2488 *J. Chem. Eng. Data* **2008,** *53,* 2488–2492

Solid−Liquid Metastable Equilibria in the Quaternary System ($NaCl + LiCl + CaCl_2 + H_2O$) at 288.15 K

Tianlong Deng* and Dan Li

College of Materials, Chemistry and Chemical Engineering, Chengdu University of Technology, Chengdu 610059, PRC, and Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, PRC

The solubility and the physicochemical properties (densities, viscosities, refractive indices, conductivities, and pH) of the liquid−solid metastable system ($NaCl + LiCl + CaCl_2 + H_2O$) at 288.15 K have been studied using the isothermal evaporation method. On the basis of the experimental data, the dry-salt phase diagram, water phase diagram, and the diagram of physicochemical properties versus composition in the system were plotted. The dry-salt phase diagram of the system includes two three-salt cosaturated points of ($CaCl_2 \cdot 6H_2O + NaCl + CaCl_2 \cdot LiCl \cdot 5H_2O$) and ($LiCl \cdot H_2O + NaCl + CaCl_2 \cdot LiCl \cdot 5H_2O$), five metastable solubility isotherm curves, and four crystallization regions corresponding to sodium chloride (NaCl), lithium chloride monohydrate ($LiCl \cdot H_2O$), calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$), and the double salt $LiCl \cdot CaCl_2 \cdot 5H_2O$. No solid solution was found. It was found that the physicochemical properties in the metastable equilibrium solution change regularly with increasing $CaCl_2$ concentration.

Introduction

There are more than 700 salt lakes, each with an area larger than 1 km^2, on the Qinghai-Tibet Plateau of China, and brines with high concentrations of potassium and boron are widely distributed in the Qaidam Basin of the Qinghai-Tibet Plateau. Recently, a huge store of oilfield brine was also discovered in the Nanyishan section of the Qaidam Basin. The hydrochemistry of the oilfield brine is of the calcium chloride type with high concentrations of sodium, potassium, lithium, borate, and calcium.[1] The oilfield brine largely consists of the complex seven-component system ($Li + Na + K + Ca + Cl + SO_4 + B_4O_7 + H_2O$).

Although the oilfield brine resources are very valuable, nothing has been reported on their potential utilization because of a lack of data on the relative solubilities and phase diagrams of the calcium-bearing systems, especially thermodynamic data on metastable equilibria.[2] To exploit these stores of brine, it is essential to make use of local climatic resources such as wind and solar energy for solar pond techniques. The climate in the region of the Qaidam Basin is windy with little rainfall and thus provides great evaporating capacity.[3] According to the statistical data from 1971 to 2000, the temperature of the brine in the Qaidam Basin from May to October in a year is between (285.35 and 291.05) K, and the average temperature is 288.15 K. Therefore, the metastable phase equilibrium, which was determined in the laboratory under conditions similar to those that occur naturally, can objectively describe the interactions among the brine minerals and reveal the crystallization path of the various salts.

The quaternary system ($NaCl + LiCl + CaCl_2 + H_2O$) is a subsystem of the seven-component system. Although the stable phase equilibria of the ternary and quaternary subsystem at 298.15 K[4,5] and the metastable quaternary systems ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K[6] and ($LiCl + MgCl_2 + Li_2SO_4 + MgSO_4 + H_2O$) at 298.15 K[7] have been previously reported, there are no reports in the literature concerning either the stable or metastable equilibria of the quaternary system at 288.15 K. In this article, the metastable solubilities and physicochemical properties of the quaternary system ($NaCl + LiCl + CaCl_2 + H_2O$) at 288.15 K are presented.

Experimental Section

Apparatus and Reagents. The isothermal evaporation equipment was designed in our laboratory. In an air-conditioned laboratory, a thermally insulated box (70 cm long, 65 cm wide, 60 cm high) was fitted with an electric fan to control the temperature. The control system consisted of three parts: an electric relay, an electrical contact thermograph, and heating lamps. When the solution temperature in the vessel was below 288.15 K, the apparatus for controlling the temperature formed a circuit, and the heating lamps began to heat. Conversely, the circuit was broken and the heating lamps stopped working when the temperature rose above 288.15 K. By this means, the solution temperature in the container could always be kept at (288.15 ± 0.2) K. The electric fan installed in the box can accelerate the rate of evaporation of the solutions. The crystals of the solid phase were analyzed with an XP-300 digital polarizing microscope (Shanghai Caikon Optical Instrument, China) and with an X-ray diffractometer (X'pert PRO, Spectris. Pte., The Netherlands). A thermostat, which can automatically control the temperature, ensured that all physicochemical parameters were strictly measured at (288.15 ± 0.1) K.

The chemicals used were of analytical purity grade and were recrystallized before use. They were all obtained from Tianjin Kermel Chemical Reagent: sodium chloride (NaCl, 99.5 mass %), lithium chloride (LiCl, 99.5 mass %), and calcium chloride ($CaCl_2 \cdot 2H_2O$, 98 mass %). Doubly deionized water (DDW) with conductivity of less than $1.0 \cdot 10^{-4}$ $S \cdot m^{-1}$ (pH 6.60) was used to prepare the series of artificial brines and for chemical analysis.

Experimental Methods. The isothermal evaporation method was used in this study. Depending on the phase equilibrium

---

* Corresponding author. E-mail: tldeng@isl.ac.cn. Tel/Fax: +86-971-6363276.

10.1021/je8000798 CCC: $40.75

Table 1. Solubility Data of the Metastable Quaternary System ($NaCl + LiCl + CaCl_2 + H_2O$) at 288.15 K

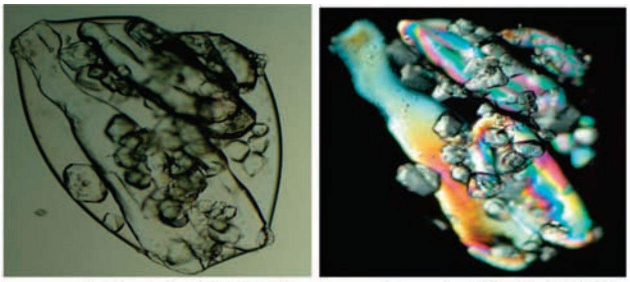
	composition of liquid phase			composition of liquid phase				
	w/mass %			g/100 g dry salt				
no.	$CaCl_2$	LiCl	NaCl	$CaCl_2$	LiCl	NaCl	H_2O	equilibrium solid phase[a]
1,E_1	40.53	0.00	0.32	99.22	0.00	0.78	144.80	NC + C6
2	40.17	0.48	0.19	98.36	1.18	0.46	144.86	NC + C6
3	39.98	0.79	0.37	97.18	1.92	0.90	143.07	NC + C6
4	39.93	0.90	0.33	97.00	2.20	0.80	142.95	NC + C6
5	39.74	0.69	1.66	94.41	1.63	3.96	137.59	NC + C6
6	39.22	0.74	2.81	91.69	1.72	6.59	133.81	NC + C6
7	35.54	4.96	2.58	82.50	11.53	5.98	132.13	NC + C6
8	32.74	8.69	1.06	77.05	20.45	2.49	135.35	NC + C6
9	32.54	8.27	1.59	76.74	19.51	3.75	135.85	NC + C6
10	31.33	10.36	0.18	74.82	24.74	0.44	138.83	NC + C6
11,E	32.04	11.11	1.53	71.71	24.86	3.43	123.81	NC + C6 + G
12	30.782	12.13	2.04	68.48	26.98	4.54	122.47	C6 + G
13	9.30	16.60	1.24	62.15	35.22	2.63	110.08	C6 + G
14,E_2	30.27	18.35	0.00	60.93	39.07	0.00	112.94	LC + G
15,E_3	26.63	24.45	0.00	52.13	47.87	0.00	95.77	LC + G
16	23.53	19.62	1.58	52.59	43.86	3.54	123.14	LC + G
17	23.72	19.76	1.18	53.11	44.24	2.64	117.04	LC + G
18	26.79	28.03	1.48	47.58	49.80	2.62	85.65	LC + G
19	22.27	27.97	0.50	41.22	55.05	3.73	108.26	LC + G
20	16.60	31.73	2.41	32.71	62.53	4.76	100.12	LC + G
21	15.06	32.21	1.95	30.60	65.45	3.95	103.37	LC + G
22	14.96	35.00	0.90	29.42	68.8	1.78	99.14	LC + G
23,F	13.68	35.56	1.25	27.09	70.43	2.48	98.44	LC + NC + G
24	13.49	22.84	4.62	32.95	55.77	11.28	140.24	NC + G
25	15.11	17.90	6.44	38.90	44.52	16.57	127.25	NC + G
26	25.46	14.57	6.65	54.55	31.2	14.25	168.77	NC + G
27	30.10	13.67	6.26	60.17	27.33	12.50	118.07	NC + G
28,E_4	0.00	42.93	2.17	0.00	95.18	4.82	122.45	LC + NC
29	1.65	41.55	1.70	3.68	92.52	3.80	122.09	LC + NC
30	1.93	40.55	1.81	4.36	91.55	4.09	122.04	LC + NC
31	3.22	33.70	2.03	8.27	86.52	5.21	134.30	LC + NC
32	9.51	35.98	2.12	19.97	75.58	5.42	117.36	LC + NC
33	11.96	33.26	2.82	24.90	69.24	5.86	133.06	LC + NC

[a] NC, NaCl; LC, $LiCl \cdot H_2O$; C6, $CaCl_2 \cdot 6H_2O$; G, $CaCl_2 \cdot LiCl \cdot 5H_2O$.

composition, the appropriate quantity of salts and DDW were calculated and mixed in clean polyethylene containers (15 cm in diameter, 6 cm high). After the salts had completely dissolved, the containers were put into the box for isothermal evaporation at (288.15 ± 0.2) K. The evaporation conditions were controlled by air flow at a velocity of (3.5 to 4.0) $m \cdot s^{-1}$, relative humidity of (20 to 30) %, and an evaporation rate of (4 to 6) $mm \cdot d^{-1}$. The conditions are reflective of those of the Qaidam Basin. Because of the metastable equilibrium, the solutions were kept without stirring for the entire evaporation process. The crystalline solid phase was periodically examined. When enough new solid phase had appeared, the wet residue was separated. One part of the solid phase was quantitatively dissolved in water and analyzed by chemical methods. The other part was dried slightly at (288.15 ± 0.2) K and was then analyzed with an XP-300D digital polarizing microscope and by X-ray diffraction. The composition of the liquid phase was analyzed by chemical methods. A 5.0 mL sample of the clarified solution from the liquid phase was taken with a pipet. This sample was filtered and diluted to 250.0 mL final volume in a volumetric flask filled with DDW to determine the concentration of the liquid-phase components. Other samples were taken from the containers in the same way and were used to measure the corresponding physicochemical properties. The remainder of the solution was allowed to evaporate and to reach a new metastable equilibrium.

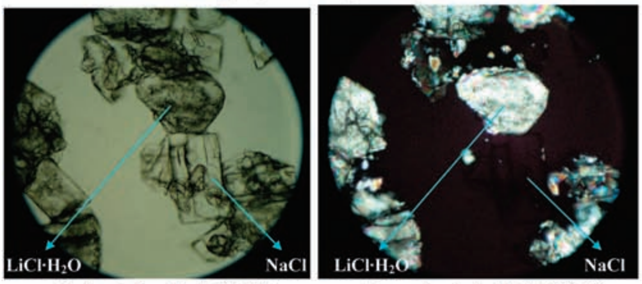
Analytical Methods. The concentration of Li^+ was measured in triplicate by ICP-AES (IRIS Intrepid ICP, Thermo Electron). The average deviation of the determination was less than ± 0.5 %. The Ca^{2+} ion concentration was determined by our previous modified titration with EDTA standard solution in the presence of alkali and Ca indicator. The uncertainty was less than ± 0.3 %.[8] The Cl^- ion concentration was measured by titration with hydrargyrum nitrate standard solution in the presence of a mixed indicator of diphenylcarbazone and bromophenol blue (uncertainty ± 0.3 %),[9] and the Na^+ ion concentration was evaluated using an ion balance combined with analytical verification using graphite furnace atomic absorption spectroscopy (GF-AAS, PE AA600, Perkin-Elmer).

The liquid-phase physicochemical properties including density, viscosity, conductivity, refractive index, and pH were measured. The pH value was measured with a PHS-3C precision pH meter supplied by Shanghai Precision & Scientific Instrument with a precision of ± 0.01. The pH meter was calibrated with standard buffer solutions that were prepared by the mixing agents of either potassium dihydrogen phosphate and sodium dihydrogen phosphate (pH 6.84) or borax (pH 9.18). The densities (ρ) were measured by a density bottle method with a precision of ± 0.2 mg. The viscosities (η) were determined using an Ubbelohde capillary viscometer, which was placed in a thermostat that electronically controlled the set temperature to (288.15 ± 0.1) K. At least five flow times for each equilibrium liquid-phase solution were measured. A stopwatch with a precision of 0.1 s was used to determine the flow time, and the results were averaged. The uncertainty of the flow time measurements was ± 0.2 s. An Abbe refractometer (model WZS-1) was used to measure the refractive index (n_D) with a precision of ± 0.0001. The conductivities (κ) were measured



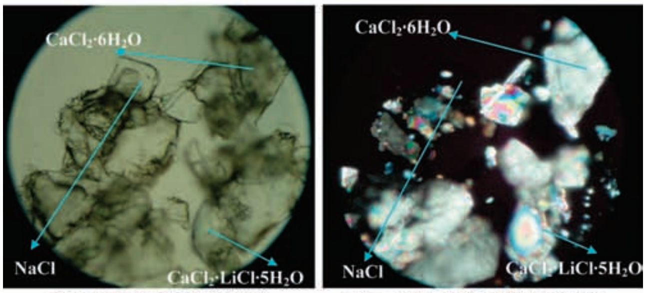
single polarized light (4×10) orthogonal polarized light (4×10)

(a) Crystals of $CaCl_2 \cdot LiCl \cdot 5H_2O$



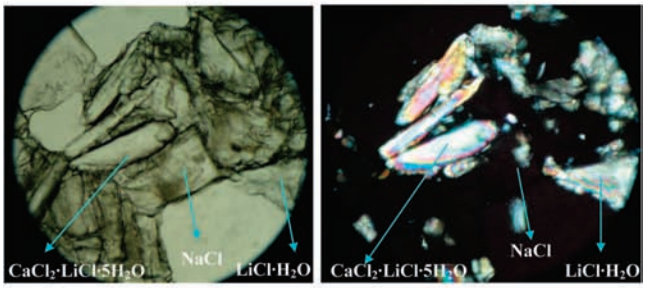
single polarized light (10×10) orthogonal polarized light (10×10)

(b) Crystals of $LiCl \cdot H_2O + NaCl$



single polarized light (10×10) orthogonal polarized light (10×10)

(c) invariant point E ($NaCl + CaCl_2 \cdot LiCl \cdot 5H_2O + CaCl_2 \cdot 6H_2O$)



single polarized light (10×10) orthogonal polarized light (10×10)

(d) invariant point F ($LiCl \cdot H_2O + NaCl + CaCl_2 \cdot LiCl \cdot 5H_2O$)

Figure 1. Identification of the invariant points for the solid phase in the reciprocal system with polarized microscopy using an oil-immersion method. (a) Crystals of $CaCl_2 \cdot LiCl \cdot 5H_2O$, (b) crystals of $LiCl \cdot H_2O + NaCl$, (c) the invariant point E ($NaCl + CaCl_2 \cdot LiCl \cdot 5H_2O + CaCl_2 \cdot 6H_2O$), and (d) the invariant point F ($LiCl \cdot H_2O + NaCl + CaCl_2 \cdot LiCl \cdot 5H_2O$).

on a conductivity meter (Orion 145A+) with a precision of ± 0.001 $S \cdot m^{-1}$. All of the measurements were maintained at (288.15 ± 0.1) K through control of the thermostat.

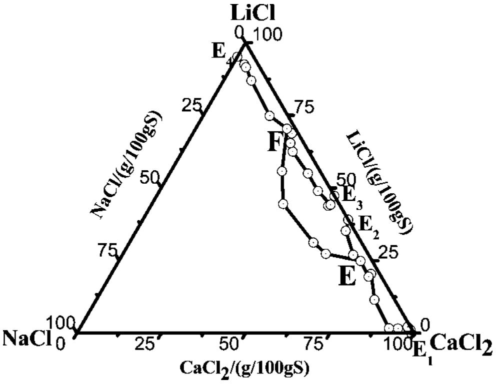


Figure 2. Metastable phase diagram of the quaternary system ($NaCl + LiCl + CaCl_2 + H_2O$) at 288.15 K.

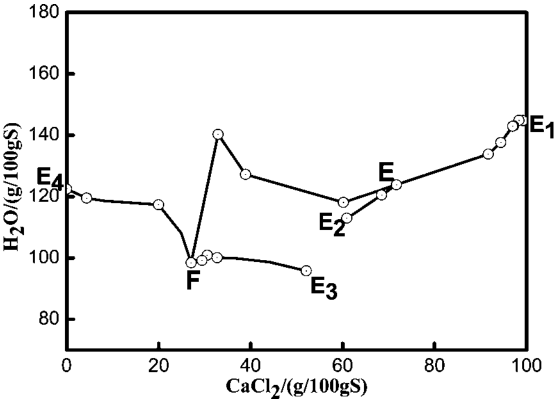
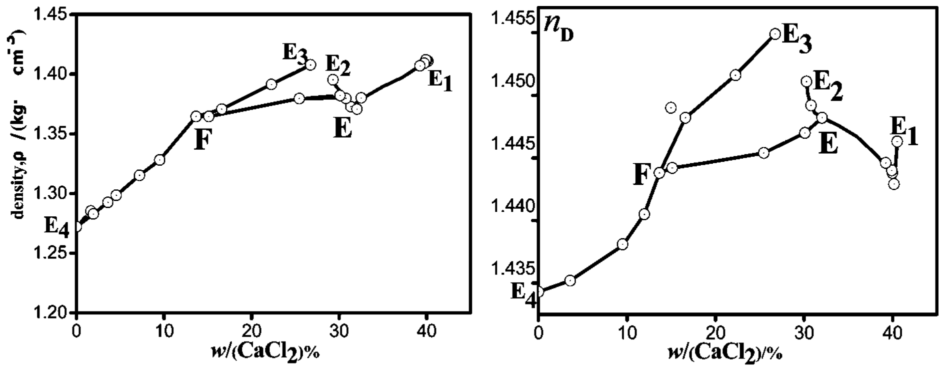


Figure 3. Water phase diagram of the system ($NaCl + LiCl + CaCl_2 + H_2O$) at 288.15 K.

Results and Discussion

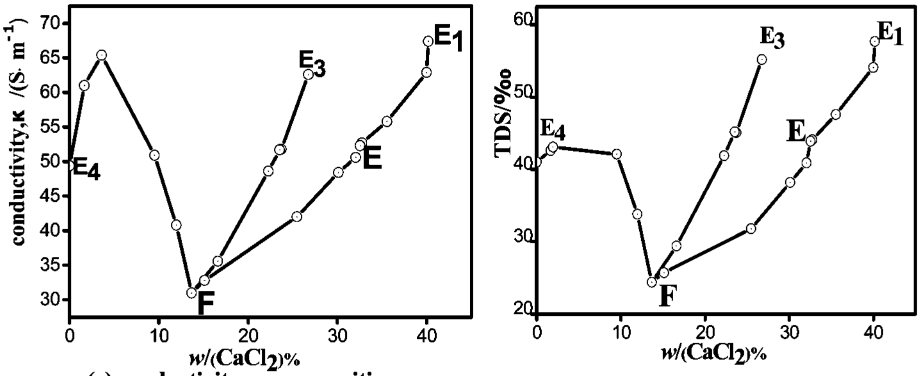
For the mineral identification, when enough new solid phase appeared, the wet residue mixtures were taken from the solution according to the experimental method. First, the optical properties of the double salt $CaCl_2 \cdot LiCl \cdot 5H_2O$ that existed in the quaternary system were identified using an oil-immersion method: a biaxial crystal (the dual optical negative crystal (i.e., $2\nu(-)$)), a small optic axial angle of 40° to 50°, and a refractive index of $Nm < 1.5228$. The refractive index of this double salt is difficult to determine exactly because the salt easily slakes, even in air. The crystal photographs of the single and orthogonal polarized light for $CaCl_2 \cdot LiCl \cdot 5H_2O$ are shown in Figure 1a. The maximum absorption peak of this double salt is about 32.0, whereas $2\theta = 0.09$ and $d = 2.8$ to 2.9 for the X-ray powder analysis. However, the crystal of lithium chloride monohydrate ($LiCl \cdot H_2O$) belongs to an optic uniaxial crystal, as in the tetragonal bipyramid and artificial synthesis types: a dual optical positive crystal (i.e., $2\nu(+)$), a refractive index of $Nm = 1.5815$ to 1.5820, and an optic axial angle of 75° (Figure 1b). The minerals NaCl and $CaCl_2 \cdot 6H_2O$ can be directly identified through the properties of the different refractive index values. Observed with XP-300D digital polarizing microscopy using an oil-immersion method, the crystal photographs of single and orthogonal polarized light on representative solid phases in the invariant points E ($NaCl + CaCl_2 \cdot LiCl \cdot 5H_2O + CaCl_2 \cdot 6H_2O$) and F ($NaCl + LiCl \cdot H_2O + CaCl_2 \cdot LiCl \cdot 5H_2O$) are presented in Figure 1c,d.

The experimental results for the solubilities and the relevant physicochemical properties of the metastable equilibria of the quaternary system ($NaCl + LiCl + CaCl_2 + H_2O$) at 288.15 K are presented in Tables 1 and 2. The ionic concentrations in the metastable equilibrium solutions are expressed as mass fractions. From the experimental data in Table 1, the experimental metastable phase diagram of the system at 288.15 K is presented in Figure 2. The phase diagram of the quaternary system in Figure 2 consists of four crystallization fields, two invariant points (points E and F), and five univariant curves. Points E and F are the invariant points of three cosaturated solid phases ($NaCl + CaCl_2 \cdot LiCl \cdot 5H_2O + CaCl_2 \cdot 6H_2O$) and (NaCl



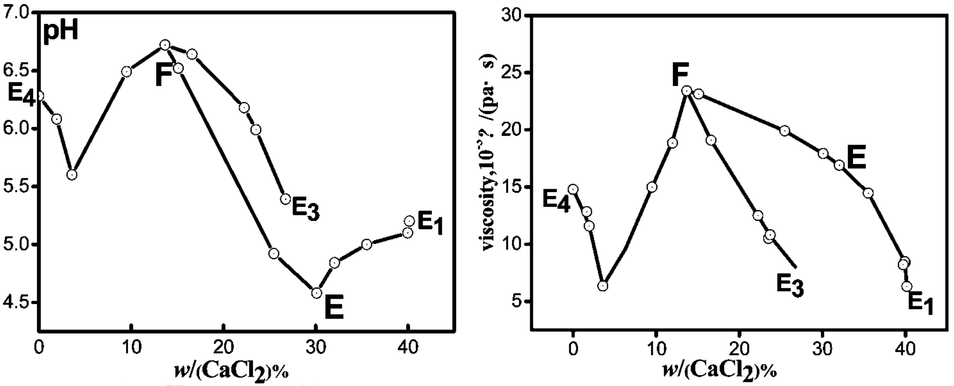
(a) density vs. composition

(b) n_D vs. composition



(c) conductivity vs. composition

(d) TDS vs. composition



(e) pH vs. composition

(f) viscosity vs. composition

Figure 4. Physicochemical properties versus composition for the metastable quaternary system (NaCl + LiCl + $CaCl_2$ + H_2O) at 288.15 K. ○, experimental value; —, experimental relationship diagram. (a,b,c,d,e,f) Density, refractive index, conductivity, TDS, pH, and viscosity, respectively, versus composition.

+ $LiCl \cdot H_2O$ + $CaCl_2 \cdot LiCl \cdot 5H_2O$) with compositions of $CaCl_2$, LiCl, and NaCl (in mass %) in the liquid phase of 32.04, 11.11, 1.53, and 13.68, 35.56, and 1.25, respectively. The five-univariant solubility isotherm curves correspond to E_1E (NaCl + $CaCl_2 \cdot 6H_2O$), E_2E ($CaCl_2 \cdot LiCl \cdot 5H_2O$ + $CaCl_2 \cdot 6H_2O$), EF (NaCl + $CaCl_2 \cdot LiCl \cdot 5H_2O$), E_3F ($CaCl_2 \cdot LiCl \cdot 5H_2O$ + $LiCl \cdot H_2O$), and E_4F (NaCl + $LiCl \cdot H_2O$). The four crystallization regions correspond to sodium chloride (NaCl), lithium chloride monohydrate ($LiCl \cdot H_2O$), calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$), and the double salt $LiCl \cdot CaCl_2 \cdot 5H_2O$. No solid solution was found in the system. The crystal region of sodium chloride is the largest, which indicates that NaCl is of low solubility, and the areas of the crystallization zones decrease in the order of $CaCl_2 \cdot LiCl \cdot 5H_2O$, $CaCl_2 \cdot 6H_2O$, and $LiCl \cdot H_2O$. The water phase diagram of the system at 288.15 K is shown in Figure 3. It shows that the values of H_2O (grams per 100 g dried salts, i.e., g/100 g·S) gradually change with increasing $CaCl_2$ (g/100 g·S). At the invariant points E and F, the water phase values reach the singularity values. On the cosaturated line of EF (i.e., NaCl + $CaCl_2 \cdot LiCl \cdot 5H_2O$) the value of H_2O (g/100 g·S) in Figure 3 increases sharply to reach a peak and then decreases gradually to point E.

On the basis of the data in Table 2, relationships of the physicochemical properties of the solution including densities, viscosities, refractive indices, conductivities, TDS (total dissolved salt), and pH with the salt concentration values are shown in Figure 4. It is found that the physicochemical properties of the equilibrium solution change smoothly with the change in calcium chloride concentration in the system. The densities and refractive indices of the aqueous solutions gradually increase with increasing calcium chloride concentration and reach the singularity values at the cosaturation points in Figure 4a,b. A similar change in behavior between conductivities and TDS as well as between pH values and viscosities in the liquid phase

Table 2. Physicochemical Property Data of the Quaternary System ($NaCl + LiCl + CaCl_2 + H_2O$) at 288.15 K

			conductivity	viscosity	density	
			κ	$10^{-3}\eta$	ρ	
no.[a]	pH	n_D	$S \cdot m^{-1}$	pa·s	$kg \cdot cm^{-3}$	TDS/‰
1,E_1	ND[b]	1.4463	ND	ND	ND	ND
2	5.20	1.4429	67.4	6.2970	1.4108	57.7
3	5.10	1.4438	62.9	8.4000	1.4112	54.1
4	5.00	1.4452	85.0	8.4703	1.4119	58.7
5	4.81	1.4429	69.4	8.1955	1.4091	59.7
6	ND	1.4446	ND	ND	1.4069	ND
7	5.00	ND	55.8	14.4526	ND	47.6
8	6.05	1.4408	52.7	6.0053	1.3839	47.8
9	6.46	1.4399	52.3	6.4112	1.3800	43.9
10	5.00	1.4381	62.9	8.4382	1.3727	53.3
11,E	4.84	1.4482	50.6	16.9022	1.3707	40.9
12	ND	1.4432	ND	ND	1.3797	ND
13	ND	1.4481	ND	ND	1.3952	ND
14,E_2	ND	1.4511	ND	ND	1.4082	ND
15,E_3	5.39	1.4549	ND	ND	1.4077	ND
16	5.99	1.4388	51.8	10.5068	1.3519	45.2
17	4.70	1.4400	51.7	10.8077	1.3544	45.1
18	5.92	1.4650	15.88	ND	1.4605	12.1
19	6.18	14516	48.6	12.4966	1.3913	41.9
20	6.64	1.4482	35.6	19.0757	1.3707	29.4
21	ND	1.4438	ND	ND	1.3543	ND
22	ND	1.4490	ND	ND	ND	ND
23,F	6.72	1.4438	31.0	23.4067	1.3645	24.4
24	ND	ND	ND	ND	ND	ND
25	6.52	1.4442	32.8	23.1584	1.3645	25.7
26	4.92	1.4454	42.0	19.9702	1.3795	31.8
27	4.58	1.4470	48.4	17.8079	1.3820	38.2
28,E_4	6.28	1.4343	49.4	14.7810	1.2922	41.0
29	6.88	1.4313	61.0	12.8415	1.2853	42.6
30	6.08	1.4298	51.1	11.5881	1.2829	43.1
31	5.60	1.4360	65.4	6.3502	1.2925	70.3
32	6.49	1.4361	50.9	14.9817	1.3281	42.1
33	7.14	1.4405	40.8	18.8492	1.4934	33.8

[a] The number order corresponds with Table 1. [b] ND, not detected.

exists. Cosaturation point F, in contrast with the trend for the conductivities and TDS of the aqueous solutions, is the lowest, whereas maximum values occur for pH values and viscosities in Figure 4 from c to f.

Conclusions

The solubilities and physicochemical properties of the liquid−solid metastable quaternary system ($NaCl + LiCl + CaCl_2 + H_2O$) at 288.15 K were determined experimentally. According to the data, the experimental metastable phase diagram and the variation of the physicochemical properties with composition were constructed for the first time. The phase diagram of the system includes two three-salt cosaturated points, five metastable solubility isotherm curves, and four crystallization regions that correspond to sodium chloride, lithium chloride monohydrate, calcium chloride hexahydrate, and the double salt $LiCl \cdot CaCl_2 \cdot 5H_2O$. No solid solution was found.

Acknowledgment

We thank Professor Z. H. Gao of the Institute of Qinghai Salt Lake for his kind help. Thanks also go to the Editor and anonymous reviewers for their active comments on the manuscript.

Literature Cited

(1) Fu, J. L.; Yu, S. S.; Li, S. J.; Ren, H. Y. Development availability for tertiary oil-field brine resources in the west of Qaidam basin. *J. Salt Lake Res.* **2005**, *13*, 17–21.

(2) Deng, T. L. Phase equilibrium for the aqueous system containing lithium, sodium, potassium, chloride, and borate ions at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 1295–1299.

(3) Zheng, X. Y.; Tang, Y.; Xu, C. *Tibet Saline Lake*; Science Press: Beijing, 1988; p 169.

(4) Smits, A.; Elgersma, J.; Hardenberg, M. *Recl. Trav. Chim Pays−Bas* **1924**, *43*, 674.

(5) Kindyakov, P. S.; Kyshtymova, E. A.; Ronova, S. T. *Tr. Mosk. Inst. Tonkoi Khim. Tekhnol.* **1958**, *7*, 32.

(6) Deng, T. L.; Wang, S. Q.; Sun, B. Metastable phase equilibrium in the aqueous quaternary system ($KCl + K_2SO_4 + K_2B_4O_7 + H_2O$) at 308.15 K. *J. Chem. Eng. Data* **2008**, *53*, 411–414.

(7) Guo, Z. Z.; Liu, Z. Q.; Chen, J. Q. Metastable phase equilibria of the quaternary system ($Li-Mg-Cl-SO_4-H_2O$) at 298.15 K. *Chin. J. Chem. Acta* **1991**, *49*, 937–943.

(8) Li, D.; Li, D. C.; Sun, B.; Deng, T. L. Titration method for calcium ion measurement in brine systems with large amounts of lithium ion coexisted. *Chem. World* **2007**, *35*, 398–402.

(9) Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. *Analytical Methods of Brines and Salts*, 2nd ed.; Science Press: Beijing, 1988.

Received for review February 1, 2008. Accepted September 19, 2008. We thank the State Key Program of National Natural Science of China (grant 20836009), the National Natural Science Foundation of China (grant 40773045), the “A Hundred Talents Program” of the Chinese Academy of Sciences (grant 0560051057), and the Specialized Research Fund for the Doctoral Program of Chinese Higher Education (grant 20060616004) for financial support.

JE8000798