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Metastable Phase Equilibrium of the Reciprocal Quaternary System $LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$ at 308.15 K

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ABSTRACT: The solubilities and the physicochemical properties including the density, viscosity, refractive index, conductivity, and pH value of the aqueous quaternary system $LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$ at 308.15 K were determined with the isothermal evaporation method. On the basis of the Jänecke indices, the dry-salt phase diagram, the water-phase diagram, and the diagrams of physicochemical properties were plotted. The dry-salt phase diagram of the system includes three three-salt cosaturation invariant points, seven univariant solubility curves, and five crystallization zones corresponding to potassium sulfate, potassium chloride, the double salt lithium potassium sulfate, lithium sulfate monohydrate, and lithium chloride monohydrate. Single-salt parameters $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\varphi)}$ for lithium sulfate, potassium sulfate, and potassium chloride, mixed electrolyte parameters θ_{Cl,SO_4} and Ψ_{K,Cl,SO_4}, and the Debye–Hükel limiting slope A^{Φ} at 308.15 K were calculated according to the temperature-dependent equations presented in the literature. On the basis of Pitzer's semiempirical equations for a mixed aqueous electrolytic solution, the extended chemical equilibrium model of Harvie was used to fit the single-salt parameters $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\varphi)}$ for lithium chloride, the mixing two-ion pair parameter of $\theta_{Li,K}$, and the mixing triplet-ion parameters of $\Psi_{Li,K,Cl}$ and Ψ_{Li,K,SO_4} in this system at 308.15 K, which are not reported in the literature. The prediction solubilities for the quaternary system agree well with the experimental values.

INTRODUCTION

There are more than 700 salt lakes, each with an area larger than 1 km^2, in the Qinghai-Tibet Plateau, China. Salt lakes of the Qaidam Basin consist of a series of lakes including Caerhan Lake, Dongtai Lake, Xitai Lake, and Yiliping Lake and are a subtype of magnesium sulfate brines famous for their abundance of lithium, potassium, magnesium, and boron resources. The brines mostly belong to the complex seven-component system of $Li + Na + K + Mg + Cl + SO_4 + B_4O_7 + H_2O$. The phenomena of supersaturation of the sulfate-type of brines are often found both in salt lakes and solar ponds.[1] To economically exploit the brine and mineral resources, it is important to adequately adopt local natural resources such as wind energy and solar energy. Therefore, simulative experimental studies on metastable phase equilibria are essential for predicting the path of mineral crystallization for the effective separation and purification of the mixture salts.

As a part of the complex system, metastable phase diagrams of some four- or five-component subsystems have been measured.[2−11] Although stable equilibrium phase diagrams of the system $LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$ at 298.15 K, 323.15 K, and 348.15 K have been measured,[12,13] the metastable phase diagram of the system at 308.15 K is not reported in the literature. Because the solubilities of salts in multicomponent salt−water systems are generally a few molal, it is necessary to use a reliable theory for aqueous solutions of electrolytes in calculating solubilities. On the basis of the semiempirical equations of Pitzer,[14,15] Harvie and co-workers have developed a chemical equilibrium model which was successfully utilized in natural waters of high ionic strength.[16−18] Song et al.[19,20] have applied the Harvie model to the calculation of metastable phase equilibrium of the salt-water system. For the system $LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$ at 308.15 K, the Pitzer single-salt parameters $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\varphi)}$ for lithium chloride, the mixing pair of $\theta_{Li,K}$, and the mixing triplet-ion parameters of $\Psi_{Li,K,Cl}$ and Ψ_{Li,K,SO_4} in wide concentrations are lacking.

In this paper, the solubility and physicochemical property data of the four-component system at 308.15 K were measured. The Pitzer single-salt parameters for lithium chloride and mixed electrolyte parameters $\theta_{Li,K}$, $\Psi_{Li,K,Cl}$, and Ψ_{Li,K,SO_4} were obtained, and the calculated solubilities of the quaternary system are presented.

EXPERIMENTAL SECTION

Apparatus and Reagents. An isothermal evaporation box was made in our laboratory. In an air-conditioned laboratory, a thermally insulated box (70 cm long, 65 cm wide, 60 cm high) with a temperature controller was used to control the temperature. An electric fan on the box was used to accelerate the evaporation of water from solutions. The solid phase minerals were identified by combined using XP-300 digital polarizing microscopy (Shanghai Caikon Optical Instrument Co. Ltd., China) and an X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands). An LCD digital hygrometer was used for the determination of relative humidity in the vaporizing chest.

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Table 1. Solubility Data of the System ($LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$) at 308.15 K

no.	composition of liquid phase, $100w_i$					Jänecke index, J[mol/100 mol dry salt]			equilibrium solid phases[a]
	Li^+	K^+	Cl^-	SO_4^{2-}	H_2O	$J(2Li^+)$	$J(SO_4^{2-})$	$J(H_2O)$	
1,G	1.26	5.32	0.00	15.29	78.13	57.21	100.00	2725.4	Arc+Db4
2	1.25	5.31	0.63	14.33	78.48	57.05	94.42	2756.9	Arc+Db4
3	1.22	5.34	1.07	13.53	78.84	56.16	90.34	2808.0	Arc+Db4
4	1.21	5.41	2.21	12.01	79.16	55.75	80.01	2813.2	Arc+Db4
5	1.20	5.40	3.30	10.46	79.64	55.59	70.09	2845.0	Arc+Db4
6	1.17	5.80	4.77	8.74	79.52	53.15	57.48	2789.3	Arc+Db4
7	1.17	6.33	6.61	6.94	78.95	51.08	43.66	2648.0	Arc+Db4
8	1.18	6.48	7.81	5.54	78.99	50.67	34.38	2611.3	Arc+Db4
9	1.20	7.31	9.59	4.25	77.65	47.97	24.66	2400.8	Arc+Db4
10	1.16	8.62	11.48	3.05	75.69	43.08	16.40	2169.0	Arc+Db4
11,A	1.25	10.05	14.25	1.72	72.73	41.29	8.16	1844.1	Arc+Db4+Syl
12,H	0.00	14.96	13.07	0.67	71.30	0.00	3.63	2069.2	Arc+Syl
13	0.12	14.55	13.30	0.70	71.33	4.51	3.73	2032.3	Arc+Syl
14	0.19	14.13	13.20	0.76	71.72	6.92	4.09	2051.3	Arc+Syl
15	0.25	13.87	13.24	0.82	71.82	9.22	4.37	2041.2	Arc+Syl
16	0.45	12.98	13.35	0.99	72.23	16.41	5.19	2019.1	Arc+Syl
17	0.58	12.49	13.46	1.10	72.37	20.62	5.67	1996.8	Arc+Syl
18	0.74	12.06	13.83	1.23	72.14	25.77	6.16	1926.9	Arc+Syl
19	0.81	11.69	13.73	1.37	72.40	28.14	6.88	1931.8	Arc+Syl
20	1.17	10.45	14.15	1.80	72.43	38.77	8.57	1842.8	Arc+Syl
21,F	3.20	1.15	0.00	23.57	72.08	94.01	100.00	1630.5	Db4+Ls
22	3.12	1.14	1.11	21.52	73.11	93.91	93.45	1693.0	Db4+Ls
23	3.09	1.06	2.36	19.48	74.01	94.23	85.91	1740.6	Db4+Ls
24	3.02	1.11	3.25	17.82	74.80	93.88	80.17	1794.8	Db4+Ls
25	3.01	1.03	4.77	15.64	75.55	94.26	70.76	1822.0	Db4+Ls
26	2.90	1.14	6.55	12.57	76.84	93.49	58.61	1910.0	Db4+Ls
27	2.93	1.08	9.02	9.38	77.59	93.86	43.42	1915.6	Db4+Ls
28	3.00	1.28	12.07	5.99	77.66	92.98	26.79	1853.2	Db4+Ls
29	3.11	1.53	14.68	3.50	77.18	91.96	14.98	1759.9	Db4+Ls
30,B	4.44	2.15	24.49	0.21	68.71	92.08	0.64	1097.2	Db4+Ls+Syl
31	1.45	9.33	14.75	1.52	72.95	46.73	7.09	1807.8	Db4+Syl
32	1.61	8.67	15.10	1.32	73.30	51.07	6.05	1795.4	Db4+Syl
33	1.92	7.59	15.85	1.17	73.47	58.81	5.17	1729.6	Db4+Syl
34	2.37	6.18	16.98	1.00	73.47	68.38	4.18	1631.1	Db4+Syl
35	2.74	5.18	18.04	0.90	73.14	74.87	3.55	1538.7	Db4+Syl
36	3.28	4.03	19.81	0.81	72.07	82.10	2.94	1390.1	Db4+Syl
37	3.61	3.34	20.91	0.76	71.38	85.91	2.63	1308.6	Db4+Syl
38	3.96	2.80	22.32	0.57	70.35	88.84	1.85	1217.7	Db4+Syl
39,E	7.71	0.00	39.35	0.03	52.91	100.00	0.059	528.8	Ls+Lc
40,D	7.53	2.26	40.51	0.0	49.70	94.95	0.00	483.0	Syl+Lc
41,C	7.47	2.24	40.14	0.04	50.11	94.95	0.083	491.0	Syl+Ls+Lc

[a] Arc, K_2SO_4; Syl, KCl; Db4, $Li_2SO_4 \cdot K_2SO_4$; Ls, $Li_2SO_4 \cdot H_2O$; Lc, $LiCl \cdot H_2O$.

The chemicals were of analytical grade and were obtained from either the Tianjin Chemical Reagent Manufactory or the Shanghai Chemical Plant: potassium chloride (KCl, $w = 0.995$ in mass fraction), lithium chloride (LiCl, $w = 0.990$), potassium sulfate (K_2SO_4, $w = 0.990$), and lithium sulfate ($Li_2SO_4 \cdot H_2O$, $w = 0.999$). The chemicals used were recrystallized with doubly deionized water (DDW) before use. DDW with a conductivity less than $1 \cdot 10^{-4}$ $S \cdot m^{-1}$ at room temperature (298.15 K) was used to prepare the series of artificially synthesized brines and for chemical analysis.

Experimental Method. According to the statistical data from 1971 to 2000, the temperature of the brine in the Qaidam Basin is between 293.15 K and 313.15 K from June to August, and the average temperature is 308.15 K. The climatic conditions in the region of Qaidam Basin are generally windy and arid with little rainfall and great evaporating capacity.[1] From an approximate knowledge of the phase equilibrium composition, an appropriate quantity of salts and DDW were mixed together to produce a series of artificial synthesized brines. These were loaded into clean polyethylene containers (16 cm diameter, 7 cm high). The

Table 2. Physicochemical Property Data of the System ($LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$) at 308.15 K

		ρ	$10^{-3}\,\eta$	κ	
no.	n_D	$kg \cdot cm^{-3}$	$Pa \cdot s$	$S \cdot m^{-1}$	pH
1,G	1.3657	1.1878	1.5541	14.89	7.37
2	1.3654	1.1802	1.5019	15.20	7.00
3	1.3657	1.1750	1.4595	15.58	7.21
4	1.3654	1.1660	1.3764	16.38	6.95
5	1.3652	1.1577	1.3178	17.28	6.93
6	1.3652	1.1528	1.2378	18.87	6.55
7	1.3679	1.1499	1.1901	ND	7.38
8	1.3682	1.1463	1.1579	ND	7.43
9	1.3710	1.1502	1.1326	ND	7.38
10	1.3741	1.1615	1.1263	ND	7.21
11,A	1.3815	1.1798	1.1567	ND	7.17
12,H	1.3772	1.1929	0.8581	ND	7.70
13	1.3741	1.1907	0.8712	ND	7.65
14	1.3745	1.1898	0.8913	ND	6.46
15	1.3749	1.1884	0.9158	ND	6.77
16	1.3761	1.1856	0.9528	ND	7.18
17	1.3789	1.1844	0.9877	ND	7.30
18	1.3779	1.1846	1.0185	ND	7.48
19	1.3782	1.1833	1.0558	ND	7.08
20	1.3813	1.1824	1.1529	ND	7.31
21,F	1.3807	1.2526	3.9241	9.41	6.49
22	1.3797	1.2334	3.3247	10.09	5.99
23	1.3801	1.2220	3.0711	10.81	7.06
24	1.3781	1.2095	2.7894	11.47	6.85
25	1.3787	1.1947	2.5165	12.47	6.95
26	1.3777	1.1756	2.1817	13.98	6.94
27	1.3795	1.1592	1.9711	15.51	6.82
28	1.3780	1.1454	1.7615	17.61	5.67
29	1.3799	1.1412	1.6891	19.37	5.87
30,B	1.4042	1.1914	2.6244	18.24	6.01
31	1.3802	1.1760	1.2121	ND	7.05
32	1.3808	1.1721	1.2403	ND	7.43
33	1.3821	1.1695	1.3211	ND	7.33
34	1.3860	1.1664	1.4561	ND	6.98
35	1.3881	1.1663	1.5806	ND	7.06
36	1.3887	1.1684	1.7709	ND	6.90
37	1.3918	1.1733	1.9465	ND	6.93
38	1.3950	1.1779	2.1450	ND	6.10
39,E	1.4461	1.3041	13.3004	7.95	5.02
40,D	1.4435	1.3277	15.4565	7.43	5.46
41,C	1.4493	1.3289	15.6941	7.51	5.76

containers were placed in the insulated box for the isothermal evaporation at (308.15 ± 0.1) K. The experimental conditions were an air flowing velocity of (3.5 to 4.0) $m \cdot s^{-1}$, a relative humidity of (20 to 30) %, and an evaporation rate of (4 to 6) $mm \cdot d^{-1}$. These conditions are similar to the climate of Qaidam Basin. The solutions were always kept in no stirring conditions to allow for the metastable evaporation, and then the crystal behavior of the solid phase was observed.

When enough new solid phases appeared (about (0.5 to 1.0) g), the wet residue mixtures were taken out from the solution. The solid phase minerals were then evaluated with combined chemical analysis through the wet residue method, observation with XP-300D digital polarizing microscopy, and further identification with X-ray diffraction. Meanwhile, a 5.0 cm^3 sample of the clear liquid phase solution was taken out from the liquid phase of each polyethylene container through a pipet and then diluted to 250.0 cm^3 in a volumetric flask with DDW for the quantitative analysis of the compositions of the liquid phase. Another aliquot of the clear liquid phase solution was used to measure the relative physicochemical properties individually. The remainder of the solution continued to be evaporated and reached a new metastable equilibrium point.

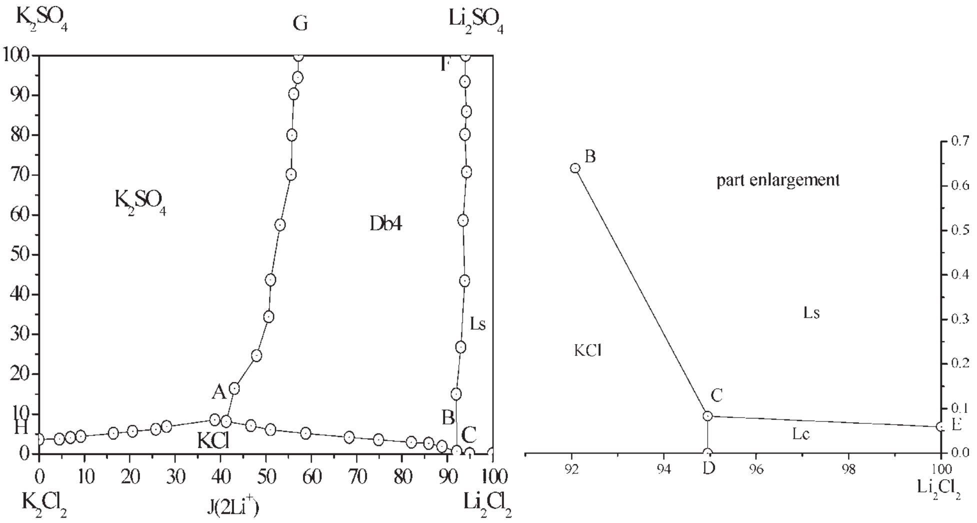


Figure 1. Dry-salt phase diagram of the system ($LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$) at 308.15 K. Arc, K_2SO_4; Syl, KCl; Db4, $Li_2SO_4 \cdot K_2SO_4$; Ls, $Li_2SO_4 \cdot H_2O$; Lc, $LiCl \cdot H_2O$.

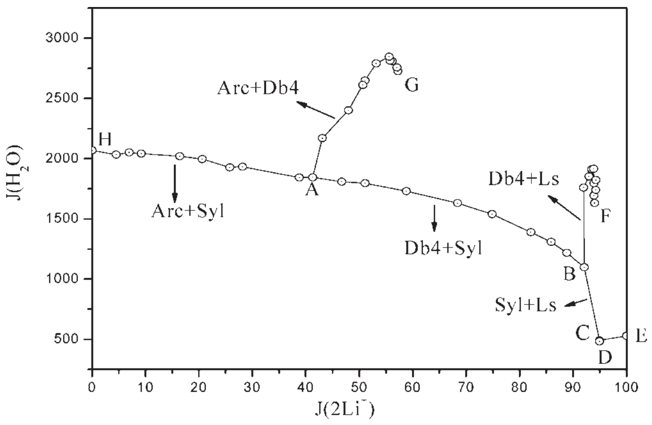


Figure 2. Water-phase diagram of the system ($LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$) at 308.15 K. Arc, K_2SO_4; Syl, KCl; Db4, $Li_2SO_4 \cdot K_2SO_4$; Ls, $Li_2SO_4 \cdot H_2O$.

Analytical Method. The concentration of Cl^- was measured by titration with a standard solution of mercury nitrate in the presence of mixed indicator (diphenyl carbazone, bromothymol, and ethanol) with an uncertainty within ± 0.3 %. The concentrations of K^+ and SO_4^{2-} were determined by the gravimetric methods with uncertainties, all within ± 0.05 %.[21] The concentration of the lithium ion was evaluated according to ion balance.

A PHS-3C precision pH meter supplied by the Shanghai Electromagnetic Instrumentation Manufactory was used to measure the pH of the equilibrium aqueous solutions. The pH meter with an uncertainty of ± 0.01 was calibrated with double standard buffer solutions by mixing potassium dihydrogen phosphate (pH = 6.84) and potassium hydrogen phthalate (pH = 4.02). The densities (ρ) were measured with a specific weighing bottle method with an uncertainty of ± 0.2 mg. The viscosities (η) were determined using an Ubbelohde capillary viscometer. 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. Conductivity (κ) measurements were carried out on a conductivity meter (Orion 145A+) with an uncertainty ± 0.01 $S \cdot m^{-1}$. Measurements of the above physicochemical properties of the equilibrium solutions were made in a thermostat maintained at (308.15 ± 0.1) K. An Abbe refractometer (model 2W) was used to measure the refractive indices (n_D) with an uncertainty of ± 0.0001. All of the measurements were maintained at the desired temperature, (308.15 ± 0.1) K, through control of the thermostat.

RESULTS AND DISCUSSION

The solubility data and the relevant physicochemical property values of the aqueous system at 308.15 K were measured, and the results are listed in Tables 1 and 2, respectively. The symbols of Arc, Syl, Db4, Ls, and Lc in Table 1 stand for K_2SO_4, KCl, $Li_2SO_4 \cdot K_2SO_4$, $Li_2SO_4 \cdot H_2O$, and $LiCl \cdot H_2O$, respectively. On the basis of the Jänecke indices (J, $J/[\text{mol}/100\ \text{mol}(2Li^+ + 2K^+ \text{ or } 2Cl^- + SO_4^{2-})]$) in Table 1, the dry-salt phase diagram and the water-phase diagram of the system at 308.15 K were plotted, as shown in Figures 1 and 2.

The phase diagram of the system ($LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$) in Figure 1 consists of five crystallization zones corresponding to potassium sulfate (K_2SO_4), potassium chloride (KCl), the double salt lithium potassium sulfate ($Li_2SO_4 \cdot K_2SO_4$), lithium sulfate monohydrate ($Li_2SO_4 \cdot H_2O$), and lithium chloride monohydrate ($LiCl \cdot H_2O$), where the double salt lithium potassium sulfate ($Li_2SO_4 \cdot K_2SO_4$) is an incongruent double salt. There are seven univariant curves corresponding to curves AH, AG, AB, BF, BC, CD, and CE, indicating the cosaturation of two salts. In Figure 1, three three-salt cosaturation points, A, B, and C, that is, isothermal invariant points, are $K_2SO_4 + Li_2SO_4 \cdot K_2SO_4 + KCl$, $Li_2SO_4 \cdot K_2SO_4 + KCl + Li_2SO_4 \cdot H_2O$, and $KCl + Li_2SO_4 \cdot H_2O + LiCl \cdot H_2O$, respectively. The crystallization area of potassium sulfate (K_2SO_4) is the largest, and the crystallized zone of lithium chloride monohydrate ($LiCl \cdot H_2O$) is the smallest. These results indicate that potassium sulfate is easy to saturate and crystallize from solution and that lithium chloride has a high solubility during isothermal evaporation.

Figure 2 shows that the Jänecke index values of the H_2O equilibrium curves saturated by the KCl solid phase gradually decrease with increasing $J(2Li^+)$, whereas those of equilibrium

Table 3. Composition and Physicochemical Properties of the Saturated Aqueous Solution of a Single Salt at 308.15 K[a]

no.	comp. liquid phase, $100w_i$	n_D	$10^{-3}\rho$ $\text{kg}\cdot\text{m}^{-3}$	$10^{-3}\eta$ $\text{Pa}\cdot\text{s}$	κ $\text{S}\cdot\text{m}^{-1}$	pH	A_i	B_i
Li_2SO_4	26.5569	1.3793	1.2338	3.6647	9.04	6.85	0.12377	0.81356
K_2SO_4	12.7201	1.3529	1.0980	0.8718	13.46	6.78	0.10648	0.78182
LiCl	46.7818	1.4398	1.2997	12.7617	7.96	5.62	0.16202	0.57307
KCl	28.0632	1.3767	1.1874	0.8426	ND	7.77	0.11040	0.63330

[a] A_i and B^i are the constants of a single salt for the refractive index and density, respectively.

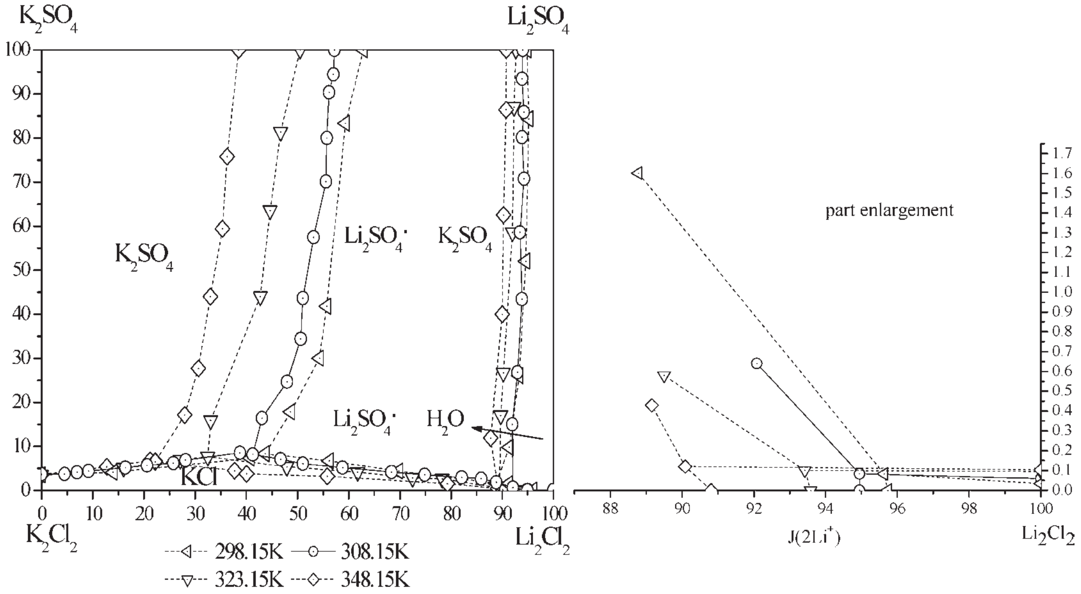


Figure 3. Comparison of the stable phase diagram at 298.15 K, 308.15 K, 323.15 K, and 348.15 K[12,13] and metastable phase diagram at 308.15 K of the quaternary system LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O.

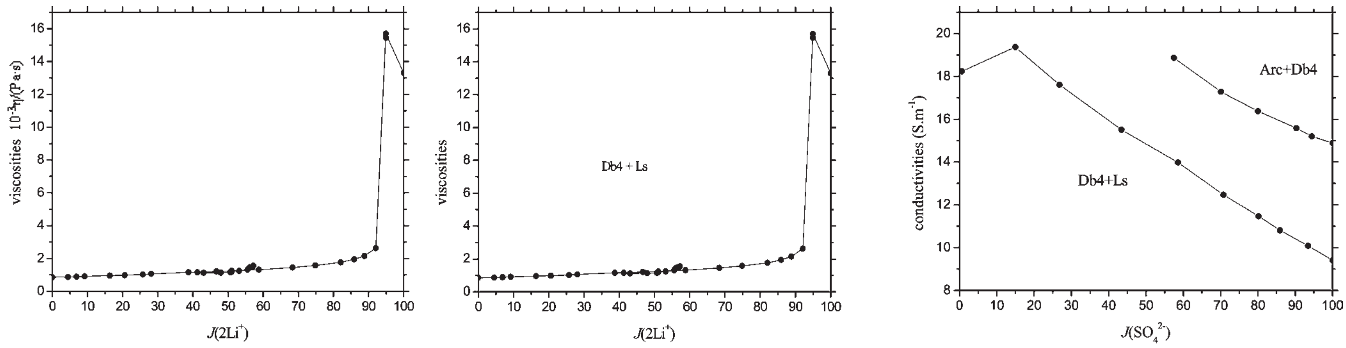
curves AG and BF saturated by the $Li_2SO_4\cdot K_2SO_4$ solid phase increase at first and then decrease with the increasing $J(2Li^+)$.

A comparison of the metastable equilibrium system (LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O) at 308.15 K with the stable equilibrium at 298.15 K, 323.15 K, and 348.15 K[12,13] is shown in Figure 3. The phase diagram of the system obtained from isothermal evaporation at 308.15 K has the same number of crystallization zones, and its position conforms to the moving sequence of stable equilibrium phase diagrams from 298.15 K to 323.15 K to 348.15 K. So it may be concluded that the isothermal evaporation process of aqueous solutions of the system at 308.15 K mainly carries on along the stable equilibrium path.

The physicochemical properties of the equilibrium solutions change regularly with changing lithium or sulfate concentration in the system as shown in Figure 4. Figure 4 parts a and b indicate that the viscosities of the equilibrium aqueous solutions gradually increase with the increase of lithium or sulfate concentration, whereas the conductivities of the equilibrium aqueous solutions have the opposite behavior. The conductivities of the equilibrium aqueous solutions of higher KCl concentration are not determined because they go beyond the maximal determinable range of 20 $\text{S}\cdot\text{m}^{-1}$ of the conductivity meter (Orion 145A+). Figure 4c illustrates the pH values of the equilibrium aqueous solutions are around 7.00 except that the pH values of points saturated by $LiCl\cdot H_2O$ are about 5. As shown in Figure 4d, the refractive indices and densities of the equilibrium aqueous solutions are increasing or decreasing with the increase of lithium or sulfate concentration, and their changing trends are more complex than other physicochemical properties. For example, the densities of the equilibrium aqueous solutions saturated by K_2SO_4 and $Li_2SO_4\cdot K_2SO_4$ decrease at first and then increase after point No. 8 with decreasing lithium concentration. Those are possibly caused by the incongruent double salt $Li_2SO_4\cdot K_2SO_4$, which is gradually transited into the solid phase K_2SO_4 when the Jänecke index values are about 50 of $2Li^+$ in these several points. Distinctly, aqueous solutions saturated by $LiCl\cdot H_2O$ have the maximal refractive indices, densities, and viscosities and minimal conductivities because lithium chloride has a high solubility, strong salting-out effect, and particle association action.

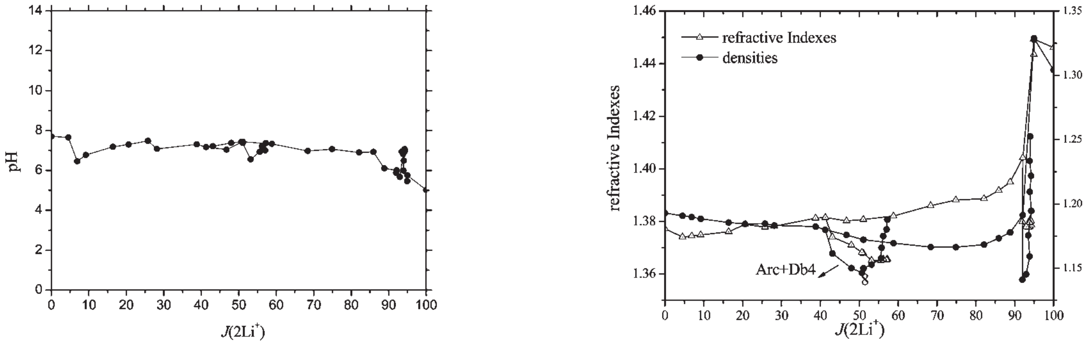
■ CALCULATION SECTION

Calculations of Refractive Indices and Densities of the Equilibrium Aqueous Solutions. Song and Du[22] put forward the calculating equations of refractive indices and densities of salt—water systems containing the lithium ion at 298.15 K. It was discovered that these equations also adapted well to the calculations of refractive indices and densities of the equilibrium aqueous solutions of the system LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O



(a) viscosity vs. composition

(b) conductivity vs. composition



(c) pH value vs. composition

(d) refractive index and density vs. composition

Figure 4. Physicochemical properties versus composition diagrams for the metastable quaternary system LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O at 308.15 K. (a) viscosity vs composition; (b) conductivity vs composition; (c) pH value vs composition; (d) refractive index and density vs composition.

at 308.15 K. Thus, these equations are the following:

$$\ln \frac{n_{308.15}}{n_{\mathrm{w}}^{308.15}} = \sum x_i \cdot A_i$$

$$\ln \frac{\rho_{308.15}}{\rho_{\mathrm{w}}^{308.15}} = \sum x_i \cdot B_i$$

In the above equations, $n_{\mathrm{w}}^{308.15} = 1.3347$ and $\rho_{\mathrm{w}}^{308.15} = 994.06$ $\mathrm{kg \cdot m^{-3}}$ are the refractive index and density of water at 308.15 K, respectively.[23] x_i is the mass fraction of salt i in the equilibrium aqueous solutions of the system. A_i and B_i are the constants of salt i for refractive index and density, respectively, which are obtained according to determined composition and refractive index and density of saturated aqueous solution of single salt i using above equations, as shown in Table 3. The mass fractions x_i of salts of liquid phases of the system are listed in Table 4 for the calculations of refractive indices and densities. All of the calculated results are presented in Table 5 and agree well with experimental values.

■ SOLUBILITY PREDICTION

Ion-Interaction Model. Pitzer and co-workers have developed an ion interaction model and published a series of papers[14,15] which gave 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 et al.[16,17] are more convenient to use in solubility calculations. 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. Additional work has centered on developing variable-temperature models, which will increase the applicability to a number of diverse geochemical systems. The primary focus has been to broaden the models by generating parameters at higher or lower temperatures.[24−26] The necessary model parameters for the activity coefficients of electrolytes in the system at 308.15 K were fit from obtained osmotic coefficients and the ternary subsystems by the multiple and single linear regression methods.

Model Parameterization. The literature[27] reported osmotic coefficients of aqueous LiCl solutions from (0.1 to 18.0) m at 273.15 K, 298.15 K, 323.15 K, 348.15 K, and 373.15 K. Thus osmotic coefficients of aqueous lithium chloride solutions from (0.1 to 18.0) m at 308.15 K may be obtained through the interpolation according to presented osmotic coefficients at other temperatures. Using the above attained osmotic coefficients of aqueous lithium chloride solutions, Pitzer single-salt parameters of $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\varphi)}$ of lithium chloride at 308.15 K are fitted. Single-salt parameters of $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\varphi)}$ of lithium sulfate, potassium sulfate, and potassium chloride, the mixing pair $\theta_{\mathrm{Cl,SO_4}}$, the mixing triplet parameter of $\Psi_{\mathrm{K,Cl,SO_4}}$, and the Debye−Hükel limiting slope $A^{\Phi} = 0.3985$ at 308.15 K are calculated on the basis of the temperature-dependent equation of parameters presented in the literature.[26,28] The mixing triplet parameter of $\Psi_{\mathrm{Li,Cl,SO_4}}$ at 298.15 K is adopted for the prediction of solubilities of the system (LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O) at 308.15 K.[29] The mixing pair $\theta_{\mathrm{Li,K}}$ and two mixing triplet parameters of $\Psi_{\mathrm{Li,K,Cl}}$ and $\Psi_{\mathrm{Li,K,SO_4}}$ are fitted using the reliable solubility data in the relative ternary subsystem at 308.15 K.[12] The obtained Pitzer parameters of the system (LiCl + KCl +

Table 4. Composition of the Liquid Phases in the System $LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$ at 308.15 K for the Calculations of Refractive Index and Density

no.	composition of liquid phase, $100w_i$				equilibrium solid phases [a]
	LiCl	KCl	Li_2SO_4	K_2SO_4	
1,G	0.0	0.0	10.0078	11.8658	Arc+Db4
2	0.4459	0.5302	9.3326	11.2082	Arc+Db4
3	0.7187	0.9813	8.6927	10.7596	Arc+Db4
4	1.9122	1.2929	7.0944	10.5348	Arc+Db4
5	3.1014	1.4762	5.4754	10.3017	Arc+Db4
6	4.3431	2.3966	3.6158	10.1201	Arc+Db4
7	5.3549	4.4861	2.3504	8.8637	Arc+Db4
8	5.3129	7.0849	2.4638	6.1534	Arc+Db4
9	5.8800	9.8278	1.8446	4.7931	Arc+Db4
10	6.0260	13.5486	1.3598	3.3790	Arc+Db4
11,A	6.8748	17.8851	1.0221	1.4938	Arc+Db4+Syl
12,H	0.0	27.4856	0.0	1.2100	Arc+Syl
13	0.5601	26.9809	0.2407	0.8851	Arc+Syl
14	0.8592	26.2444	0.3635	0.8070	Arc+Syl
15	1.1814	25.7712	0.4475	0.7786	Arc+Syl
16	2.3626	23.9155	0.5186	0.9741	Arc+Syl
17	3.1195	22.8147	0.5168	1.1684	Arc+Syl
18	4.0546	21.9461	0.6303	1.2315	Arc+Syl
19	4.4718	21.0172	0.6364	1.4838	Arc+Syl
20	6.4655	18.3762	0.9159	1.8058	Arc+Syl
21,F	0.0	0.0	25.3601	2.5633	Db4+Ls
22	0.7344	1.0511	23.7937	1.3171	Db4+Ls
23	2.3393	0.8436	21.4205	1.3855	Db4+Ls
24	3.4112	0.8415	19.4559	1.4851	Db4+Ls
25	5.2320	0.8339	17.0648	1.3289	Db4+Ls
26	7.1594	1.1917	13.6700	1.1402	Db4+Ls
27	10.3870	0.7002	9.7319	1.5887	Db4+Ls
28	13.7882	1.1435	5.9010	1.5074	Db4+Ls
29	16.8922	1.1559	2.7097	2.0579	Db4+Ls
30,B	27.0262	3.9662	0.1429	0.1610	Db4+Ls+Syl
31	8.0551	16.8612	1.0610	1.0843	Db4+Syl
32	9.1168	15.7148	0.9048	0.9567	Db4+Syl
33	11.1801	13.6736	0.7457	0.9420	Db4+Syl
34	14.0124	11.0727	0.6228	0.8349	Db4+Syl
35	16.3262	9.2280	0.5467	0.7672	Db4+Syl
36	19.6494	7.0948	0.4987	0.6843	Db4+Syl
37	21.7441	5.7227	0.4039	0.7470	Db4+Syl
38	23.9765	4.7676	0.2349	0.6643	Db4+Syl
39,E	47.0581	0.0	0.03596	0.0	Ls+Lc
40,D	45.9912	4.3033	0.0	0.0	Syl+Lc
41,C	45.5678	4.2679	0.0518	0.0	Syl+Ls+Lc

[a] Arc, K_2SO_4; Syl, KCl; Db4, $Li_2SO_4 \cdot K_2SO_4$; Ls, $Li_2SO_4 \cdot H_2O$; Lc, $LiCl \cdot H_2O$.

Table 5. Calculated Refractive Index and Density Data of the System $LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O$ at 308.15 K

no.	n_D			$10^{-3}\ \rho/(kg \cdot m^{-3})$		
	exp.	cal.	relative error	exp.	cal.	relative error
1,G	1.3657	1.3685	0.2050	1.1878	1.1832	−0.3873
2	1.3654	1.3682	0.2051	1.1802	1.1776	−0.2203
3	1.3657	1.3678	0.1538	1.1750	1.1726	−0.2043
4	1.3654	1.3678	0.1758	1.1660	1.1656	−0.03431
5	1.3652	1.3677	0.1831	1.1577	1.1575	−0.01728
6	1.3652	1.3684	0.2344	1.1528	1.1533	0.04337
7	1.3679	1.3698	0.1389	1.1499	1.1521	0.1913
8	1.3682	1.3699	0.1243	1.1463	1.1474	0.09596
9	1.3710	1.3723	0.09482	1.1502	1.1531	0.2521
10	1.3741	1.3754	0.09461	1.1615	1.1640	0.2152
11,A	1.3815	1.3805	−0.07239	1.1798	1.1814	0.1356
12,H	1.3772	1.3776	0.02904	1.1929	1.1943	0.1174
13	1.3741	1.3780	0.2838	1.1907	1.1936	0.2436
14	1.3745	1.3777	0.2328	1.1898	1.1906	0.06724
15	1.3749	1.3778	0.2109	1.1884	1.1898	0.1178
16	1.3761	1.3780	0.13807	1.1856	1.1863	0.05904
17	1.3789	1.3783	−0.04351	1.1844	1.1850	0.05066
18	1.3779	1.3793	0.1016	1.1846	1.1865	0.1604
19	1.3782	1.3792	0.07256	1.1833	1.1848	0.1268
20	1.3813	1.3806	−0.05068	1.1824	1.1842	0.1522
21,F	1.3807	1.3810	0.02173	1.2526	1.2466	−0.479
22	1.3797	1.3798	0.00725	1.2334	1.2322	−0.09729
23	1.3801	1.3791	−0.07246	1.2220	1.2188	−0.2619
24	1.3781	1.3783	0.01451	1.2095	1.2078	−0.1406
25	1.3787	1.3780	−0.05077	1.1947	1.1955	0.06696
26	1.3777	1.3768	−0.0653	1.1756	1.1767	0.09357
27	1.3795	1.3772	−0.1667	1.1592	1.1614	0.1898
28	1.3780	1.3788	0.05806	1.1454	1.1504	0.4365
29	1.3799	1.3811	0.08696	1.1412	1.1460	0.4206
30,B	1.4042	1.4011	−0.2208	1.1914	1.1930	0.1343
31	1.3802	1.3810	0.05796	1.1760	1.1783	0.1956
32	1.3808	1.3812	0.02897	1.1721	1.1743	0.1877
33	1.3821	1.3824	0.02171	1.1695	1.1713	0.1539
34	1.3860	1.3844	−0.1154	1.1664	1.1689	0.2143
35	1.3881	1.3866	−0.1081	1.1663	1.1694	0.2658
36	1.3887	1.3906	0.1368	1.1684	1.1747	0.5392
37	1.3918	1.3931	0.09340	1.1733	1.1782	0.4176
38	1.3950	1.3963	0.09319	1.1779	1.1838	0.5009
39,E	1.4461	1.44051	−0.38682	1.3041	1.30214	−0.15014
40,D	1.4435	1.4448	0.09020	1.3277	1.3296	0.1410
41,C	1.4493	1.4439	−0.3762	1.3289	1.3266	−0.1723

$Li_2SO_4 + K_2SO_4 + H_2O$) at 308.15 K are presented in Table 6. The balance constants K of $Li_2SO_4 \cdot H_2O$ and $LiCl \cdot H_2O$ at 308.15 K are calculated through their solubility data of saturated aqueous solutions in Table 3 and single-salt parameters in Table 6, respectively. The balance constant of KCl is simultaneously acquired when the mixing pair $\theta_{Li,K}$ and mixing triplet parameter of $\Psi_{Li,K,Cl}$ are fitted using the solubility data of the ternary system ($LiCl + KCl + H_2O$) at 308.15 K.[13] The balance constants of K_2SO_4 and $Li_2SO_4 \cdot K_2SO_4$ at 308.15 K are gained according to the solubility data of the cosaturated points of the ternary system ($Li_2SO_4 + K_2SO_4 + H_2O$) in Table 1 and Pitzer parameters in Table 6. These balance constants of equilibrium solid salts of $LiCl \cdot H_2O$, $Li_2SO_4 \cdot H_2O$, KCl, K_2SO_4, and $Li_2SO_4 \cdot K_2SO_4$ correspond to 150 700, 2.701, 8.572, 0.01476, and 0.001211, respectively.

Calculated Solubilities. Using the chemical equilibrium model and the above parameters, the calculated results of the solubility are shown in Figure 5 with dashed lines. It is shown that the calculated

Table 6. Pitzer Parameters of the System LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O at 308.15 K

species	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	θ	Ψ	ref
LiCl	0.2011991	−0.2281616	−0.0040318			this work
KCl	0.053302	0.23159	−0.0013506			26
Li_2SO_4	0.1349971	1.3078500	−0.00472651			28
K_2SO_4	0.070021	0.80718	−0.018800			26
Li^+,K^+				−0.0722246		this work
Cl^-,SO_4^{2-}				0.07000		26
Li^+,Cl^-,SO_4^{2-}					−0.01236	29
K^+,Cl^-,SO_4^{2-}					−0.0028566	26
Li^+,K^+,Cl^-					−0.00310205	this work
Li^+, K^+,SO_4^{2-}					0.00485573	this work

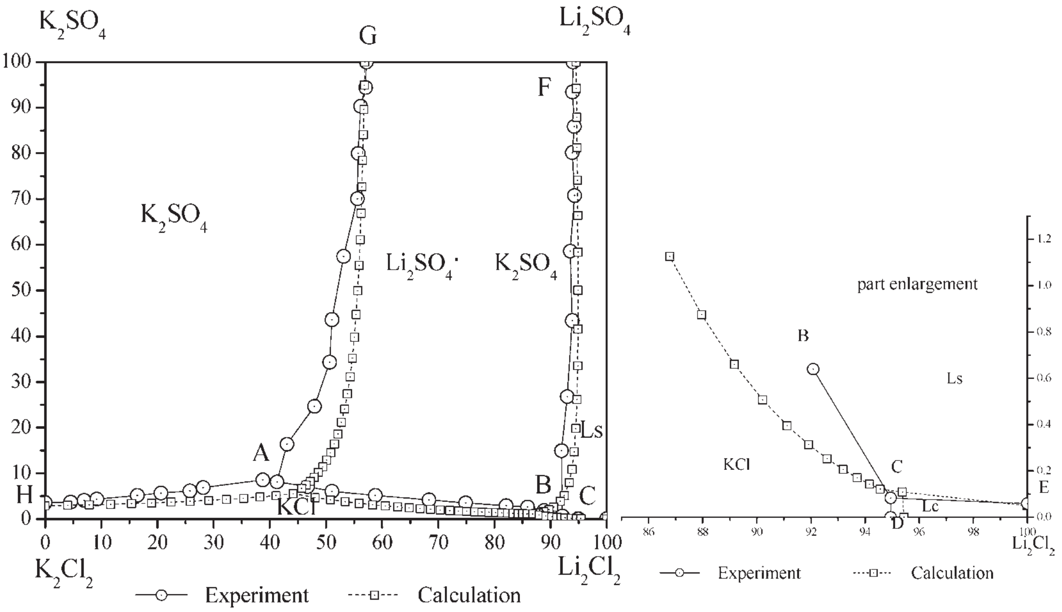


Figure 5. Comparison of the experimental and calculated phase diagram of the system LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O at 308.15 K. Arc, K_2SO_4; Syl, KCl; Db4, $Li_2SO_4\cdot K_2SO_4$; Ls, $Li_2SO_4\cdot H_2O$; Lc, $LiCl\cdot H_2O$.

and the determined values are in good agreement. This means that the parameters fitted in this work are reliable. Especially when the lithium ion is the dominant component in the system, the predictive values using the chemical equilibrium model significantly coincided with experimental values. However, when the liquid composition is located in the univariant curve of K_2SO_4 and $Li_2SO_4\cdot K_2SO_4$, the discrepancy between the predictive values and the experimental measurements is relatively large, as shown in Figure 5 with the dashed line. The possible reason is that the fitted mixing triplet parameter $\Psi_{Li,K,SO4}$ was evaluated from the solubility data of the relative subsystems because of less solubility data and lacking osmotic coefficient data. Further work on the osmotic coefficient data should be carried out to improve the calculated accuracy of the solubility.

CONCLUSIONS

Solubilities and physicochemical properties of the liquid−solid metastable equilibria of the system LiCl + KCl + Li_2SO_4 + K_2SO_4 + H_2O at 308.15 K are determined experimentally. According to the data measured, the experimental metastable phase diagram and the diagrams of physicochemical properties versus composition are constructed for the first time. On the basis of the temperature-dependent equations in the literature, single-salt parameters of lithium sulfate, potassium sulfate, and potassium chloride, the mixing pair $\theta_{Cl,SO4}$, the mixing triplet parameter of Ψ_{K,Cl,SO_4}, and the Debye−Hükel limiting slope A^{Φ} = 0.3985 at 308.15 K are acquired satisfactorily. The single-salt Pitzer parameters of lithium chloride, the mixing pair $\theta_{Li,K}$, and two mixing triplet parameters of $\Psi_{Li,K,Cl}$ and Ψ_{Li,K,SO_4} are fitted at 308.15 K. The balance constants of salts containing lithium in the system at 308.15 K are obtained according to the determined solubilities of subsystems and gained Pitzer parameters. The predictive metastable solubilities with the extended Pitzer model agree well with the experimental data.

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