.62	5.10	1291.4	NaCl + KCl + S_B + borax
16	0.29	2.96	5.93	33.77	0.51	56.54	0.40	8.09	91.51	2.36	669.9	NaCl + KCl + S_A
17, G	0.00	1.74	6.91	37.39	0.31	53.53	0.00	4.46	95.73	1.29	570.7	NaCl + KCl + S_A
18	1.78	6.18	1.23	18.13	4.55	68.13	6.38	44.09	49.53	55.04	2106.4	NaCl + borax + S_B
19	1.51	5.95	1.31	16.72	4.20	69.12	5.37	42.19	52.43	50.50	2123.8	NaCl + borax + S_B
20	1.80	4.35	2.88	19.10	2.77	69.70	4.99	24.00	71.01	25.92	1666.6	NaCl + borax + S_B
21	1.78	3.65	2.65	19.97	2.51	69.44	4.58	18.72	76.70	21.83	1543.1	NaCl + borax + S_B
22	1.83	3.38	2.88	20.87	2.50	68.55	4.47	16.44	79.08	20.62	1445.1	NaCl + borax + S_B
23	1.97	2.25	4.41	26.54	1.80	63.03	3.52	8.00	88.48	10.85	970.9	NaCl + borax + S_B
24, F	0.74	0.00	6.19	33.48	1.34	58.25	1.05	0.00	98.95	6.44	714.9	NaCl + borax + S_B
25	0.91	5.88	3.25	22.65	0.68	66.63	1.85	23.83	74.32	4.67	1169.9	NaCl + KCl + S_A
26	0.75	2.80	4.77	27.95	0.83	62.90	1.25	9.30	89.45	4.68	905.5	NaCl + S_A + S_B
27, E	0.41	0.00	6.47	34.12	0.72	68.29	0.56	0.00	99.44	3.32	687.8	NaCl + S_A+ S_B

[a] S_A − $LiCl{\cdot}H_2O$; S_B − $Li_2B_4O_7{\cdot}3H_2O$; borax − $Na_2B_4O_7{\cdot}10H_2O$.

Table 2. Physicochemical Property Data of the Five-Component System at 298.15 K

no.[a]	pH	n_D	$\Lambda/(S{\cdot}m^{-1})$	$10^{-3}\eta/(Pa{\cdot}s)$	$10^{-3}\rho/(kg{\cdot}m^{-3})$
1	ND[b]	ND	ND	ND	1.2001
2	ND	ND	ND	ND	1.2370
3	ND	ND	ND	ND	1.2536
4, D	ND	ND	ND	ND	1.2332
5	8.30	1.3861	5.20	1.71	1.2354
6	8.36	1.3876	5.22	1.68	1.2339
7	8.34	1.3865	5.28	1.75	1.2355
8	8.29	1.3860	5.40	1.76	1.2386
9	8.21	1.3868	5.58	1.87	1.2392
10, K	8.09	1.3875	5.80	1.95	1.2409
11	8.01	1.3869	5.60	1.91	1.2196
12	7.93	1.3871	5.70	1.82	1.2207
13	7.42	1.3861	5.90	1.86	1.2028
14	7.52	1.3870	5.92	1.91	1.2061
15, H	6.57	1.3901	5.95	2.35	1.1830
16	6.21	1.3809	5.68	2.11	1.1943
17, G	ND	ND	ND	ND	1.3222
18	8.03	1.3821	4.33	1.78	1.1819
19	7.94	1.3850	5.01	1.78	1.1846
20	7.92	1.3868	5.25	1.82	1.1872
21	7.83	1.3879	5.13	1.86	1.1899
22	7.50	1.3885	5.15	1.88	1.1956
23	6.74	1.3921	5.11	1.92	1.1961
24, F	6.63	1.3992	5.21	1.93	1.2094
25	6.37	1.3821	5.35	1.94	1.2258
26	6.13	1.3828	5.41	1.99	1.2222
27, E	6.09	1.3881	5.61	2.35	1.2296

[a] The no. column corresponds to the no. column in Table 1. [b] ND means not detected.

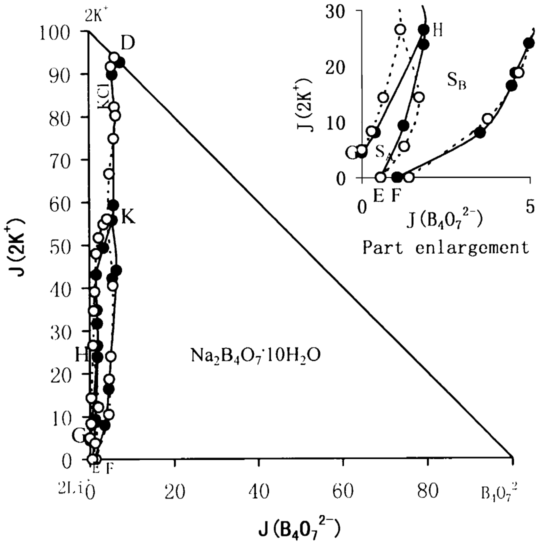

Figure 1. Dry-salt phase diagram of the Li^+, Na^+, K^+/Cl^-, $B_4O_7^{2-}$ + H_2O system at 298.15 K. ●, Experimental value; —, experimental isotherm curve; ○, calculated value; - - -, predictive isotherm curve; S_A, $LiCl{\cdot}H_2O$ crystallization zone; S_B, $Li_2B_4O_7{\cdot}3H_2O$ crystallization zone; $J_B = J_B/[mol/100\ mol(2Li^+ + 2K^+ + B_4O_7^{2-})]$.

After equilibrium was achieved, the rotary system was allowed to rest for 1 h to separate the solid phase from the liquid phase before sampling. The liquid phases were taken out, and a quantitative analysis was performed. The solid phases were filtered through a 0.22-μm membrane by vacuum filtration at (298.15 ± 0.1) K. The filtrate was used to measure the relative physicochemical properties individually. One part of the solid phases was qualitatively dissolved in water and analyzed by chemical methods. The other part was dried at (298.15 ± 0.1) K, ground into powder, and then analyzed by X-ray diffraction.

Analytical Method. The liquid-phase concentrations of Na^+, K^+, and Li^+ were determined by atomic absorption spectrometry (precision ±0.06 mass %, Medal WYD-YII). The Cl^- concentration was measured by titration with a standard solution of $AgNO_3$ in the presence of three drops of 0.1% (w/v) $KCrO_4$ as an indicator (precision ±0.01 mass %). The $B_4O_7^{2-}$ concentration was determined by neutralization titration in excess propanetriol; the precision of the measurement was ±0.03 mass %.[18]

A PHS-3C precision pH meter supplied by the Shanghai Electromagnetic Instrumentation Manufactory was used

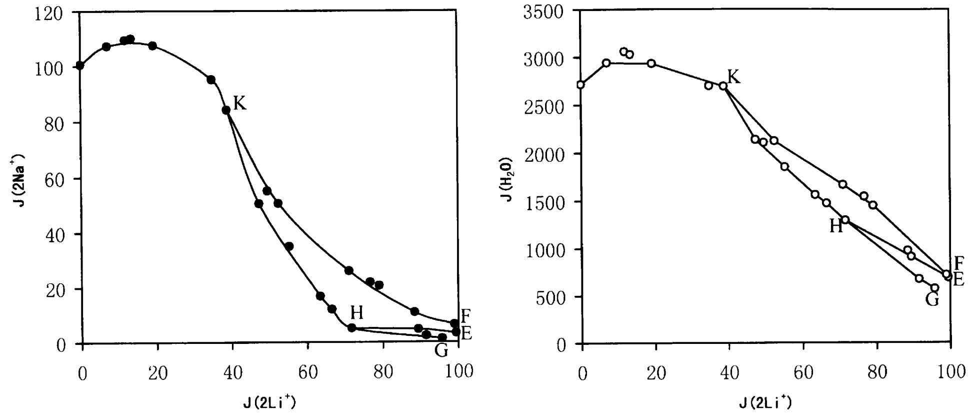

Figure 2. Sodium and water phase diagrams of the Li^+, Na^+, K^+/Cl^-, $B_4O_7^{2-} + H_2O$ system at 298.15 K. (Left) sodium diagram; (right) water diagram; $J_B = J_B/[mol/100\ mol(2Li^+ + 2K^+ + B_4O_7^{2-})]$.

to measure the pH of the equilibrium aqueous solutions. The pH meter was calibrated with standard buffer solutions of either mixing phosphate of potassium dihydrogen phosphate (pH 6.863) or borax (pH 9.183) respectively; which one is used depends on the position of each complex (precision ±0.01). The densities (ρ) were measured with a specific weighing bottle method correction for the floating force of air with a precision of ±0.2 mg. The viscosities (η) were determined using an Ubbelohde capillary viscometer. The viscometer was placed in a thermostat that electronically controlled the set temperature at (298.15 ± 0.1) K. No fewer than three flow times for each equilibrium liquid-phase solution were measured, and the results were averaged. The uncertainty of the flow time measurements was ±0.01 s. An Abbe refractometer (model WZS-1) was used to measure the refractive index (n_D) with an accuracy of ±0.0001. The thermostat temperature was constant to ±0.1 K. Conductivity (Λ) measurements were carried out on a conductivity meter (DDS-11A) with an accuracy of $\pm 0.01\ S\cdot m^{-1}$. Measurements were made in a water bath maintained at (298.15 ± 0.1) K.

Results and Discussion

The solubility data and the relevant physicochemical property data of the aqueous system containing lithium, sodium, potassium, chloride, and borate ions at 298.15 K were measured, and the results are shown in Tables 1 and 2, respectively. On the basis of the Jãneche index (J_B, $J_B/[mol/100\ mol(2Li^+ + 2K^+ + B_4O_7^{2-})]$) in Table 1, the experimental solubility isothermal phase diagram of the system at 298.15 K was plotted, as shown in Figure 1.

The phase diagram of the system in Figure 1 consists of four crystallization zones in which all are saturated with sodium chloride corresponding to potassium chloride (KCl), lithium chloride monohydrate ($LiCl\cdot H_2O$), lithium borate trihydrate, ($Li_2B_4O_7\cdot 3H_2O$) and borax ($Na_2B_4O_7\cdot 10H_2O$). Points K and H are two four-salt consaturation points, that is, isothermal invariant points. There are five isotherm curves corresponding to curves HG, HE, HK, KF, and DK, indicating the cosaturation of three salts. The crystallization area of borax is the largest, and the crystallized zone of lithium chloride monohydrate is the smallest. These results indicate that borax is easy to saturate and crystallize from solution and that lithium chloride has a high solubility. There are no solid solutions or double salts formed in the system.

Figure 2 is the relevant sodium diagram (Figure 2a) and water diagram (Figure 2b) of the system at 298.15 K. Figure 2a indicates that the Jãneche index values of $J(2Na^+)$ in the corner with high lithium ionic concentrations are lower than those located in the other zones of the dry-salt diagram for the strong salting-out effect of lithium chloride. Figure 2b shows that the Jãneche index values of $J(H_2O)$ gradually decrease with increasing $J(2Li^+)$.

Table 3. Pitzer Ion-interaction Parameters for the Five-Component System at 298.15 K[a]

Single-Salt Parameters

cation	anion	$\beta_{MX}^{(0)}$	$\beta_{MX}^{(1)}$	C_{MX}^{ϕ}	ref
Li^+	Cl^-	0.20818	−0.07264	0.0	8
K^+	Cl^-	0.04835	0.2122	−0.00084	12
Na^+	Cl^-	0.07722	0.25183	0.00106	22
Li^+	$B_4O_5(OH)_4^{2-}$	−0.331042	−0.152813	0.01012	this work
K^+	$B_4O_5(OH)_4^{2-}$	−0.022	0.0	0.0	13
Na^+	$B_4O_5(OH)_4^{2-}$	−0.11	−0.4	0.0	13

Mixing Ion-Interaction Parameters

parameters	value	ref
$\theta_{Na,K}$	−0.012	12
$\theta_{Li,Na}$	0.012	23
$\theta_{Li,K}$	−0.022	19
$\theta_{Cl,B4O5(OH)4}$	0.074	13
$\Psi_{Li,Na,Cl}$	0.1	24
$\Psi_{Na,K,Cl}$	−0.0018	12
$\Psi_{Li,K,Cl}$	−0.01	24
$\Psi_{Na,K,B4O5(OH)4}$	0.289823	19
$\Psi_{Li,K,B4O5(OH)4}$	0.115485	this work
$\Psi_{Li,Na\ B4O5(OH)4}$	0.493558	this work
$\Psi_{Li,Cl\ B4O5(OH)4}$	0.010115	this work
$\Psi_{Na,Cl,B4O5(OH)4}$	0.025	13
$\Psi_{K,Cl,B4O5(OH)4}$	0.0185245	19

[a] Adjustable parameters are $\alpha_1 = 2.0$ and $\alpha_2 = 0.0$; $b = 1.2$.

The physicochemical properties of the equilibrium solution change regularly with changing borate concentration in the system. Table 2 indicates that the viscosities and refractive indexes of the equilibrium aqueous solutions gradually increase with increasing borate concentration, whereas the trend for the pH, conductivities, and densities of the equilibrium aqueous solutions is reversed.

Prediction of Solubilities

Ion-Interaction Model. Pitzer[9,10] has published a series of papers and given a set of expressions for osmotic coefficients of the solution and mean activity coefficient of electrolytes in the solution. Expressions of the chemical equilibrium model for conventional single-ion activity coefficients derived by Harvie[12] were used to calculate the solubilities of the Li^+, Na^+, K^+/Cl^-, $B_4O_7^{2-} + H_2O$ system. A complete discussion of these equations can be found in

Table 4. $\mu°/RT$ Values of the Species in the Five-Component System at 298.15 K

species	$\mu°/RT$	ref	species	$\mu°/RT$	ref
H_2O	−95.6635	12	$LiCl \cdot H_2O$	−254.5962	8
Li^+	−118.0439	8	NaCl	−154.99	12
Na^+	−105.651	12	KCl	−164.84	12
K^+	−113.957	12	$Na_2B_4O_5(OH)_4 \cdot 8H_2O$	−2224.16	13
Cl^-	−52.955	12	$K_2B_4O_5(OH)_4 \cdot 2H_2O$	−1663.47	13
$B_4O_5(OH)_4^{2-}$	−1239.10	13	$Li_2B_4O_5(OH)_4 \cdot H_2O$	−19 160.23	this paper

the appendixes of Felmy and Weare[13] and Harvie.[12] Using the activity coefficients and the solubility products of the equilibrium solid phases allowed us to identify the coexisting solid phases and their compositions at equilibrium. The necessary model parameters for the activity coefficients of electrolytes in the system were fit from the ternary subsystems by a multiple linear regression method.

Model Parametrization. According to the identification of XRD,[19] IR,[20] and thermogravimetric analysis,[21] the borate exists in a stratified structural unit of $[B_4O_5(OH)_4]^{2-}$ in the closed stable equilibria aqueous system at 298.15 K. The complete structural formulas of the botrate minerals of lithium, sodium, and potassium in the equlibria solid phases are $Li_2[B_4O_5(OH)_4] \cdot H_2O$, $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$, and $K_2[B_4O_5(OH)_4] \cdot 2H_2O$, respectively. The single-salt parameters of lithium borate ($\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ}) and the mixing triplet parameters of $\Psi_{Li,Cl,B4O5(OH)4}$, $\Psi_{Li,K,B4O5(OH)4}$, and $\Psi_{Li,Na,B4O5(OH)4}$, all of which were not reported in the literature, are fit using the reliable solubility data in the relative ternary subsystem.[14−17] The Pitzer single-salt parameters, Pitzer mixing ion-interaction parameters, and $\mu°/RT$ values of the species in the quaternary system at 298.15 K used in this study are presented in Tables 3 and 4. The standard deviation of the fit (sd) and the multiple correction coefficient (R) for the best values of these fitted ion-interaction parameters for a single electrolyte of lithium borate, which is a measure of the closeness of the fit to a linear relationship, are 0.0488 and 0.9982, respectively, when the maximum molality of lithium borate fitted in this study is 0.183 m. The $\mu°/RT$ value of lithium borate presented in Table 4 was calculated for the first time and combined the fitted single-salt parameters of lithium borate and the solubility of the binary system of lithium borate in water.

Calculated Solubilities. Using the chemical equilibrium model and the above parameters, the calculated results of the solubility are shown in Figure 1 with dashed lines. It is shown that the predicted values using the chemical equilibrium model agree well with experimental values. For such a complicated five-component system with high ionic strengths (to 19.219 m), this agreement indicates that the parameters obtained in this work are reliable and that the chemical equilibrium model of Harvie is capable of predicting equilibiria in the system studied.

Conclusions

The experimental solubility data and the relevant physicochemical property data of the aqueous system of lithium, sodium, potassium, chloride, and borate at 298.15 K were determined. According to the solubility data measured, the isothermal phase diagram was constructed. The single-salt Pitzer parameter of lithium borate and the mixing ion interaction parameters of $\Psi_{Li,Cl,\ B4O5(OH)4}$, $\Psi_{Li,K,B4O5(OH)4}$, and $\Psi_{Li,Na,B4O5(OH)4}$ were fit. The maximum molality of lithium borate fit in this study was 0.183 mol/kg of solvent. The calculated solubilities agree well with the experimental values.

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