Solid-Liquid Equilibrium for Quaternary System Na₂SO₄-NaCl-H₂O₂-H₂O at 283.15 K

Hong-Kun Zhao, Rong-Rong Li, Dao-Sen Zhang, Qiu-Hong Zhang, and Cao Tang

The solid-liquid phase equilibrium for the quaternary system Na_2SO_4-$NaCl$-H_2O_2-H_2O was studied at 283.15 K by Schreinemaker's wet residues method. The solubility data for the quaternary system were measured, and the phase diagram was constructed. When the concentration of hydrogen peroxide employed in the experiments was below 50 mass%, four solid phases were present in the quaternary system, which corresponded to $NaCl$, $Na_2SO_4 \cdot 10H_2O$, $Na_2SO_4 \cdot 0.5$-$H_2O_2 \cdot H_2O$, and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$. The phase diagram of the quaternary system included two invariant points and four crystalline zones. The crystalline region of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ was larger than those of $NaCl$, $Na_2SO_4 \cdot 10H_2O$, or $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$.

1. Introduction

$4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ is a compound obtained in aqueous solution by reaction of Na_2SO_4, $NaCl$, and H_2O_2. The crystalline compound has good properties as a whitener, it dissolves quickly, and its solubility in cold water is high. In addition, it can be prepared from nontoxic salts that are abundant, inexpensive, and used regularly in washing powder formulations. Adams and Pritchard[1,2] studied its clathrate structure and confirmed that the $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ with the cage structure was more stable than sodium percarbonate and sodium perborate. Subsequently, the preparation methods and applications have been reported in the literature.[3-9] Recently, Cosgrove and William studied its thermal decomposition behavior.[10] Forner and coworkers[11] discussed the industrial process for obtaining the stable compound $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$.

It is well known that solid-liquid phase equilibrium data are important in crystallization processes. The preparation process of the $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ is based on the phase diagram of the quaternary system Na_2SO_4-$NaCl$-H_2O_2-H_2O. The solid-liquid phase equilibrium data are very important in the design of equipment for separation processes in the chemical industry. However no solubility data for the quaternary system can be found in the literature.[12] In order to obtain a higher yield of the compound $4Na_2SO_4 \cdot 2H_2O_2 \cdot$-$NaCl$, the reaction is usually performed at relative low temperature. In this work, we studied the solid-liquid equilibrium of the quaternary system Na_2SO_4-$NaCl$-H_2O_2-H_2O at

283.15 K. The objective of this research was to generate and analyze the phase diagram of quaternary system using the Schreinemakers wet residue method,[13] based on the following: The tie line joining the composition of the pure solid and of the saturated liquid in equilibrium with it is the locus of all intermediate compositions corresponding to varying amounts of solid and liquid phase. This includes the composition of the liquid phase and of crystals wet with mother liquor. A straight line drawn through a pair of points representing such compositions on a phase diagram is a segment of the tie line and therefore passes through the composition of the pure solid. The lines drawn through several such pairs of composition, each corresponding to a different original mixture, have a common intersection at the composition of the pure solid phase.

2. Materials and Experimental

2.1 Materials

The chemicals used are of analytical grade. The hydrogen peroxide (≤ 50 mass%) is purchased from the Puyang chemical plant and does not contain stabilizers. The other chemicals are provided by the Beijing Chemical Plant and used without further purification: sodium sulfate (≥99.9 mass%), sodium chloride (≥99.9 mass%). The water used to prepare solutions is twice-distilled water (conductivity <5 μS/cm).

2.2 Procedure

A thermostat was used in this experiment, with a device for rotating several bottles at a time. The isothermal dissolution method was used during experiments. Excess sodium sulfate and/or sodium chloride was dissolved in 25 mL of aqueous hydrogen peroxide with various concentrations (0-50 mass%). The saturated solution was transferred to a conical flask. The conical flask was stoppered and placed in a thermostat at (283.15 ± 0.01 K). To ensure

Hong-Kun Zhao, Rong-Rong Li, Dao-Sen Zhang, Qiu-Hong Zhang, and Cao Tang, College of Chemistry & Chemical Engineering, YangZhou University, Yangzhou, Jiangsu 225002, People's Republic of China. Contact e-mail: hkzhao@zzu.edu.cn.

Table 1 Mass fraction solubilities of the system sodium chloride-hydrogen peroxide, water at 283.15 K

No.	Mass fraction of liquid phase, %		Mass fraction of moist solid phase, %		Density of liquid phase, g/mL	Solid phase
	NaCl	H_2O_2	NaCl	H_2O_2		
1	20.74	34.25	93.73	2.99	1.3119	NaCl
2	20.67	32.27	93.69	2.93	1.2927	NaCl
3	20.67	28.16	92.82	2.74	1.274	NaCl
4	21.66	22.45	93.46	2.48	1.2665	NaCl
5	21.66	18.8	93.19	2.37	1.2531	NaCl
6	22.63	15.65	93.22	2.41	1.2387	NaCl
7	23.94	11.04	93.13	2.33	1.2384	NaCl
8	25.39	6.86	92.89	2.29	1.2189	NaCl
9	26.29	0	93.09	2.16	1.2017	NaCl

Table 2 Mass fraction solubilities of the system sodium sulfate-hydrogen peroxide, water at 283.15 K

No.	Mass fraction of liquid phase, %		Mass fraction of moist solid phase, %		Density of liquid phase, g/mL	Solid phase
	H_2O_2	Na_2SO_4	H_2O_2	Na_2SO_4		
1	36.16	23.91	11.97	73.71	1.4095	$Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$
2	33.23	24.47	11.6	74.01	1.3845	$Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$
3	30.75	24.98	11.23	73.78	1.3741	$Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$
4	25.98	26.25	10.66	75.23	1.3728	$Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$
5	22.65	27.12	11.13	74.09	1.3455	$Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$
6	20.17	27.85	7.95	62.23	1.3326	$Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ + $Na_2SO_4 \cdot 10H_2O$
7	19.74	27.49	4.77	53.04	1.3492	$Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ + $Na_2SO_4 \cdot 10H_2O$
8	18.81	24.24	2.9	40.8	1.2896	$Na_2SO_4 \cdot 10H_2O$
9	16.5	21.44	2.82	41.13	1.2525	$Na_2SO_4 \cdot 10H_2O$
10	13.9	18.23	2.77	41.09	1.2201	$Na_2SO_4 \cdot 10H_2O$
11	9.93	14.29	2.43	41.11	1.1612	$Na_2SO_4 \cdot 10H_2O$
12	7.12	12.72	2.34	40.5	1.1543	$Na_2SO_4 \cdot 10H_2O$
13	4.35	10.68	2.38	40.19	1.1115	$Na_2SO_4 \cdot 10H_2O$
14	0	8.35	0	40.23	1.0628	$Na_2SO_4 \cdot 10H_2O$

Table 3 Mass fraction solubilities of the system sodium sulfate-sodium chloride, water at 283.15 K

No.	Mass fraction of liquid phase, %		Mass fraction of moist solid phase, %		Density of liquid phase, g/mL	Solid phase
	NaCl	Na_2SO_4	NaCl	Na_2SO_4		
1	24.74	0	91.42	0.12	1.1803	NaCl
2	24.36	1.51	91.28	0.19	1.1997	NaCl
3	23.99	2.63	90.09	0.2	1.2176	NaCl
4	23.23	3.76	90.87	0.17	1.2245	NaCl
5	22.89	3.75	58.31	14.62	1.2289	NaCl + $Na_2SO_4 \cdot 10H_2O$
6	20.6	3.36	32.64	2.06	1.2201	$Na_2SO_4 \cdot 10H_2O$
7	18.72	3.01	33.15	1.73	1.2043	$Na_2SO_4 \cdot 10H_2O$
8	14.51	3.39	34.84	1.98	1.1677	$Na_2SO_4 \cdot 10H_2O$
9	11.19	3.65	34.96	1.44	1.1448	$Na_2SO_4 \cdot 10H_2O$
10	7.03	4.8	37.79	1.36	1.125	$Na_2SO_4 \cdot 10H_2O$
11	2.94	6.77	38.13	1.05	1.1031	$Na_2SO_4 \cdot 10H_2O$
12	0	8.28	39.62	0	1.0813	$Na_2SO_4 \cdot 10H_2O$

2.3 Analysis

The hydrogen peroxide concentration was determined by titrating the acidified solution with standard potassium permanganate. The sodium chloride concentration was titrated with a standard solution of silver nitrate in the presence of three drops of 0.1% (w/v) potassium chromate as an indicator. The sodium sulfate concentration was determined by titrating with a standard solution of barium chloride in the presence of sodium alizarinsulfonate as an indicator.[14] The densities (ρ) of equilibrium liquid phase were measured with a specific weighting bottle calibrated by the floating force of air with a precision of ±0.2 mg. The solute and the solvent were prepared using an electronic balance that had a range of measurement up to 120 g, with an uncertainty of ±0.0001 g. Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis (precision 0.01%).

3. Results and Discussion

The solubility of the ternary systems NaCl-H_2O_2-H_2O, Na_2SO_4-H_2O_2-H_2O, Na_2SO_4NaCl-H_2O at 283.15 K cannot be found in the literature.[12] In this work, the solubility data for the three ternary systems are determined experimentally. The measured solubility of the ternary systems and the quaternary system Na_2SO_4-NaCl-H_2O_2-H_2O at 283.15 K are shown in Tables 1, 2, 3, 4, respectively. The phase diagrams of these systems at 283.15 K are plotted in Fig. 1 to 5.

3.1 Ternary System

Figures 1 to 3 are phase diagrams of the ternary systems, NaCl-H_2O_2-H_2O, Na_2SO_4-H_2O_2-H_2O, and Na_2SO_4-NaCl-H_2O at 283.15 K, respectively. It can be seen from Fig. 1 that NaCl-H_2O_2-H_2O is a simple ternary system. The

that sampling was performed under equilibrium conditions, a preliminary test was carried out in which the liquid concentration and the density were measured as a function of time. Two types of experiment were carried out, one starting from a supersaturated solution, in which the solid phase precipitated to reach equilibrium and the other, starting from a nonsaturated solution, in which solid dissolved to reach equilibrium. The results showed that for both cases about 4 h was sufficient to reach equilibrium. In our experiments, sampling was performed after a minimum of 5 h. The composition of the solid phase was determined by Schreinemaker's method.[13] After the equilibrium was achieved, the solid phase and the liquid phase were separated by filtration at 283.15 K and then analyzed, respectively.

Table 4 Mass fraction solubilities of the quaternary system sodium sulfate-sodium chloride-hydrogen peroxide, water at 283.15 K

| | Mass fraction, % | | | | | | | | Jãneck index, kg/100 kg dry-salt | | | | | | | | | |
| | Liquid phase | | | | Moist solid phase | | | | Liquid phase | | | | Moist solid phase | | | | Density of liquid | |
No.	Na$_2$SO$_4$	NaCl	H$_2$O$_2$	H$_2$O	Na$_2$SO$_4$	NaCl	H$_2$O$_2$	H$_2$O	Na$_2$SO$_4$	NaCl	H$_2$O$_2$	H$_2$O	Na$_2$SO$_4$	NaCl	H$_2$O$_2$	H$_2$O	phase, g/mL	Solid phase
1	1.59	19.29	36.29	42.83	36.08	36.29	15.15	12.48	2.78	33.74	63.48	74.92	41.22	41.46	17.31	14.26	1.3179	B + A
2	1.47	19.89	30.98	46.99	40.75	39.58	7.89	11.78	4.05	37.52	58.43	88.63	46.19	44.87	8.94	13.36	1.3003	
3	2.1	20.84	26.72	50.34	31.63	48.28	6.09	14	4.22	41.97	53.81	101.42	36.78	56.14	7.08	16.27	1.2849	
4	3.87	21.21	21.61	53.31	40.18	49.33	6.59	3.9	8.29	45.43	46.28	114.18	41.81	51.33	6.86	4.06	1.2725	
5	3.02	21.74	17.72	57.52	17.74	71.27	4.33	6.66	7.11	51.18	41.71	135.4	19.01	76.36	4.64	7.14	1.2566	
6	2.98	23.57	14.48	58.97	31.58	48.22	6.13	14.07	7.26	57.44	35.3	143.74	36.75	56.12	7.13	16.37	1.2504	
7	3.04	24.85	12.36	59.75	58.1	26.03	8.35	7.52	7.55	61.74	30.77	148.45	62.82	28.15	9.03	8.13	1.2448	
8	3.8	24.19	7.84	64.17	38.83	44.1	8.13	8.94	10.6	67.51	21.89	179.11	42.64	48.43	8.93	9.82	1.2343	
9	4.78	23.16	4.88	67.18	67.87	23.09	7.1	1.94	14.56	70.57	14.87	204.69	69.21	23.55	7.24	1.98	1.2241	
10	5.59	22.98	3.77	67.66	69.97	19.42	7.18	3.44	17.29	71.06	11.66	209.21	72.46	20.11	7.44	3.55	1.2284	
11	4.09	24.53	0.62	70.76	27.42	33.64	0.073	38.87	13.99	83.89	2.12	242	44.85	55.03	0.12	63.58	1.2064	N$_{10}$ + Aeee
12	5.03	24.2	1.04	69.73	23.85	42.6	0.18	33.37	16.62	79.92	3.46	230.31	35.79	63.94	0.27	50.08	1.2093	
13	5.05	24.28	1.82	68.85	22.38	43.58	0.21	33.83	16.21	77.95	5.84	221.03	33.82	65.87	0.31	51.13	1.2131	
14	7.27	24.36	2.16	66.21	32.38	22.68	0.52	44.42	21.52	72.09	6.39	211.43	58.25	40.81	0.94	79.92	1.212	
15	5.65	23.63	3.62	67.1	26.01	28.99	1.21	43.79	17.17	71.82	11	203.95	46.27	51.57	2.15	77.9	1.2163	
16	5.21	23.36	4.57	66.76	42.04	17.45	1.88	36.82	15.97	70.28	13.75	200.84	68.5	28.43	3.06	62.95	1.2193	
17	5.08	22.55	4.72	67.65	63.41	6.79	5.39	24.51	15.7	69.71	14.59	209.12	83.89	8.98	7.13	32.29	1.2283	N$_{10}$ + B
18	6.4	21.59	5.87	66.14	57.36	7.04	5.17	30.43	18.9	63.76	17.34	195.33	82.45	10.12	7.43	43.74	1.2232	
19	6.65	20.38	7.21	65.76	50.94	4.38	3.13	41.55	19.42	59.52	21.06	192.06	87.15	7.49	5.36	71.09	1.2125	
20	6.93	17.23	8.24	67.6	57.04	5.52	5.09	32.35	21.39	53.18	25.43	208.64	84.32	8.16	7.52	47.82	1.2339	
21	8.54	16.58	9.89	64.99	54.82	4.46	4.57	36.14	24.39	47.36	28.25	185.63	85.86	6.99	7.16	56.62	1.2239	
22	10.44	16.12	11.54	61.9	50.45	4.32	4.21	41.02	27.4	42.31	30.29	162.47	85.54	7.32	7.14	69.55	1.2304	
23	11.35	12.25	13.11	63.29	47.08	3.53	4.17	45.22	30.92	33.37	35.71	172.41	85.94	6.44	7.61	82.55	1.2368	
24	11.95	12.07	13.09	62.89	52.4	5.54	4.98	37.08	32.2	32.52	35.27	169.47	83.28	8.81	7.91	58.93	1.2442	
25	14.16	11.13	14.01	60.7	52.06	3.93	4.51	39.5	36.03	28.32	35.65	154.45	86.05	6.5	7.45	65.29	1.2448	
26	14.5	9.47	15.36	60.67	58.12	4.19	5.36	32.34	36.87	24.08	39.05	154.28	85.89	6.19	7.92	47.78	1.2456	
27	15.16	8.85	15.94	60.05	64.65	7.56	8.55	19.24	39.62	21.57	38.81	143.52	80.05	9.36	10.59	23.82	1.2565	
28	14.29	7.41	16.3	62	60.57	5.08	6.4	27.96	37.61	19.5	42.89	163.16	84.07	7.05	8.88	38.79	1.257	
29	19.06	5.6	17.15	58.19	57.6	4.45	6.16	31.79	45.59	13.39	41.02	139.18	84.45	6.52	9.03	46.61	1.3257	
30	21.75	1.45	32.14	44.66	82.88	0.54	13.66	2.92	39.3	2.62	58.08	80.7	85.37	0.56	14.07	3.01	1.3542	B + C
31	21.95	1.85	30.64	45.56	75.36	3.86	11.25	9.53	40.32	3.4	56.28	83.69	83.3	4.27	12.44	10.53	1.3473	
32	22.76	2.31	26.24	48.69	76.81	4.14	10.93	8.12	44.36	4.5	51.14	94.89	83.6	4.51	11.9	8.84	1.3266	
33	20.56	1.37	34.76	43.31	75.72	2.27	13.41	8.6	36.27	2.41	61.32	76.43	82.85	2.48	14.67	9.42	1.3118	
34	23.09	3.48	23.08	50.35	71.54	2.69	11.88	13.89	46.5	7.01	46.49	101.42	83.08	3.12	13.8	16.13	1.3076	
35	20.61	4.64	17.61	57.14	59.62	4.58	6.61	29.19	48.09	10.83	41.09	133.32	84.2	6.47	9.33	41.22	1.2897	
36	20.84	3.88	18.02	57.26	60.72	5.07	7.23	26.97	48.76	9.08	42.16	133.97	83.16	6.94	9.9	36.95	1.29	
37	25.4	3.37	19.25	51.98	53.33	0.56	4.1	42.01	52.89	7.02	40.09	108.22	91.96	0.97	7.07	72.45	1.3251	N$_{10}$ + C
38	26.11	1.93	19.21	52.75	55.29	3.66	6.6	34.44	55.26	4.08	40.66	111.64	84.35	5.58	10.07	52.56	1.3108	
39	25.68	1.52	18.83	53.97	70.52	7.2	10.62	11.55	55.79	3.3	40.97	117.25	79.85	8.14	12.01	13.07	1.3257	
40	25.76	1.05	19.5	53.69	54.84	0.39	7.09	37.68	55.63	2.27	42.11	115.94	88	0.63	11.38	60.46	1.3006	

A, NaCl; B, 4Na$_2$SO$_4$·2H$_2$O$_2$·NaCl; C, Na$_2$SO$_4$·0.5H$_2$O$_2$·H$_2$O; N$_{10}$, Na$_2$SO$_4$·10H$_2$O

solubility of NaCl at 283.15 K varies a little with the concentration of hydrogen peroxide aqueous solution. Figure 2 is the phase diagram of the ternary system Na$_2$SO$_4$-H$_2$O$_2$-H$_2$O at 283.15 K. It shows that two hydrates are presented when the concentration of H$_2$O$_2$ is less than 50 mass %. The analytical results indicate that one hydrate is Na$_2$SO$_4$·0.5H$_2$O$_2$·H$_2$O, and the other is Na$_2$SO$_4$·10H$_2$O. In the ternary system Na$_2$SO$_4$-NaCl-H$_2$O, there is no crystalline region of anhydrous sodium sulfate in the system at 283.15 K as shown in Fig. 3.
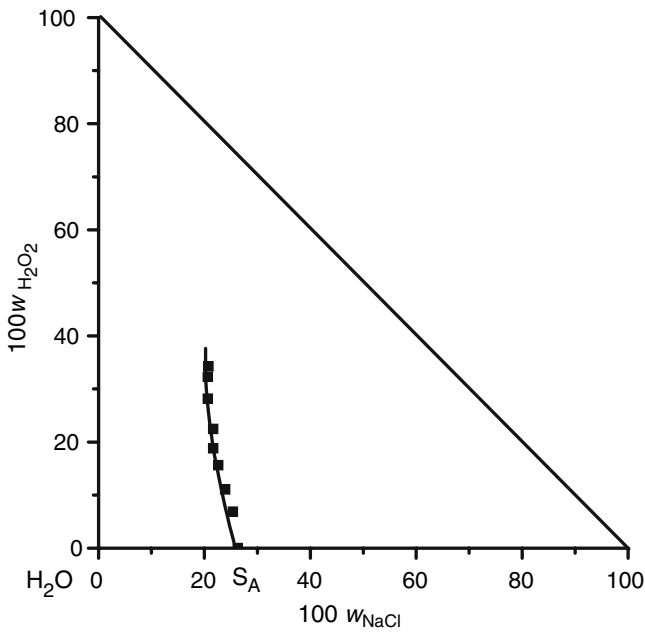
Fig. 1 Phase diagram for the system sodium chloride-hydrogen peroxide-water at 283.15 K. S_A, solubility of NaCl in water at 283.15 K; w, mass fraction
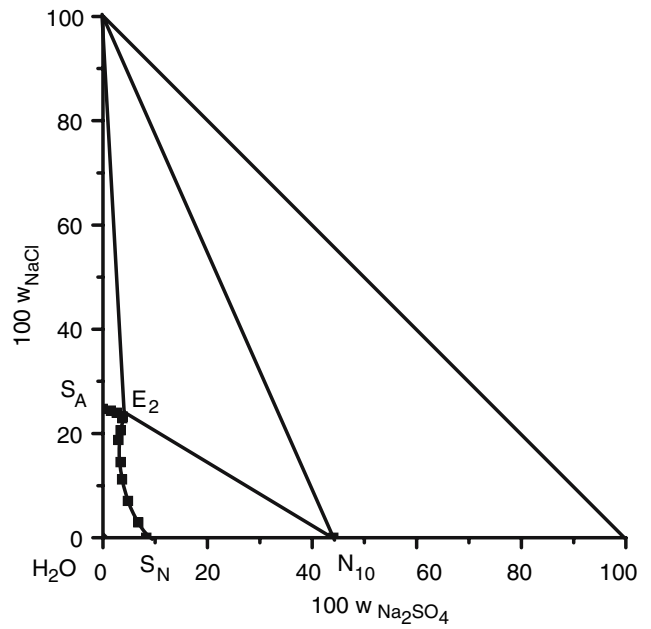

Fig. 3 Phase diagram for the system sodium sulfate-sodium chloride-water at 283.15 K. N_{10}, $Na_2SO_4 \cdot 10H_2O$; E_2, cosaturated point; S_N, solubility of $Na_2SO_4 \cdot 10H_2O$ in water at 283.15 K; S_A, solubility of NaCl in water at 283.15 K; w, mass fraction
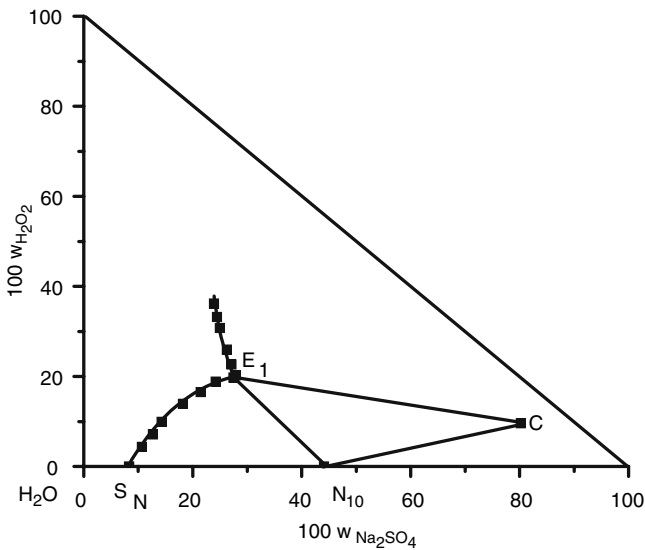

Fig. 2 Phase diagram for the system sodium sulfate-hydrogen peroxide-water at 283.15 K. N_{10}, $Na_2SO_4 \cdot 10H_2O$; C, $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$; E_1, cosaturated point; S_N, solubility of $Na_2SO_4 \cdot 10H_2O$ in water at 283.15 K; w, mass fraction

3.2 Quaternary System

The phase diagrams of the quaternary system Na_2SO_4-NaCl-H_2O_2-H_2O at 283.15 K are given in Fig. 4 and 5. It can be seen that when the concentration of hydrogen peroxide employed in the experiments is below 50 mass%,
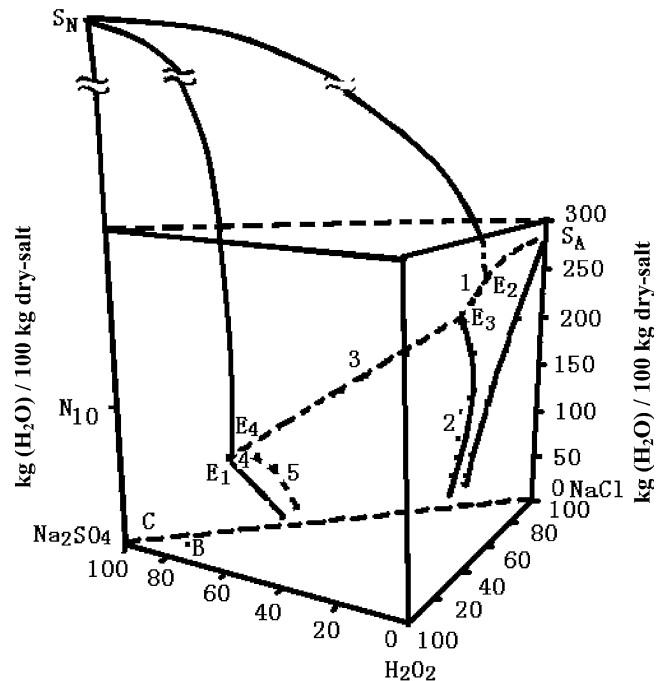

Fig. 4 Phase diagram for the quaternary system sodium sulfate-sodium chloride-hydrogen peroxide-water at 283.15 K. C, $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$; B, $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$; E_3, cosaturated point of a solution with solid phases NaCl, $Na_2SO_4 \cdot 10H_2O$, and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$; E_4, cosaturated point of a solution with solid phases $Na_2SO_4 \cdot 10H_2O$, $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, and $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$; B, C, S_A, N_{10}, and S_N have the same meanings as those described in Figures 1 to 3
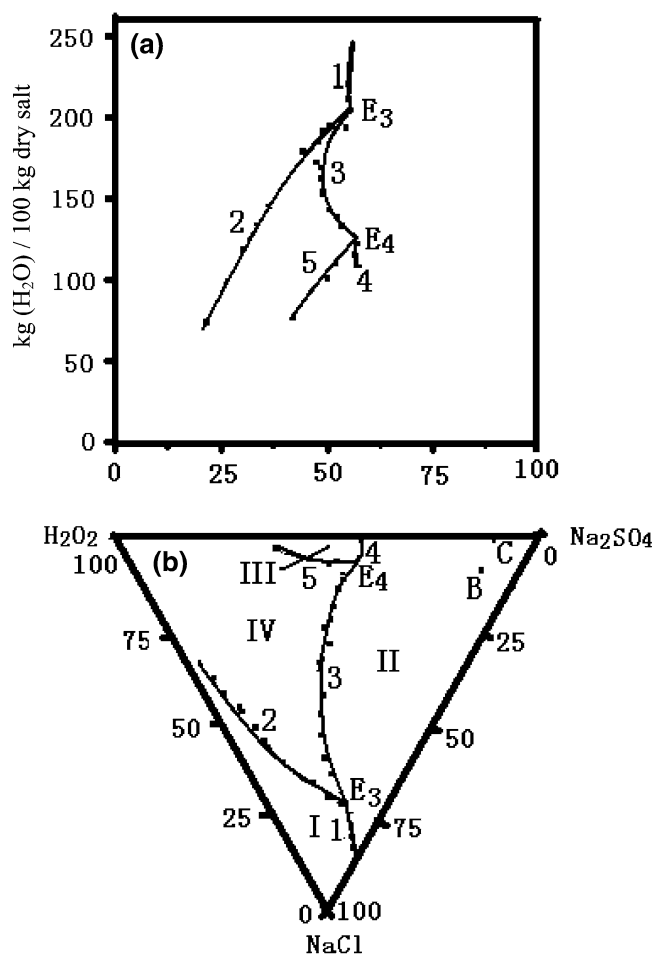
Fig. 5 Jãneck projection of the phase diagram for the quaternary system sodium sulfate-sodium chloride-hydrogen peroxide-water at 283.15 K. (a) Aqueous phase diagram. (b) Dry salt phase diagram. I, NaCl crystallization zone; II, $Na_2SO_4 \cdot 10H_2O$ crystallization zone; III, $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ crystallization zone; IV, $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ crystallization zone; B and C have the same meanings as those described in Fig. 4

there are four solids formed in the system, which correspond to $Na_2SO_4 \cdot 10H_2O$, NaCl, $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, respectively. There are five cosaturation curves of two components: curve 1, corresponding to the coexistence of crystals $Na_2SO_4 \cdot 10H_2O$ and NaCl with the saturated solution; curve 2, corresponding to the coexistence of crystals NaCl and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ with the saturated solution; curve 3, corresponding to the coexistence of crystals $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ and $Na_2SO_4 \cdot 10H_2O$ with the saturated solution; curve 4, corresponding to the coexistence of crystals $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ and $Na_2SO_4 \cdot 10H_2O$ with the saturated solution; curve 5, corresponding to the coexistence of crystals $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ and $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ with the saturated solution.

The quaternary diagram is divided into four crystallization zones by five curves: I, corresponding to the equilibrium of crystal NaCl with saturated solution; II, corresponding to the equilibrium of crystal $Na_2SO_4 \cdot 10H_2O$ with saturated

solution; III, corresponding to the equilibrium of crystal $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ with saturated solution; IV, corresponding to the equilibrium of crystal $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ with saturated solution. The crystalline region of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ is the largest one among the four crystallization regions. The results indicate that the compound $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ can be easily prepared at 283.15 K.

As shown in Fig. 4 and 5, there are two invariant points E_3 and E_4. E_3 corresponds to coexistence of solids NaCl, $Na_2SO_4 \cdot 10H_2O$, and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, and E_4 corresponds to coexistence of solids $Na_2SO_4 \cdot 10H_2O$, $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$, and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$. E_3 and E_4 are invariant points at 288 K.

4. Conclusion

The phase equilibrium for the quaternary system Na_2SO_4-NaCl-H_2O_2-H_2O and its subsystems at 283.15 K was studied by Schreinemaker's wet residues method. The phase diagram was constructed based on the measured solubility. At studied temperature, four solid phases formed in the quaternary system Na_2SO_4-NaCl-H_2O_2-H_2O that corresponded to $Na_2SO_4 \cdot 10H_2O$, NaCl, $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$, and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, respectively. The phase diagram of the quaternary system included two invariant points and four crystalline zones. The crystalline region of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ is larger than those of other three solids. The phase diagram of the system Na_2SO_4-NaCl-H_2O_2-H_2O provide the fundamental basis for the preparation and separation out of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$ from the reaction system.

References

1. J.M. Adams and R.G. Pritchard, The Crystal Structure of $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, *Acta Crystallogr.*, 1978, **B34**(5), p 1428-1432, in English
2. J.M. Adams, R.G. Pritchard, and J.M. Thomas, A Novel Tunnel Structure Containing Enclathrated Hydrogen Peroxide: $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, *J. Chem. Soc., Chem. Commun.*, 1978, **3**, p 288-289, in English
3. Y. Ito and T. Mashiko, "Stable Sodium Sulfate-Hydrogen Peroxide-Sodium Chloride Adduct and Process for Preparing Same," U.K. patent 1,480,884, July 27, 1977, in English
4. Y. Nakagawa, S. Sugiura, and K. Matsunaga, "Detergent Composition Containing Novel Bleaching Agent," U.S. patent 3,979,312, September 7, 1976, in English
5. Y. Nakagawa, S. Sugiura, and K. Matsunaga et al., "Bleaching Composition," U.S. patent 3,979,313, September 7, 1976, in English

6. Y. Ito and T. Mashiko, "Stable Sodium Sulfate-Hydrogen Peroxide-Sodium Chloride Adduct and Process for Preparing Same," U.S. patent 4,005,182, January 25, 1977, in English

7. W. Doetsch, H. Honig, and R. Siegel, "Hydrogen Peroxide Adduct and Process for Preparation and Use Thereof," U.S. patent 4,400,367, August 23, 1983, in English

8. Y. Ito, "Process for Preparing Stabilized Adduct of Sodium Sulphate-Hydrogen Peroxide-Sodium Chloride," J.P. patent 60051611, August 31, 1985, in Japanese

9. B.J. Forner and P.R. Artlgas, "Process for Obtaining Granules of a Stable Adduct of Sodium Sulphate and Hydrogen Peroxide Containing Sodium Chloride," E.P. patent 1,258,454, November 20, 2002, in English

10. S.D. Cosgrove and J. William, Chemistry of Sulfate Chloride Perhydrates. Part 1. Thermal Decomposition of $4Na_2SO_4 \cdot$ $NaCl \cdot 2H_2O_2$ and the Formation of $Na_2SO_4(III)$, *J. Mater. Chem.*, 1998, **8**(2), p 413-417, in English

11. B.J. Forner and P.R. Artlgas, "Industrial Process for Obtaining a Stable Adduct of Na_2SO_4, NaCl and H_2O_2," E.P. patent 1,258,455, November 20, 2002, in English

12. H. Stephen and T. Stephen, *Solubility of Inorganic and Organic Compounds*. Pergamon, Oxford, 1979

13. H. Schott, A Mathematical Extrapolation for the Method of Wet Residues, *J. Chem. Eng. Data*, 1961, **6**(3), p 324-324, in English

14. H.K. Zhao, C. Tang, D.S. Zhang, W.L. Xu, Y.Q. Wang, and P.M. Jian, Solubility and Phase Diagram for the Quaternary System $Na_2CO_3 + Na_2SO_4 + H_2O_2 + H_2O$ at 293 K, *J. Chem. Eng. Data*, 2006, **51**(5), p 1567-1570, in English