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Metastable Phase Equilibrium in the Aqueous Ternary System ($KCl-CaCl_2-H_2O$) at (288.15 and 308.15) K

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The solubility and the physicochemical properties (density and refractive index) in the liquid–solid metastable system ($KCl-CaCl_2-H_2O$) at (288.15 and 308.15) K were determined using the isothermal evaporation method. Based on the experimental data, the metastable phase diagrams and the diagrams of physicochemical properties vs composition in the system at (288.15 and 308.15) K were plotted. In the metastable phase diagrams of the ternary system at (288.15 and 308.15) K, there are in all one invariant point, two univariant curves, and two crystallization zones, corresponding to potassium chloride, antarcticite ($CaCl_2 \cdot 6H_2O$) at 288.15 K, and potassium chloride, and calcium chloride tetrahydrate ($CaCl_2 \cdot 4H_2O$), at 308.15 K. This system at both temperatures belongs to a simple eutectic type, and neither double salts nor solid solution were found. Based on the extended Harvie−Weare (HW) models and temperature-dependent equations at (288.15 and 308.15) K, respectively, the values of the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$,and C^{φ} for KCl and $CaCl_2$, the mixed ion-interaction parameters $\theta_{K,Ca}$ and $\Psi_{K,Ca,Cl}$, the Debye–Hückel parameter A^{φ}, and the standard chemical potentials of the minerals in the ternary system were obtained by fitting. Using the temperature-dependent equations and the standard chemical potentials of the minerals respectively, the predictive solubilities for the ternary system at both temperatures are presented. A comparison between the calculated and experimental results at each temperature shows that the predicted solubilities obtained with the extended HW model agree well with experimental data.

Introduction

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

Although all of these oilfield brine resources are very valuable, nothing has been reported on potential multipurpose utilization because of a lack of data on the relative solubilities and phase diagrams of the cadmium-bearing systems, especially the thermodynamic data on metastable equilibria.[2] In order to exploit these 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 Caidamu Basin is windy, with little rainfall, so it provide great evaporating capacity.[3] Therefore, the metastable phase equilibrium, determined in the laboratory in conditions similar to those occurring naturally could objectively demonstrate the interaction of brine-mineral and reveal the crystallized path of salts.

The ternary system ($KCl-CaCl_2-H_2O$) is a subsystem of the six-component system. Although some stable phase equilibrium on this ternary system at (288.15 and 308.15) K had been previously reported,[4–8] the ternary system in metastable equilibria neither at 288.15 K nor at 308.15 K is reported in the literature to describe the metastable behavior. In this paper, the metastable solubilities and physicochemical property data of the ternary system at two temperatures and the predictive solubilities based on the extended Harvie−Weare (HW) models are presented.

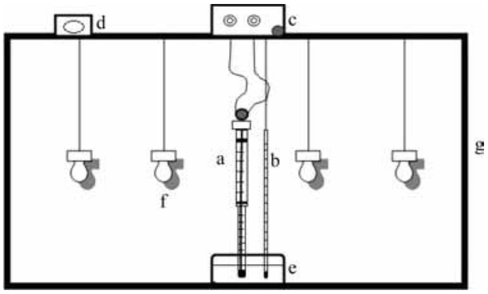

Figure 1. Fellow-chart of the isothermal evaporation chamber: a, electrical contact thermograph; b, precise thermometer; c, electric relay; d, electric fan; e, evaporating container; f, heating lamp; g, isothermal container.

Experimental Section

Apparatus and Reagents. The isothermal evaporation instruments were designed in our laboratory. In an air-conditioned laboratory, a thermal insulation material box (70 cm long, 65 cm wide, 60 cm high) with an electric fan was installed with an apparatus to control the temperature, which includes three parts: an electric relay, an electrical contact thermograph, and heating lamps as shown in Figure 1. When the solution temperature in the vessel was under the required temperature

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Table 1. Solubility Data of the Metastable Ternary System ($KCl-CaCl_2-H_2O$) at 288.15 K

	liquid phase composition w_b (mass %)		wet solid phase composition w_b (mass %)		density		
no.	KCl	$CaCl_2$	KCl	$CaCl_2$	$10^{-3}\rho/(kg \cdot m^{-3})$	n_D	solid phase
1, A	24.82	0.00	ND[a]	ND	1.1678	1.3646	KCl
2	21.58	2.94	ND	ND	1.1788	ND	KCl
3	17.71	7.60	ND	ND	1.1923	ND	KCl
4	16.86	8.56	ND	ND	1.1957	1.3791	KCl
5	11.69	15.39	36.22	11.05	1.2246	ND	KCl
6	10.63	16.44	ND	ND	1.2277	1.3919	KCl
7	6.06	25.04	44.14	14.82	1.2827	1.4097	KCl
8	3.16	26.37	ND	ND	1.2921	1.4129	KCl
9	3.46	35.46	29.48	25.88	1.3764	1.4359	KCl
10	2.99	36.17	ND	ND	1.3862	1.4382	KCl
11	3.15	36.96	ND	ND	1.3943	1.4406	KCl
12	2.69	38.06	39.77	23.49	1.4056	1.4439	KCl
13, E	1.99	39.80	18.14	37.11	1.4259	1.4490	$CaCl_2 \cdot 6H_2O$ + KCl
14	1.28	39.99	0.73	46.87	1.4196	1.4480	$CaCl_2 \cdot 6H_2O$
15	0.00	40.37	ND	ND	1.4163	1.4472	$CaCl_2 \cdot 6H_2O$
16, B		40.46	ND	ND	1.4099	1.4451	$CaCl_2 \cdot 6H_2O$

[a] ND means not detected.

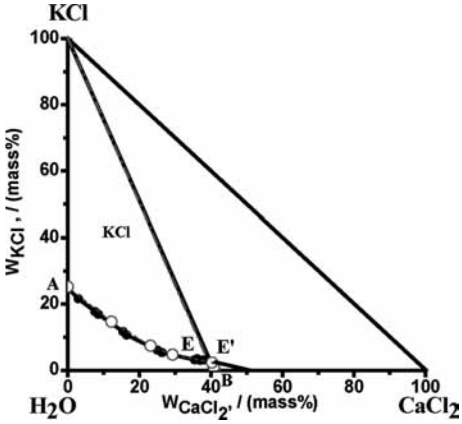
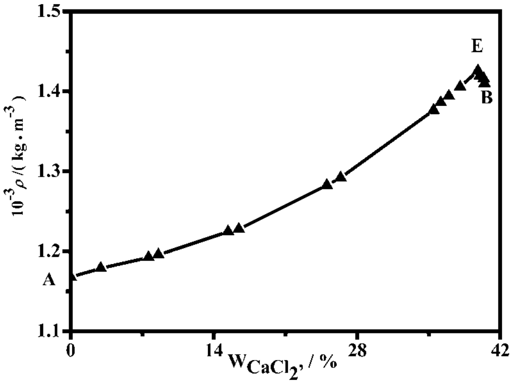
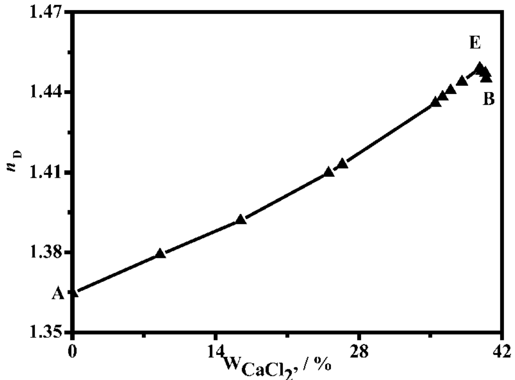


Figure 2. Experimental and calculated metastable phase diagrams for the ternary system ($KCl-CaCl_2-H_2O$) at 288.15 K. ●, experimental value; ○, calculated value.



(a) Density value-composition



(b) Refractive index value-composition

Figure 3. Physicochemical properties vs composition in the metastable ternary system ($KCl-CaCl_2-H_2O$) at 288.15 K. ▲, experimental value; —, experimental relationship diagram; (a) density composition; (b) refractive index composition.

[(288.15 or 308.15) 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. Therefore, the solution temperature in the container could always be kept at the required temperature within ± 0.3 K. The electric fan installed on the box can accelerate the evaporation velocity of the solutions. The solid phase crystals were analyzed combined with an XP-300 Digital Polarizing Microscopy (Shanghai Caikon Optical Instrument Co. Ltd., China) and with an X-ray diffractometer (X'pert PRO, Spectris. Pte. Ltd., The Netherlands). A thermostat, which can automatically control the temperature, ensured that all physicochemical parameters were strictly measured at (288.15 ± 0.1) K or (308.15 ± 0.1) K.

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

Experimental Methods. The isothermal evaporation method was used in this study. According to phase equilibrium composition, the appropriate quantity of salts and DDW was calculated and mixed into clean polyethylene containers (15 cm in diameter, 6 cm high). After the salts completely dissolved, the containers were put into the box for the isothermal evaporation at (288.15 or 308.15) K. The evaporation conditions were controlled with an air flow velocity of (3.5 to 4.0) $m \cdot s^{-1}$, elative humidity of (20 to 30) %, and evaporation rate of (4 to 6) $mm \cdot day^{-1}$, just like the climate of the Caidamu Basin. The solutions were kept without stirring during the whole evaporation process so as not to disturb the metastable equilibrium, and the crystal solid phase was observed periodically. When enough new solid phase appeared, the wet residue mixtures were separated from the solution. Then, one part of the solid phase was quantitatively dissolved in water and analyzed by chemical methods. The other part was slightly dried at (288.15 or 308.15)

Table 2. Solubility Data of the Metastable Ternary System ($KCl-CaCl_2-H_2O$) at 308.15 K

	liquid phase composition w_b (mass %)		wet solid phase composition w_b (mass %)		density	
no.	KCl	$CaCl_2$	KCl	$CaCl_2$	$10^{-3}\rho/(kg \cdot m^{-3})$	solid phase
1, A	28.24	0.00	ND[a]	ND	1.2364	KCl
2	24.51	3.61	ND	ND	ND	KCl
3	21.35	7.10	ND	ND	1.2400	KCl
4	15.62	13.46	8.88	44.88	1.2482	KCl
5	15.29	13.74	ND	ND	1.2649	KCl
6	10.84	19.97	ND	ND	1.2758	KCl
7	6.84	27.28	ND	ND	1.2887	KCl
8	5.42	31.54	ND	ND	1.2975	KCl
9	4.63	34.80	ND	ND	1.3231	KCl
10	4.19	36.13	ND	ND	1.3430	KCl
11	4.41	36.79	ND	ND	1.3570	KCl
12	4.50	40.19	42.90	23.82	1.3653	KCl
13	4.43	44.55	17.80	38.21	ND	KCl
14, E	6.79	50.715	60.31	30.55	1.5691	$CaCl_2 \cdot 4H_2O$ + KCl
15, B	0.00	53.04	ND	ND	1.5171	$CaCl_2 \cdot 4H_2O$

[a] ND means not detected.

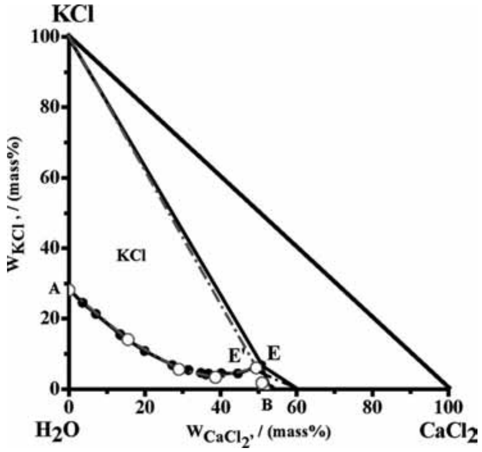


Figure 4. Experimental and calculated metastable phase diagrams for the ternary system ($KCl-CaCl_2-H_2O$) at 308.15 K. ●, experimental value; ○, calculated value.

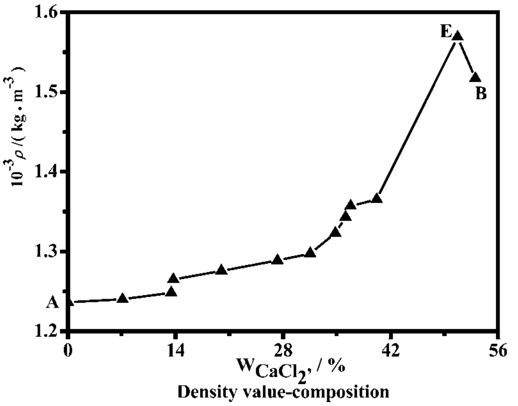


Figure 5. Densities vs composition in the ternary system ($KCl-CaCl_2-H_2O$) at 308.15 K. ▲, experimental value; —, experimental relationship diagram.

K, then analyzed with XP-300D Digital Polarizing Microscopy and further with X-ray diffraction. The compositions of the liquid phase were analyzed by the chemical analysis methods. A 5.0 mL sample of the clarified solution was taken from the liquid phase with a pipet through a filter and diluted to 250.0 mL final volume in a volumetric flask filled with DDW to determine the concentration of the liquid-phase components. Some other solutions, which were taken from the containers in the same manner, were used to measure the corresponding physicochemical properties of solutions in this sampling. The remainder of the solution was further evaporated until it reached a new metastable equilibrium.

Analytical Methods. The concentration of the Ca^{2+} ion was determined by titration with EDTA standard solution in the presence of alkali and a Ca-indicator. The uncertainty was less than ± 0.3 %. The Cl^- ion concentration was measured by titration with hydrargyrum nitrate standard solution in the presence of a mixed indicator of diphenylcarbazone and bromphenol blue (uncertainty of ± 0.3 %),[9] and K^+ was evaluated according to ion balance.

The measurements of the liquid-phase physicochemical properties were corresponding to density and refractive index. 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 to measure the refractive index (n_D) with an accuracy of ± 0.0001. All the measurements were maintained at the desired temperature with ± 0.1 K through control of the thermostat.

Results and Discussion

Ternary System ($KCl-CaCl_2-H_2O$) at 288.15 K. The experimental data on the metastable solubilites and the relevant physicochemical properties of the ternary system ($KCl-CaCl_2-H_2O$) at 288.15 K are presented in Table 1. The ion concentration values in the metastable equilibrium solution are expressed in mass fraction. According to the experimental data in Table 1, the metastable phase diagram of the system at 288.15 K is plotted, as shown in Figure 2 with solid lines.

In Figure 2 with solid lines, points A and B are the metastable solubilities of the single-salts of potassium chloride and antarcticite. Point E is a eutectic point of potassium chloride and antarcticite (KCl + $CaCl_2 \cdot 6H_2O$). There are two isotherm evaporation curves corresponding to curves AE and BE, indicating the saturation of single salts. The metastable phase diagram consisted of two crystallization regions corresponding to the large area of KCl and the relative small area of $CaCl_2 \cdot 6H_2O$. The system obviously belongs to a simple eutectic type, and neither double salts nor solid solutions are found.

On the basis of experimental data in Table 1, relationship of the solution physicochemical properties with the concentration of calcium chloride is shown in Figure 3. It can be found that the densities and refractive indexes of the aqueous solutions, in the ternary system, changed gradually and regularly with the

Table 3. Pitzer Equation Parameters and the Standard Chemical Potential for the Minerals, in the Ternary System at (288.15 and 308.15) K

T/K	single salts	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}
288.15	KCl	0.04193432	0.18885136	−0.00014796
288.15	$CaCl_2$	0.30046792	1.67591161	−0.00092417
308.15	KCl	0.05330204	0.23159070	−0.00135059
308.15	$CaCl_2$	0.30668075	1.74671108	0.00066042

T/K	A^{φ}	$\Theta_{K,Ca}$	$\Psi_{K,Ca,Cl}$	species	KCl	$CaCl_2 \cdot nH_2O$	H_2O
288.15	0.38564641	−0.00466067	−0.00127055	μ^0/RT	1.80375161	8.21919939[a]	0.15506872
308.15	0.39853455	0.17560	−0.04024181	μ^0/RT	2.32402855	−111.6515319[b]	−31.50522977

[a] $CaCl_2 \cdot 6H_2O$ [b] $CaCl_2 \cdot 4H_2O$.

Table 4. Comparison of the Experimental and Calculated Solubilities in the Eutectic Point of the Ternary System ($KCl-CaCl_2-H_2O$) at (288.15 and 308.15) K

		composition of liquid phase w_b (mass %)			
T/K	no.	KCl	$CaCl_2$	H_2O	equilibrium solid phase
288.15	exptl	2.69	39.80	57.51	$KCl + CaCl_2 \cdot 6H_2O$
288.15	calcd	2.31	40.33	34.89	$KCl + CaCl_2 \cdot 6H_2O$
308.15	exptl	6.79	50.715	42.495	$KCl + CaCl_2 \cdot 4H_2O$
308.15	calcd	6.03	49.38	44.59	$KCl + CaCl_2 \cdot 4H_2O$

content change of calcium chloride and reached the maximum value at eutectic point E.

Ternary System ($KCl-CaCl_2-H_2O$) at 308.15 K. The experimental data on the metastable solubilites and the solution densities of the ternary system ($KCl-CaCl_2-H_2O$) at 308.15 K are presented in Table 2. According to the experimental data in Table 2, the metastable phase diagram of the system at 308.15 K is plotted, as shown in Figure 4 with solid lines.

In Figure 4 with solid lines, points A and B are the metastable solubilities of the single-salts of potassium chloride and calcium chloride tetrahydrate. Point E is a eutectic point of potassium chloride and calcium chloride tetrahydrate ($KCl + CaCl_2 \cdot 4H_2O$). There are two isothermal evaporation curves corresponding to curves AE and BE, indicating the saturation of single salts. The metastable phase diagram consisted of two crystallization regions corresponding to the large area of KCl and the relative small area of $CaCl_2 \cdot 4H_2O$. Obviously, the system belongs to the simple eutectic type, and neither double salts nor solid solutions are found.

On the basis of experimental data in Table 2, the relationship of the solution densities with the concentration of calcium chloride is shown in Figure 5. It can be found that the solution density of the ternary system changed regularly with the content of calcium chloride and reached the maximum value at eutectic point E.

Comparison of the Ternary System at (288.15 and 308.15) K. In the metastable phase diagrams of the ternary system ($KCl-CaCl_2-H_2O$) at two temperatures, it is shown that the calcium chloride crystallization zones are corresponding to antarcticite ($CaCl_2 \cdot 6H_2O$) at 288.15 K and calcium chloride tetrahydrate ($CaCl_2 \cdot 4H_2O$) at 308.15 K. Comparison of the metastable diagrams at (288.15 and 308.15) K shows that the solubilities of potassium chloride and calcium chloride become larger as the temperature increases, and correspondingly, the crystallization zones, especially of calcium chloride, become larger. This information can be used to recover potassium or remove calcium.

Solubility Prediction

Ion-Interaction Model. Pitzer and co-workers have developed an ion interaction model and published a series of papers[10,11] 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[12,13] 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.[14–16]

Model Parametrization. A low-temperature thermochemical model for the system $Na-K-Ca-Mg-Cl-SO_4-H_2O$ is presented by Spencer[15] for concentrated electrolyte solutions over temperature ranges from (–213.15 to 298.15) K. Standard chemical potentials for the reactions of mineral solids and solutions were fitted simultaneously with the solution model parameters. The temperature-dependent equation for the system are shown as follows

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

A hightemperature thermochemical model for the system $Na-K-Ca-Cl-SO_4-H_2O$ is presented by Greenberg[16] for concentrated electrolyte solutions over temperature ranges from (273.15 to 523.15) K. The standard chemical potential of calcium chloride tetrahydrate is presented by Christov and Møller.[17] The temperature-dependent equation for the system are shown as follows

$$P(T) = a_1 + a_2T + a_3/T + a_4 \ln T + a_5/(T - 263) + a_6T^2 + a_7/(680 - T) + a_8/(T - 227)$$

Using the two temperature-dependent equations, Pitzer single-salt parameters, Pitzer mixing ion-interaction parameters, the Debye–Hückel parameter A^{φ}, and the standard chemical potentials of the minerals in the system at (288.15 and 308.15) K are fitted as shown in Table 3.

Calculated Solubility. Based on the Pitzer ion-interaction model and its extended HW models of aqueous electrolyte solution, the solubilities of the ternary system at (288.15 and 308.15) K have been calculated by using the temperature-dependent equations and the standard chemical potentials of the minerals. On the basis of calculated solubilities, the comparisons of the metastable experimental phase diagrams of the ternary system with the predicted phase diagrams at (288.15 and 308.15) K are plotted in Figure 2 and Figure 4 with dashed lines, respectively. A comparison between the calculated and experimental solubilities in the invariant point E at (288.15 and 308.15) K is shown in Table 4.

In Figures 2 and 4, the results show that the experimental and calculated solubilities have a good agreement at both temperatures. Those results indicate that the parameters obtained from the temperature-dependent equations in this work are reliable and that the standard chemical potentials of the minerals evaluated using the extended HW models are capable of predicting the metastable solubility of the ternary systems at different temperatures.

Conclusions

Solubilities and physicochemical properties of the liquid–solid metastable equilibria of the ternary system ($KCl-CaCl_2-H_2O$) at (288.15 and 308.15) K are determined experimentally. According to the data measured, the experimental metastable phase diagram and the diagrams of physicochemical properties vs composition are constructed in the first time. Based on the temperature-dependent equations in the literature, Pitzer single-salt parameters, mixing ion-interaction parameters, the Debye–Hückel parameter A^{φ}, and standard chemical potentials of the minerals in the system at both temperatures could be fitted satisfactorily. After the solubility predictions for the ternary system at (288.15 and 308.15) K, the results demonstrate that both Pitzer parametrizations based on the temperature-dependent equations and the standard chemical potentials of the minerals in the ternary system at the two temperatures are reliable. The predictive metastable solubilities with the extended HW models agree well with the experimental data.

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