Articles

Metastable Phase Equilibrium in the Reciprocal Quaternary System (NaCl + $MgCl_2$ + Na_2SO_4 + $MgSO_4$ + H_2O) at 273.15 K

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Experimental studies on the metastable solubilities and the physicochemical properties (density, refractive index, conductivity, and pH value) in the aqueous reciprocal quaternary system (NaCl + $MgCl_2$ + Na_2SO_4 + $MgSO_4$ + H_2O) at 273.15 K were determined with the isothermal evaporation method. According to the experimental results, the dry-salt-phase diagram, water-phase diagram, and physicochemical properties versus composition diagrams were plotted. It was found that there are two three-salt cosaturated points, five metastable solubility isotherm curves, and four metastable crystallization fields corresponding to sodium chloride, epsomite, mirabilite, and bischofite. Neither solid solutions nor double salts were found. On the basis of Pitzer's semiempirical equation for a mixed aqueous electrolytic solution, the extended HW model (Harvie and Meare) and the temperature-dependent equation were used for fitting the Pitzer single-salt parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ} for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$, the mixing ion-interaction parameters $\theta_{\mathrm{Na,Mg}}$, $\theta_{\mathrm{Cl,SO4}}$, $\Psi_{\mathrm{Na,Mg,Cl}}$, $\Psi_{\mathrm{Na,Mg,SO4}}$, $\Psi_{\mathrm{Na,Cl,SO4}}$, and $\Psi_{\mathrm{Mg,Cl,SO4}}$, and the Debye−Hückel parameter A^{ϕ} in the system at 273.15 K, which are not reported in the literature. In addition, the average equilibrium constants of metastable equilibrium solids at 273.15 K were obtained with the method of the activity product constant. The prediction of solubilities for the reciprocal quaternary system are then demonstrated. A comparison between the calculated and experimental results shows that the predictive solubilities obtained with the extended HW model agree well with experimental data.

Introduction

Salt lakes are widely distributed in the west of China, especially in the area of the Qinghai-Xizang (Tibet) Plateau. Salt Lakes of the Qaidam Basin consist of a series of lakes including Dong-xi-tai Lake, Da-xiao-chaidan Lake, and Yiliping Lake and are a subtype of magnesium sulfate brines famous for their abundance of lithium, potassium, magnesium, and boron resources.[1] The natural salt lake brines are mostly similar with the seawater system. The climate conditions in the region of the Qaidam Basin are generally windy, arid, little rainfall, and great evaporating capacity. To economically exploit the brine and mineral resources, it is important to adequately adopt the local natural resources such as the energy of the wind and sun, i.e., solar pond techniques. Therefore, metastable phase equilibrium research is essential to predict the crystallized path of evaporation of the salt lake brine. Although the metastable equilibrium of the seawater system (Na + K + Mg + Cl + SO_4 + H_2O) from (293.15 to 373.15) K has been reported,[2−5] the reciprocal quaternary system (NaCl + $MgCl_2$ + Na_2SO_4 + $MgSO_4$ + H_2O) at 273.15 K is not reported in the literature to describe the metastable behavior. The average temperature in winter in the Qaidam Basin is about 273.15 K, so the metastable phase equilibrium of this quaternary system at 273.15 K is essentially needed to separate and purify the minerals of mirabilite or epsomite through the temperature effect.

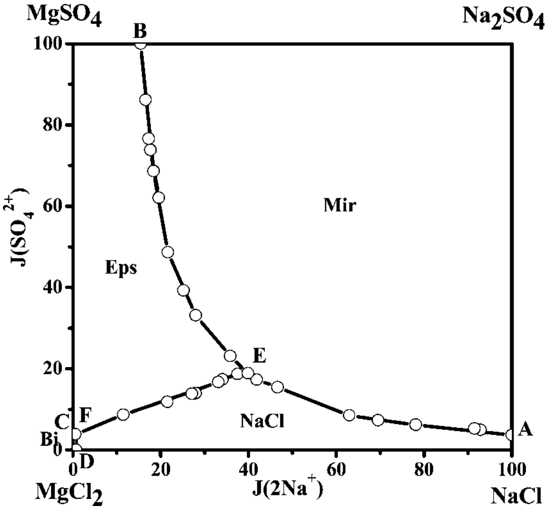

Figure 1. Metastable equilibrium phase diagram for the quaternary system (NaCl + $MgCl_2$ + Na_2SO_4 + $MgSO_4$ + H_2O) at 273.15 K. ○, experimental value; —, experimental isotherm curve; Mir, $Na_2SO_4\cdot10H_2O$; Eps, $MgSO_4\cdot7H_2O$; Bi, $MgCl_2\cdot6H_2O$.

Because the solubilities of salts in a multicomponent salt−water system are generally a few molal, it is necessary to use a reliable

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Table 1. Metastable Equilibrium Solubility of the Reciprocal Quaternary System ($NaCl + MgCl_2 + Na_2SO_4 + MgSO_4 + H_2O$) at 273.15 K

	composition of liquid phase w_b (mass %)				Jänecke index J_b/[mol/100 mol dry salt]			
no.	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	$2Na^+$	SO_4^{2-}	H_2O	equilibrium solid phase[a]
1,A	10.48	0.00	15.57	0.80	100	3.67	1781.55	NaCl + Mir
2	9.86	0.40	15.56	1.09	92.88	4.91	1757.89	NaCl + Mir
3	9.73	0.48	15.55	1.16	91.48	5.21	1753.19	NaCl + Mir
4	8.32	1.23	15.42	1.37	78.10	6.16	1764.41	NaCl + Mir
5	7.55	1.75	15.53	1.65	69.51	7.27	1727.76	NaCl + Mir
6	6.89	2.14	15.42	1.94	63.01	8.51	1719.20	NaCl + Mir
7	5.36	3.24	14.99	3.71	46.65	15.43	1614.00	NaCl + Mir
8	4.84	3.55	14.74	4.18	41.88	17.29	1605.00	NaCl + Mir
9,E	4.65	3.71	14.60	4.59	39.88	18.85	1585.24	NaCl + Mir + Eps
10	4.36	3.83	14.55	4.53	37.54	18.70	1599.75	NaCl + Eps
11	4.00	4.10	14.98	4.25	34.07	17.33	1578.73	NaCl + Eps
12	3.89	4.15	15.07	4.09	33.13	16.68	1584.01	NaCl + Eps
13	3.30	4.50	15.70	3.41	27.93	13.80	1579.14	NaCl + Eps
14	3.19	4.54	15.65	3.42	27.11	13.90	1585.22	NaCl + Eps
15	2.60	4.99	16.35	2.98	21.57	11.85	1550.61	NaCl + Eps
16	1.44	5.89	17.74	2.27	11.44	8.63	1472.94	NaCl + Eps
17,F	0.091	8.85	24.97	1.34	0.54	3.81	981.71	NaCl + Eps + Bi
18,B	1.41	5.74	0.00	19.00	15.47	100	2072.58	Mir + Eps
19	1.48	3.95	1.91	16.10	16.56	86.14	2184.54	Mir + Eps
20	1.51	3.83	3.17	14.02	17.29	76.58	2255.52	Mir + Eps
21	1.56	3.83	3.55	13.59	17.71	73.84	2245.12	Mir + Eps
22	1.65	3.87	4.35	12.87	18.40	68.59	2195.62	Mir + Eps
23	1.75	3.81	5.24	11.61	19.58	62.07	2211.39	Mir + Eps
24	2.00	3.81	7.30	9.36	21.66	48.65	2147.59	Mir + Eps
25	2.42	3.81	9.02	7.90	25.17	39.24	2036.68	Mir + Eps
26	2.76	3.76	10.19	6.83	27.97	33.09	1975.76	Mir + Eps
27	3.72	3.52	12.31	5.02	35.87	23.12	1853.73	Mir + Eps
28,C	0.0	8.88	24.97	1.28	0.00	3.65	985.22	Eps + Bi
29,D	0.11	8.80	25.86	0.0	0.68	0.00	992.79	NaCl + Bi

[a] Mir, $Na_2SO_4 \cdot 10H_2O$; Eps, $MgSO_4 \cdot 7H_2O$; Bi, $MgCl_2 \cdot 6H_2O$.

Table 2. Physicochemical Property Data of the Reciprocal Quaternary System

no.[a]	density $10^{-3}\rho$ ($kg \cdot m^{-3}$)	conductivity k ($S \cdot m^{-1}$)	n_D	pH
1,A	1.215	1.16	1.3836	6.92
2	1.2183	1.126	1.3850	6.86
3	1.2191	1.075	1.3853	–[b]
4	1.2201	0.992	1.3868	–
5	1.2232	0.946	1.3885	–
6	1.2254	0.912	1.3896	6.70
7	1.245	0.776	1.3943	–
8	1.2484	0.712	1.3952	–
9,E	1.2496	0.708	1.3961	6.50
10	1.2502	0.7	1.3959	–
11	1.2508	0.692	1.3971	–
12	1.2512	0.69	1.3970	6.31
13	1.2521	0.676	1.3980	–
14	1.2526	0.674	1.3979	–
15	1.2574	0.652	1.3998	6.00
16	1.2682	0.612	1.4041	5.52
17,F	1.3406	0.292	1.4302	4.64
18,B	1.2358	0.262	1.3777	6.86
19	1.2261	0.323	1.3780	6.83
20	1.2187	0.39	1.3778	–
21	1.2184	0.405	1.3782	–
22	1.2176	0.423	1.3795	6.73
23	1.2154	0.46	1.3799	–
24	1.2139	0.537	1.3823	–
25	1.2196	0.575	1.3853	–
26	1.2225	0.624	1.3871	6.58
27	1.2321	0.695	1.3896	–
28,C	1.3396	0.296	1.4300	4.92
29,D	1.3309	0.318	1.4292	5.21

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

theory for aqueous solution of electrolytes in calculating solubilities.[6] On the basis of the semiempirical equations of Pitzer,[7−9] which gave a set of expressions for osmotic coefficients of the solution and mean activity coefficient of electrolytes in the solution, Harvie and Weare[10,11] have extended the electrolyte solution theory model, which reliably predicts mineral solubilities in complex brine systems from low to high concentrations at 298.15 K. This extended HW model was successfully utilized for the stable solubility predictions of the major seawater ions of the $Na + K + Mg + Cl + SO_4 + H_2O$ five-component system[8,11] and the ternary and quaternary subsystems of the $Na{-}K{-}Ca{-}Mg{-}H{-}Cl{-}SO_4{-}CO_2{-}B(OH)_4{-}H_2O$ in Searles Lake, California.[12] Additional work has centered on developing a variable-temperature model, which will increase the applicability to a number of diverse geochemical systems. The primary focus has been to broaden the model to generate parameters at higher or lower temperatures.[13−17] A low-temperature thermochemical model for the system $Na + K + Ca + Mg + Cl + SO_4 + H_2O$ is presented by Spencer, who concentrated electrolyte solutions over temperatures ranging from (213.15 to 298.15) K.[16,17] The temperature-dependent equations for the system are shown in eq 1

$$P(T) = a_1 + a_2T + a_6T^2 + a_9T^3 + a_3/T + a_4 \ln T \qquad (1)$$

Using the Pitzer parameters and the standard chemical potential of the aqueous solution species and minerals allows us to identify the coexisting solid phases and their compositions at equilibrium. But for the metastable solubility prediction in the metastable reciprocal quaternary system ($NaCl + MgCl_2 + Na_2SO_4 + MgSO_4 + H_2O$) at 273.15 K, there is no report on how to obtain the metastable equilibrium contents of solids in solution due to the fact that the standard chemical potential of the species and minerals in the aqueous solution is unsuitable for the next metastble solubility prediction. In this paper, experimental data on the metastable solubilities and the physicochemical properties of the reciprocal quaternary system ($NaCl + MgCl_2 + Na_2SO_4 + MgSO_4 + H_2O$) at 273.15 K are presented together with predictive solubilities based on the extended HW model.

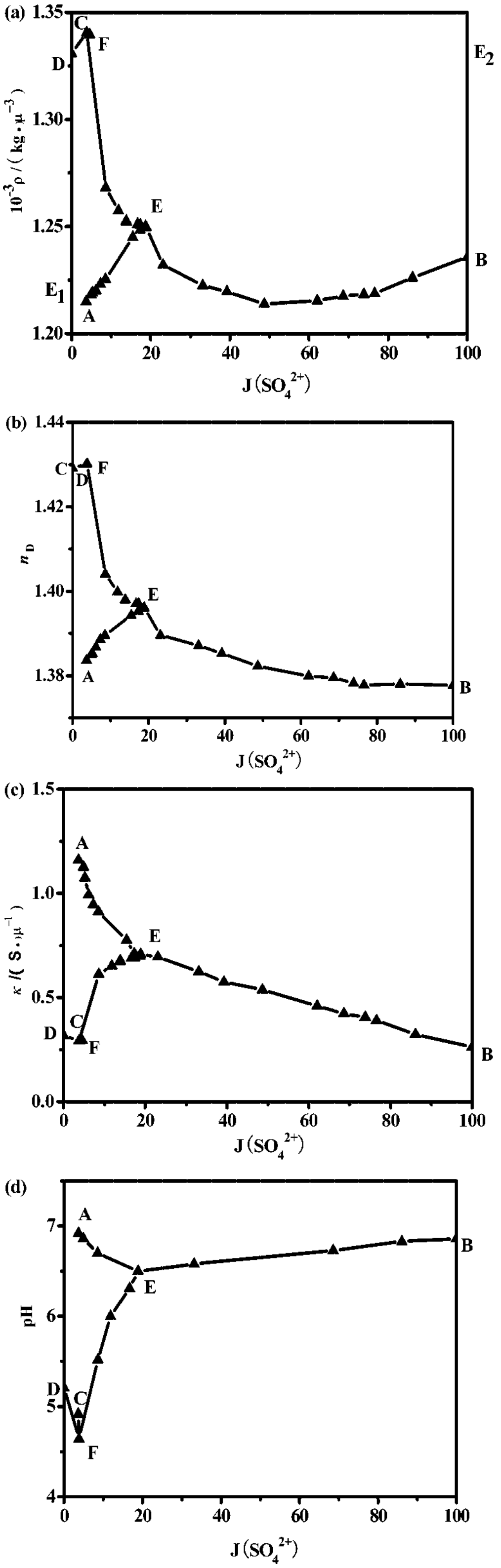

Figure 2. Property versus composition diagrams for the metastable quaternary system ($NaCl + MgCl_2 + Na_2SO_4 + MgSO_4 + H_2O$) at 273.15 K. ▲, experimental data point; —, experimental relationship diagram; (a), density versus composition; (b), refractive index versus composition; (c), conductivity versus composition; (d), pH versus composition.

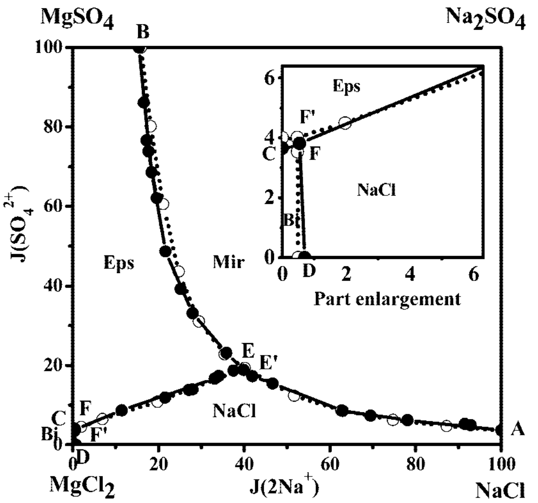

Figure 3. Comparison of the experimental and calculated metastable solubilities for the reciprocal quaternary system ($NaCl + MgCl_2 + Na_2SO_4 + MgSO_4 + H_2O$) at 273.15 K. ●, experimental value; ○, calculated value; Mir, $Na_2SO_4 \cdot 10H_2O$; Eps, $MgSO_4 \cdot 7H_2O$; Bi, $MgCl_2 \cdot 6H_2O$.

Experimental Section

Apparatus and Reagents. The isothermal evaporation box was made in our laboratory. In an air-conditioned laboratory, a thermal insulation material box (70 cm long, 65 cm wide, 60 cm high) has double-temperature controlling systems, where one is a cryogenic system through a refrigerating compressor and the other is a heating system through an electric incandescent lamp. The temperature-controlling apparatus is made up of an electrical relay, an electrical contact thermograph, and heating lamps. When the solution temperature in the container was under (273.15 ± 0.2) K, the apparatus for controlling the temperature formed a circuit, and the heating lamp began to heat. Conversely, the circuit was broken, and the heating lamp stopped working while the refrigerating compressor worked. Therefore, the temperature in the box could always be kept at (273.15 ± 0.2) K. An electric fan installed on the box always worked to accelerate the evaporation quantity of water from the solutions. The solid-phase minerals were identified using an XP-300 digital polarizing microscope (Shanghai Caikon Optical Instrument Co., Ltd., China) and an X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands).

The chemicals used were of analytical grade and recrystallized before use. They were all obtained from the Tianjin Kermel Chemical Reagent Ltd.: sodium chloride (NaCl, 99.5 mass %), sodium sulfate (Na_2SO_4, 99.0 mass %), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, 99.0 mass %), magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, 99.0 mass %). Doubly deionized water (DDW) with a conductivity less than $1 \cdot 10^{-4}\ S \cdot m^{-1}$ was used to prepare the series of artificial brines and for chemical analysis.

Experimental Method. The isothermal evaporation method was used in this study. According to phase equilibrium composition, the appropriate quantity of salts and DDW were mixed together as a series of artificial synthesized brines and loaded into clean polyethylene containers (15 cm in diameter, 6 cm high) and then put into the box for the isothermal evaporation at (273.15 ± 0.2) K. The experimental conditions were: an air flowing velocity of (3.0 to 4.0) $m \cdot s^{-1}$, a relative humidity of (30 to 35) %, and an evaporation rate of (1.0 to 3.0) $mm \cdot day^{-1}$. The conditions are reflective of those of the Qaidam Basin. For metastable evaporation reasons, no stirring was applied to the solutions. The crystal behavior of the solid phase was observed periodically. When enough new solid phase appeared, the wet residue mixtures were taken from the solution. Then solids were approximately evaluated with combined chemical analysis, observed using oil-immersion by XP-300D

Table 3. Single Salt and Mixing Ion-Interaction Parameters in the Solution of the Quaternary System at 273.15 K

single salts	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}
NaCl	0.05320098	0.24192667	—	0.00435853
Na_2SO_4	−0.06193906	0.84007261	—	0.01794157
$MgCl_2$	0.36156828	1.29414728	—	0.00930166
$MgSO_4$	0.08551602	2.28375420	14.35411781	0.08952181

A^{ϕ}	$\theta_{Na,Mg}$	$\theta_{Cl,SO4}$	$\Psi_{Na,Mg,Cl}$	$\Psi_{Na,Mg,SO4}$	$\Psi_{Na,Cl,SO4}$	$\Psi_{MgCl,SO4}$
0.37812446	0.0700	0.05044263	−0.00892147	−0.01900825	−0.00172301	−0.02494434

Table 4. Average Equilibrium Constants of Minerals Existing in the Quaternary System at 273.15 K

species	NaCl	$Na_2SO_4 \cdot 10H_2O$	$MgCl_2 \cdot 6H_2O$	$MgSO_4 \cdot 7H_2O$
$K_{aver.}$	31.9795094	0.0029354	57783.5747977	0.0067024

Table 5. Comparison of the Experimental and Calculated Solubilities in the Invariant Points for the Reciprocal Quaternary System ($NaCl + MgCl_2 + Na_2SO_4 + MgSO_4 + H_2O$) at 273.15 K

	comp. of liquid phase w_b (mass %)				Jänecke index J_b/[mol/100 mol dry salt]		
no.[a]	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	$2Na^+$	SO_4^{2-}	equilibrium solid phase[b]
E	4.65	3.71	14.60	4.59	39.08	18.85	NaCl + Mir + Eps
E′	4.67	3.68	14.47	4.71	40.13	19.36	NaCl + Mir + Eps
F	0.091	8.85	24.97	1.34	0.54	3.81	NaCl + Eps + Bi
F′	0.080	8.87	24.95	1.41	0.47	4.01	NaCl + Eps + Bi

[a] Points E and F, the experimental values; points E′ and F′, the calculated data. [b] Mir, $Na_2SO_4 \cdot 10H_2O$; Eps, $MgSO_4 \cdot 7H_2O$; Bi, $MgCl_2 \cdot 6H_2O$.

digital polarizing microscopy, and further identified with X-ray diffraction. Meanwhile, a 5.0 mL sample of the clarified solution was taken from the liquid phase of each polyethylene container through a filter pipet and then diluted to a 250.0 mL final volume in a volumetric flask filled with DDW for quantitative analysis of the composition of the liquid phase. Some of the filtrate was used to measure the relative physicochemical properties individually according to the analytical method. The remainder of the solution continued to be evaporated to reach a new metastable equilibrium point.

Analytical Method. The composition of SO_4^{2-} in the liquids was analyzed by the gravimetric method of barium chloride with a precision within ± 0.05 mass %. The Mg^{2+} ion concentration was determined by titration with EDTA standard solution in the presence of the indicator of Eriochrome Black-T with a precision within ± 0.3 mass %. The Cl^- ion concentration was determined by titration with mercury nitrate standard solution in the presence of a mixed indicator of diphenylcarbazone and bromophenol blue with a precision of ≤ ± 0.3 mass %.[18]

A PHS-3C precision pH meter supplied by the Shanghai Precision & Scientific Instrument Co., Ltd., was used to measure the pH of the equilibrium aqueous solutions (precision of ± 0.01). The pH meter was calibrated with standard buffer solutions: either a mixture of potassium dihydrogen phosphate and disodium hydrogen phosphate (pH 6.98) or potassium hydrogen phthalate (pH 4.00). The densities (ρ) were measured with a density bottle method with a precision of ± 0.2 mg. An Abbe refractometer (model WZS-1) was used for measuring the refractive index (n_D) with a precision of ± 0.0001. Conductivities (κ) were measured with an Orion 145A+ conductivity meter (Thermo Electron Corporation, America) with a precision of ± 0.001 $S \cdot m^{-1}$. Measurements for the physicochemical parameters of density, refractive index, conductivity, and pH were conducted in a thermostat that electronically controlled the set temperature at (273.15 ± 0.1) K.

Results and Discussion

The experimental data on the metastable solubilities and the relevant physicochemical properties of the quaternary system ($NaCl + MgCl_2 + Na_2SO_4 + MgSO_4 + H_2O$) at 273.15 K are presented in Tables 1 and 2, respectively. The ion concentration values in the metastable equilibrium solution are expressed as a Jänecke index [J_b/(mol/100 mol dry salt)]. According to the experimental data in Table 1, the metastable equilibrium phase diagram of the system at 273.15 K is shown in Figure 1.

The metastable phase diagram of the system at 273.15 K in Figure 1 consists of two invariant points, with cosaturated salts at E ($NaCl + Na_2SO_4 \cdot 10H_2O + MgSO_4 \cdot 7H_2O$) and F ($NaCl + MgSO_4 \cdot 7H_2O + MgCl_2 \cdot 6H_2O$) and four crystallization zones corresponding to sodium chloride (NaCl), mirabilite ($Na_2SO_4 \cdot 10H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), and bischofite ($MgCl_2 \cdot 6H_2O$). There are five univariant curves corresponding to AE, BE, CF, DF, and EF, indicating the cosaturation of two salts. The crystallization area of bischofite is the smallest, and the crystallized zone of mirabilite is the largest. These results indicate that mirabilite is easy to saturate and crystallize from solution, so it could be separated and purified from brines through freezing in winter. Neither solid solutions nor double salts were found in the quaternary metastable system.

On the basis of the experimental data in Table 2, relationships between the solution physicochemical properties (density, refractive index, conductivity, and pH) and mass fraction of sulfate are found, as shown in Figure 2. It can be seen that the physicochemical properties change regularly with the mass fraction changes of sulfate.

Solubility Prediction

Using the temperature-dependent eq 1,[16,17] Debye−Hückel parameter A^{ϕ}, Pitzer single-salt parameters, and Pitzer mixing ion-interaction parameters in the system at 273.15 K were fitted in Table 3. According to the data of metastable experimental solubilities, the average equilibrium constants of minerals that exist in the quaternary system at 273.15 K were fitted with the method of the activity product constant in each metastable solution (Table 4).

On the basis of the Pitzer ion-interaction model and its extended HW model of aqueous electrolyte solution, the solubilities of the quaternary system at 273.15 K have been calculated using the average equilibrium constants of solids. On the basis of the calculated solubilities, comparisons between the metastable experimental phase diagram with a solid line and the predictive phase diagrams with a dashed line for the quaternary system at 273.15 K are shown in Figure 3. A comparison of the calculated and experimental metastable solubilities at the invariant points E and F is in Table 5.

In Figure 3, the results show that the calculated and experimental phase diagrams are in good agreement. These results indicate that the parameters obtained in this work from the temperature-dependent equation are reliable and that the average equilibrium constants of solids evaluated using the extended HW model are capable of predicting the metastable equilibria in this reciprocal quaternary system.

Conclusions

Metastable equilibria of the reciprocal quaternary system ($NaCl + MgCl_2 + Na_2SO_4 + MgSO_4 + H_2O$) at 273.15 K were studied with the isothermal evaporation method. Solubilities and the physicochemical properties were determined experimentally. The results show that neither solid solutions nor double salts were formed in this quaternary system. Depending on the temperature-dependent equation, the values of the Debye−Hückel parameter A^{ϕ}, single-salt, and mixing ion-interaction Pitzer parameters in the system at 273.15 K were obtained. Using the average equilibrium constants of equilibrium solids, the solubilities of the quaternary system were calculated with the extended HW model. A comparison of the experimental and calculated solubilities shows that the predictive data obtained with the extended HW model agree well with experimental results.

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