JOURNAL OF CHEMICAL & ENGINEERING DATA

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Equilibria in the Quaternary System KCl−NaCl−$CaCl_2$−H_2O at 283.15 K

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ABSTRACT: The solubilities and physicochemical properties in the quaternary system KCl−NaCl−$CaCl_2$−H_2O at 283.15 K have been measured with the isothermal method. The dry-salt phase diagram, water-phase diagram, and physicochemical properties vs composition in the system were plotted according to the measured data. The system contained only the forms of single salts, and no double salts or solid solution were found. On the basis of the extended Harvie−Weare (HW) model and the temperature coefficients of the single-salt parameters obtained from the calorimetric data, the Pitzer parameters for KCl, NaCl, and $CaCl_2$ and the mixed ion-interaction parameters at 283.15 K were obtained. In addition, the average equilibrium constants of the solids at the same temperature were obtained using a method derived from the activity coefficient model of the electrolyte solution theory. Using the average equilibrium constants of the solids at equilibrium, the solubility predictions for the quaternary system are presented. A comparison between the calculated and experimental results suggests that the predicted solubility data obtained with the extended HW model agree well with the experimental data.

INTRODUCTION

Sintering dust arrested by electrostatic precipitators in the sinter plant of integrated iron and steel companies has been found enriched with potassium chloride up to 30 % to 50 % (by weight).[1,2] Water leaching was proposed to extract the potassium chloride from the sintering dust, and the leaching solution can be considered as a quaternary system KCl−NaCl−$CaCl_2$−H_2O after sulfide precipitation for removing the slight amount of dissolved heavy metal impurities.

As an alternative method to obtain a potassium chloride product, evaporation-cooling crystallization needs solubility data of the quaternary system KCl−NaCl−$CaCl_2$−H_2O at temperatures over a wide range. However, there are only some solubility data of this quaternary system and its ternary subsystems KCl−NaCl−H_2O, KCl−$CaCl_2$−H_2O, and NaCl−$CaCl_2$−H_2O between (291.15 and 368.15) K,[3−7] although the metastable equilibria of the quaternary system at 288.15 K have been experimentally measured and also calculated with the Pitzer and extended Harvie−Weare (HW) models.[8,9] Equilibria of the quaternary system KCl−NaCl−$CaCl_2$−H_2O at 283.15 K were investigated in this paper. Both the measured solubility data and the predicted solubilities based on the extended HW model are presented.

EXPERIMENTAL SECTION

The experiments were carried out as equilibrium investigations. Samples were prepared by mixing the individual salts and water in suitable proportions in closed plastic bottles. The bottles were shaken in an air-bath, which was electrically heated and carefully insulated. The air of the bath was vigorously stirred by means of fans. The temperature was constant to within 0.1 °C. After three or four days, the sample was passed through a glass filter with pore size of 0.22 μm, without taking the bottle containing the sample or the filter out of the thermostat. Small amounts of the solution and the solid phase were immediately weighed for analysis. One of the components was added to the pure filtered solution, and the experiments were repeated as before.

The compositions of both the solid phase and the liquid phase were determined by chemical methods. The concentration of K^+ and Na^+ was determined using a flame photometer FP640 after being diluted step by step until the concentration was at or near the middle of the standard curve. The K^+ concentration in some samples was also analyzed by gravimetric methods using sodium tetraphenyl borate and compared with that obtained by FP640. The relative error was about ± 5 %. The concentration of Cl^- was determined using an ion chromatograph (792 basic IC made by Metrohm). The average deviation was less than ± 1 %. The Ca^{2+} concentration was determined by titration with ethylene diamine tetraacetic acid (EDTA), and the uncertainty was within ± 0.3 %. The concentration of Na^+ was also evaluated by ion balance and compared with the value measured by FP640, and the average deviation was within 5 %. The pH value of the liquid phase was measured with a PHS-3C precision pH meter. The densities (ρ) were measured with a density bottle with a precision of ± 0.0002 $g \cdot cm^{-3}$.

RESULTS AND DISCUSSION

The experimental results for the solubilities and the relevant physicochemical properties of the stable equilibria of the quaternary system KCl−NaCl−$CaCl_2$−H_2O at 283.15 K are presented in Tables 1 and 2. The solubilities of salts in the

Received: July 14, 2010
Accepted: February 25, 2011
Published: March 11, 2011

Table 1. Quaternary System $KCl-NaCl-CaCl_2-H_2O$ at 283.15 K

	weight percent, solution			Jänecke index, J_b (g/100 g of S)			
no.	KCl	NaCl	$CaCl_2$,	KCl	$CaCl_2$	H_2O	solid phase
$1E_1$	8.71 ± 0.43	21.66 ± 1.08	0	28.68 ± 1.43	0	229.2 ± 11.4	KCl + NaCl
2	8.05 ± 0.40	18.79 ± 0.93	2.77 ± 0.01	27.19 ± 1.35	9.35 ± 0.02	237.7 ± 11.8	KCl + NaCl
3	7.89 ± 0.39	17.65 ± 0.88	4.26 ± 0.01	26.48 ± 1.32	14.30 ± 0.04	235.5 ± 11.7	KCl + NaCl
4	7.33 ± 0.36	14.27 ± 0.71	8.30 ± 0.02	24.52 ± 1.22	27.76 ± 0.08	234.4 ± 11.7	KCl + NaCl
5	6.91 ± 0.34	12.33 ± 0.61	10.45 ± 0.03	23.27 ± 1.16	35.20 ± 0.10	236.8 ± 11.8	KCl + NaCl
6	6.35 ± 0.32	10.51 ± 0.52	13.95 ± 0.04	20.61 ± 1.03	45.28 ± 0.13	224.5 ± 11.2	KCl + NaCl
7	4.84 ± 0.24	6.21 ± 0.31	20.98 ± 0.06	15.11 ± 0.75	65.50 ± 0.19	212.2 ± 10.6	KCl + NaCl
8	3.97 ± 0.19	4.27 ± 0.21	25.27 ± 0.07	11.85 ± 0.59	75.41 ± 0.22	198.4 ± 9.9	KCl + NaCl
9	3.18 ± 0.16	2.50 ± 0.12	28.86 ± 0.08	9.21 ± 0.46	83.56 ± 0.25	189.5 ± 9.4	KCl + NaCl
10	2.25 ± 0.11	0.84 ± 0.04	34.66 ± 0.10	5.96 ± 0.29	91.81 ± 0.27	164.9 ± 8.2	KCl + NaCl
11E	1.954 ± 0.097	0.697 ± 0.034	36.99 ± 0.11	4.93 ± 0.24	93.31 ± 0.27	152.2 ± 7.6	KCl + NaCl + C6[a]
12	1.316 ± 0.065	0.700 ± 0.035	39.11 ± 0.11	3.20 ± 0.16	95.10 ± 0.28	143.1 ± 7.1	NaCl + C6
13	0.760 ± 0.038	0.645 ± 0.032	38.73 ± 0.11	1.89 ± 0.09	96.50 ± 0.29	149.1 ± 7.4	NaCl + C6
14	0.737 ± 0.036	0.674 ± 0.033	38.31 ± 0.11	1.86 ± 0.09	96.45 ± 0.29	151.7 ± 7.5	NaCl + C6
$15E_2$	0	0.533 ± 0.026	35.19 ± 0.10	0	98.51 ± 0.29	179.9 ± 8.9	NaCl + C6
16	0.337 ± 0.016	0.626 ± 0.031	39.45 ± 0.12	0.83 ± 0.04	97.62 ± 0.29	147.4 ± 7.3	NaCl + C6
17	2.125 ± 0.106	0.468 ± 0.023	38.62 ± 0.12	5.16 ± 0.25	93.71 ± 0.28	142.6 ± 7.1	KCl + C6
$18E_3$	2.051 ± 0.102	0	38.47 ± 0.11	5.06 ± 0.25	94.94 ± 0.28	146.7 ± 7.3	KCl + C6
19	2.131 ± 0.106	0.314 ± 0.015	38.44 ± 0.11	5.21 ± 0.26	94.02 ± 0.28	144.5 ± 7.2	KCl + C6
20	2.110 ± 0.105	0.344 ± 0.017	39.17 ± 0.12	5.07 ± 0.25	94.10 ± 0.28	140.2 ± 7.0	KCl + C6

[a] C6, $CaCl_2 \cdot 6H_2O$.

Table 2. pH and Density Data of the Liquid Phase in the Quaternary System $KCl-NaCl-CaCl_2-H_2O$ at 283.15 K

no.	pH	$\rho/(g \cdot cm^{-3})$
$1,E_1$	6.68	1.2341
2	6.56	1.2385
3	6.58	1.2426
4	6.42	1.2525
5	6.25	1.2592
6	6.17	1.2732
7	5.90	1.2896
8	5.70	1.3132
9	5.61	1.3312
10	ND[a]	1.3900
11E	5.05	1.4289
12	4.65	1.3775
13	4.56	1.3901
14	4.56	ND
$15E_2$	ND	1.3878
16	4.62	1.3815
17	4.61	1.4163
$18E_3$	ND	1.4243
19	ND	1.4162
20	ND	ND

[a] ND = not detected.

equilibria are expressed as a weight percentage. The experimental phase diagram of the system at 283.15 K was plotted, as shown in Figure 1. The phase diagram consists of one invariant point E, three crystallized regions of single salts KCl, NaCl, and $CaCl_2 \cdot 6H_2O$, and three invariant solubility isotherm curves that correspond to E_1E, E_2E, and E_3E. This phase diagram is similar to the metastable equilibria phase diagram of the same quaternary system at 288.15 K.[8]

The water diagram of the system at 283.15 K is shown in Figure 2, which presents the projection of the invariant curves (Jänecke diagram) of this quaternary system at 283.15 K. According to the data in Table 2, the relationships between the physicochemical properties of the solution (pH and density) and the weight percentage of $CaCl_2$ are illustrated in Figure 3. As obtained in the literature,[8,9] the pH and density of the equilibrium solution change smoothly between E1 and E with the increase of calcium chloride concentration. The pH of the solution begins to sharply decrease when the calcium chloride concentration increases after point E. The density of the solution gets a maximal value at point E. The obtained special features of point E together suggest the accuracy of the solubility measurement.

■ SOLUBILITY PREDICTIONS

Calculation of Single Salt Parameters. In this work, solubility prediction of the quaternary system at 283.15 K was done on the basis of expressions about osmotic coefficients of the solution and mean activity coefficients of electrolytes in the solution proposed by Pitzer.[10,11] The electrolyte parameters, including the Pitzer single salt parameters $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\Psi)}$ and mixed salt parameters θ and Ψ, in those expressions were initially given by Pitzer and Kim in 1974 and subsequently supplemented by Harvie and Wear (HW) in 1984.[12−14] However, these parameters for both single salt and mixed-ion interactions are all

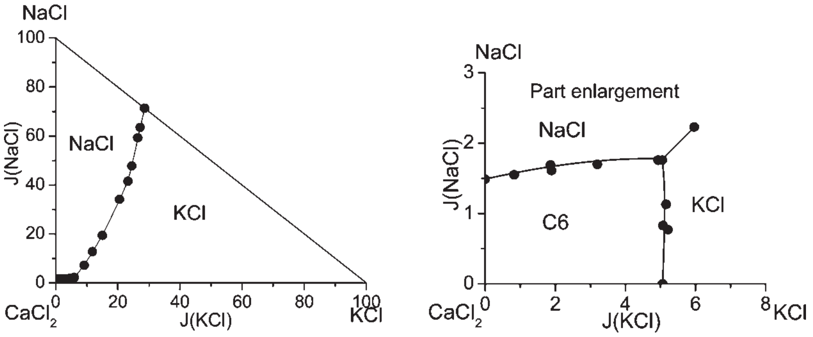

Figure 1. Phase diagram of the quaternary system KCl−NaCl−$CaCl_2$−H_2O at 283.15 K.

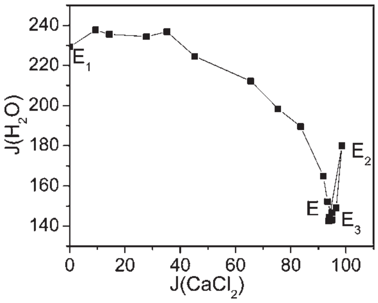

Figure 2. Water-phase diagram of the system KCl−NaCl−$CaCl_2$−H_2O at 283.15 K.

obtained from standard conditions at 298 K. So it is necessary to get the values of the parameters for the quaternary system KCl−NaCl−$CaCl_2$−H_2O at 283.15 K first. These parameters are not only affected by the structure of the electrolytes and interaction of mixed ions but also influenced by temperature of the system. It is reported that the single parameters $\beta^{(0)}$, $\beta^{(1)}$, and $C^{(\Psi)}$ at any temperature T can be calculated by the following equations when there is no remarkable temperature deviation from 298 K.[15−18]

$$\beta_T^{(0)} = \beta_{298}^{(0)} + \int_{298}^{T} \frac{\partial \beta^{(0)}}{\partial T}\, dT \qquad (1)$$

$$\beta_T^{(1)} = \beta_{298}^{(1)} + \int_{298}^{T} \frac{\partial \beta^{(1)}}{\partial T}\, dT \qquad (2)$$

$$C_T^{(\varphi)} = C_{298}^{(\varphi)} + \int_{298}^{T} \frac{\partial C^{(\varphi)}}{\partial T}\, dT \qquad (3)$$

where $\beta_T^{(0)}$, $\beta_T^{(1)}$, and $C_T^{(\varphi)}$ are Pitzer single parameters at temperature T; $\beta_{298}^{(0)}$, $\beta_{298}^{(1)}$, and $C_{298}^{(\varphi)}$ are Pitzer single parameters at 298 K; and $(\partial\beta)^{(0)}/(\partial T)$, $(\partial\beta)^{(1)}/(\partial T)$, and $(\partial C)^{(\varphi)}/(\partial T)$, listed in Table 3, are the partial derivatives of the single parameters with respect to temperature T. So the Pitzer single parameters of KCl, NaCl, and $CaCl_2$ at 283.15 K were thus obtained, as shown in Table 4.

Calculation of Mixed-Ion Interaction Parameters. The mixed-ion interaction parameters given by Pitzer and HW were also obtained at 298 K. In this paper, the Pitzer mixed ion-interaction parameters $\theta_{K,Na}$, $\theta_{K,Ca}$, $\theta_{Na,Ca}$ $\Psi_{K,Na,Cl}$, $\Psi_{K,Ca,Cl}$, and $\Psi_{Na,Ca,Cl}$ are calculated on the basis of solubility data of binary systems of KCl−NaCl−H_2O, KCl−$CaCl_2$−H_2O, and NaCl−$CaCl_2$−H_2O at 283.15 K with resort to multiple linear regression by the least-squares method. The results are listed in Table 5, and a comparison between the parameters fitted in this paper and those parameters reported at (298.15 and 288.15) K are also shown. At the same time, the equilibrium constants of the three salts, KCl, NaCl, and $CaCl_2 \cdot 6H_2O$, are obtained as presented in Table 6.

On the basis of the Pitzer equations and extended HW model and those fitted parameters of both single salt and mixed-ion interaction and the equilibrium constants, solubilities of the quaternary system KCl−NaCl−$CaCl_2$−H_2O at 283.15 K are calculated. Comparison between the experimental phase diagram and those calculated is shown in Figure 4. The results in Figure 4 show that the predicted solubilities of the quaternary system agree well with the experimental ones, indicating that the parameters and the equilibrium constants are fitted reliably.

■ CONCLUSIONS

The equilibrium of the quaternary system KCl−NaCl−$CaCl_2$−H_2O at 283.15 K was determined experimentally with the isothermal method. The density and pH of the equilibrium solution were also measured. On the basis of the experimental data, the dry-salt phase diagram of the system includes one three-salt cosaturated point, three equilibrium solubility isothermal curves, and three crystallization zones of KCl, NaCl, and $CaCl_2 \cdot 6H_2O$. No double salts or solid solution were found. On the basis of the Pitzer equations and extended HW model, single salt parameters and mixed-ion interaction parameters were fitted using multiple linear regression using the least-squares method according to the solubility data of the three binary systems (KCl−NaCl−H_2O, KCl−$CaCl_2$−H_2O, and NaCl−$CaCl_2$−H_2O) at 283.15 K. Solubility predictions of the quaternary system KCl−NaCl−$CaCl_2$−H_2O at 283.15 K have been made using the average equilibrium constants of the solids. The results demonstrate that the Pitzer parametrizations based on the temperature coefficients and the average equilibrium constants of the solids as a judgment of the quaternary system equilibrium are reliable. The calculated solubilities with the extended HW model through the average equilibrium constants agree well with the experimental data.

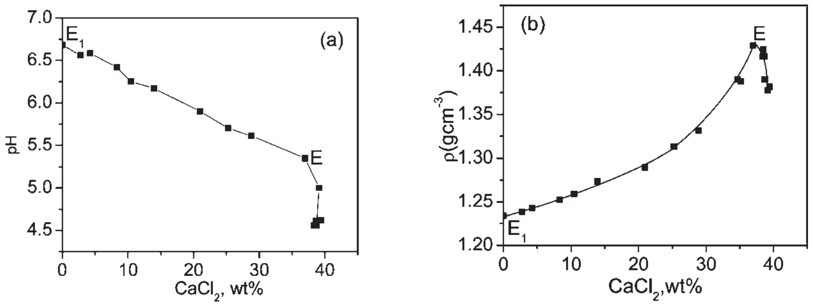

Figure 3. Relationship between physicochemical properties and weight percent of $CaCl_2$ in the equilibrium quaternary system: (a) pH and (b) density.

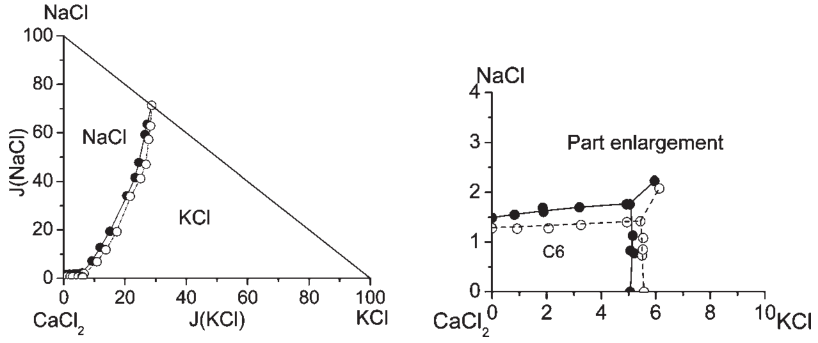

Figure 4. Comparison of experimental and calculated solubilities for the equilibrium phase diagram of the quaternary system at 283.15 K: ●, experimental; ○, calculated; C6, $CaCl_2 \cdot 6H_2O$.

Table 3. Temperature Coefficients of Pitzer Single Electrolyte Ion-Interaction Parameters

species	$(\partial\beta)^{(0)}/(\partial T)\cdot 10^4$	$(\partial\beta)^{(1)}/(\partial T)\cdot 10^4$	$(\partial C)^{(\varphi)}/(\partial T)\cdot 10^5$
KCl	5.794	10.71	−5.095
NaCl	7.159	7.005	−10.54
$CaCl_2$	−1.725	39.0	-

Table 4. Pitzer Single Electrolyte Ion-Interaction Parameters at 283.15 K

species	$\beta^{(0)}$	$\beta^{(1)}$	$C^{(\varphi)}$
KCl	0.037919	0.207345	0.000324
NaCl	0.066482	0.241322	0.002641
$CaCl_2$	0.328378	1.32562	−0.00174

Table 5. Pitzer Mixed Ion-Interaction Parameters of the Quaternary System

T (K)	$\theta_{K,Na}$	$\theta_{K,Ca}$	$\theta_{Na,Ca}$	ref.
283.15	$-4.33\cdot 10^{-3}$	$7.025\cdot 10^{-3}$	$5.460\cdot 10^{-2}$	this work
288.15	$-4.661\cdot 10^{-2}$	$6.865\cdot 10^{-2}$	$5.000\cdot 10^{-2}$	3
298.15	$-1.200\cdot 10^{-2}$	$3.200\cdot 10^{-2}$	$7.000\cdot 10^{-2}$	4
T (K)	$\Psi_{K,Na,Cl}$	$\Psi_{K,Ca,Cl}$	$\Psi_{Na,Ca,Cl}$	ref.
283.15	$-2.241\cdot 10^{-3}$	$-2.025\cdot 10^{-2}$	$-2.628\cdot 10^{-4}$	this work
288.15	$-3.668\cdot 10^{-3}$	$-1.271\cdot 10^{-3}$	$-1.271\cdot 10^{-3}$	3
298.15	$-1.800\cdot 10^{-3}$	$-2.500\cdot 10^{-2}$	$1.400\cdot 10^{-2}$	4

Table 6. Average Equilibrium Constants of Salts of the Quaternary System at 283.15 K

species	KCl	NaCl	$CaCl_2\cdot 6H_2O$
$K_{aver.}$	6.260	2.626E1	2.879E3

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Funding Sources

The authors would like to thank the National Natural Science Foundation of China (No. 50974018) and Ministry of Education (No. 108007) for the financial support.

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