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Phase Diagram of the Quaternary System Sodium Sulfate + Sodium Chloride + Hydrogen Peroxide + Water and Its Subsystems: Experimental Data

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Phase diagrams of the quaternary system sodium sulfate + sodium chloride + hydrogen peroxide + water and its subsystems sodium chloride + hydrogen peroxide + water, sodium sulfate + hydrogen peroxide + water, and sodium sulfate + sodium chloride + water were studied at a temperature of 288.15 K using the moist method. In this paper, the solubility data, the densities, and the refractive indexes of the liquid phase of the quaternary system and its subsystems were measured. The phase diagrams of these systems were constructed, and there are four solid phases in the diagrams. The quaternary phase diagram includes two cosatured points, five univariant curves, and four crystallization regions corresponding to NaCl, $Na_2SO_4 \cdot 10H_2O$, $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$, and $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$.

Introduction

Hydrogen peroxide adducts of inorganic compounds generally include sodium percarbonate, sodium perborate, and some phosphate−hydrogen peroxide adducts. These adducts are mainly used for bleaching, sterilization, and the like. The fields of use of these hydrogen peroxide adducts are frequently limited by the properties of the starting inorganic compounds, and because most of the above-mentioned hydrogen peroxide adducts have a very high alkalinity in aqueous solutions, various limitations are imposed on the uses of these adducts. In view of the fact that sodium sulfate is neutral and nontoxic and is a substance that is available at a low cost and is now used in large quantities as a builder for synthetic detergents, it is considered that if it is possible to prepare a stable sodium sulfate−hydrogen peroxide adduct on an industrial scale, significant advantages will be attained. However, because the stability of sodium sulfate−hydrogen peroxide adducts, which are represented by the general formula $Na_2SO_4 \cdot mH_2O_2 \cdot nH_2O$[1] is very poor, processes for preparing the same and processes of using this hydrogen peroxide adduct have scarcely been reported in the art.

The stable sodium sulfate−hydrogen peroxide−sodium chloride adduct with formula $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, which is also named PSC, was first synthesized by the Kao Soap Co. Ltd and Nippon Peroxide Co. Ltd.[2] The PSC adduct is a new type of neutral assistant for synthetic detergents with pH 6−8 in aqueous solutions. In the clathrate structure of this adduct,[3,4] each of the Na^+ ions is surrounded in a distorted octahedron formed by five oxygen atoms and one chloride ion and another Na^+ ion is surrounded in a tetragonal prism formed by oxygen atoms. Therefore, the PSC with the cage structure is more stable than sodium percarbonate and sodium perborate.[5] The synthetic process of PSC has been reported in DE2530529,[2] GB1480884,[5] US3739312,[6] US3739313,[7] US4005182,[8] US440367,[9] and JP6051611.[10] It is well-known that the preparing process of the PSC adduct is based on the phase diagram of the quaternary system $Na_2SO_4 + NaCl + H_2O_2 + H_2O$. Although the ternary diagrams of the subsystems $Na_2SO_4 + NaCl + H_2O$ and $Na_2SO_4 + H_2O_2 + H_2O$ have been investigated, no research was reported on the phase diagram of the quaternary system.[11] It is important to investigate the phase diagram for designing and optimizing the preparing process of the PSC adduct. The objective of this research is to generate and analyze the phase diagrams of the quaternary system and its ternary subsystems. Meanwhile, the densities and refractive indexes of the liquid phase are also measured.

Materials and Experimental Method

Materials. The hydrogen peroxide used was a Puyang product not containing stabilizers. The other chemicals were of reagent quality. The water used to prepare solutions was twice distilled water.

Experiments. The isothermal dissolution method was used during experiments. A known mass of 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 288.15 K. To obtain the time of equilibrium achieved, 15 flasks containing the same solution were used. A 5.0 mL sample of the clarified solution was taken from the liquid phase of each conical flask with a pipet at regular intervals and diluted to 50 mL of final solution in a volumetric flask filled with twice distilled water. If the compositions of the liquid phase in the bottle became constant, this indicated that the equilibrium was achieved. Generally, it took about 6 h to be at equilibrium. After the equilibrium was achieved, the solid and the liquid phases were separated by filtration and then analyzed, respec-

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Table 1. Mass Fraction Solubilities *w* of the System Sodium Chloride (1) + Hydrogen Peroxide (2) + Water (3) at 288.15 K

	liquid phase		moist solid phase				
no.	$100w_1$	$100w_2$	$100w_1$	$100w_2$	density of liq phase/ $g \cdot mL^{-1}$	refractive index	solid phase
1	20.29	37.41	93.18	3.48	1.3212	1.3985	NaCl
2	20.78	33.87	92.89	3.51	1.3123	1.3965	NaCl
3	21.17	31.59	93.16	3.22	1.2997	1.3950	NaCl
4	21.37	27.22	93.44	3.09	1.2822	1.3930	NaCl
5	21.26	29.84	92.96	3.08	1.2903	1.3942	NaCl
6	22.01	23.9	93.07	2.79	1.2930	1.3914	NaCl
7	23.23	16.74	93.38	2.50	1.2252	1.3784	NaCl
8	24.07	12.09	92.39	2.39	1.2358	1.3962	NaCl
9	25.01	5.43	93.25	2.07	1.2172	1.3938	NaCl
10	26.33	0.00	93.66	2.06	1.2057	1.3904	NaCl

tively. To avoid appreciable decomposition of hydrogen peroxide, the temperature in this study was selected at 288.15 K.

Analysis. The moist solid samples were dissolved in water, and aliquot portions of the solutions so obtained and those of the liquid-phase samples were used for the 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. The densities (ρ) were measured with a specific weighing bottle calibrated by the floating force of air with a precision of ±0.2 mg. An Abbe refractometer (model WZS-1) was used to measure the refractive index (η_D) with an accuracy of ±0.0001. The accuracy of the thermostat temperature was ±0.1 K. Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis.

In these studies, X-ray diffraction and infrared absorption spectroscopy were also employed to determine whether the solid phase is pure or compound.

Results and Discussion

The measured solubility and the relative physicochemical property data of the ternary systems $Na_2SO_4 + NaCl + H_2O$, $NaCl + H_2O_2 + H_2O$, and $Na_2SO_4 + H_2O_2 + H_2O$ and the quaternary system $Na_2SO_4 + NaCl + H_2O_2 + H_2O$ are shown in Tables 1−4, respectively. The measured solubility and isothermal phase diagrams of these four systems at 288.15 K were given in Figures 1−4, respectively.

Ternary System $NaCl + H_2O_2 + H_2O$. It can be seen from Figure 1 that $NaCl + H_2O_2 + H_2O$ is a simple ternary system. No solid solutions and double salts were formed in the system. Only sodium chloride salted out. The single-saturation curve TS_A in Figure 1 serves as a boundary between a region of homogeneous unsaturated solutions and a region where precipitation occurs. Along the curve the solution is saturated with sodium chloride. It can also be found in Figure 1 that the solubility of sodium chloride undergoes a slight decrease with increase of the concentrations of H_2O_2.

Table 2. Mass Fraction Solubilities *w* of the System Sodium Sulfate (1) + Hydrogen Peroxide (2) + Water (3) at 288.15 K

	liquid phase		moist solid phase				
no.	$100w_1$	$100w_2$	$100w_1$	$100w_2$	density of liq phase/ $g \cdot mL^{-1}$	refractive index	solid phase[a]
1	24.86	36.02	73.86	12.25	1.4080	1.3961	C
2	25.53	32.68	74.26	12.16	1.3982	1.3940	C
3	25.65	30.23	75.4	11.78	1.3881	1.3918	C
4	26.9	25.82	75.01	11.88	1.3800	1.3919	C
5	29.16	21.55	73.78	11.59	1.3653	1.3884	C
6	29.98	17.71	59.27	8.42	1.3484	1.3899	N_{10} + C
7	30.02	17.49	51.14	4.77	1.3483	1.3896	N_{10} + C
8	26.69	15.7	40.81	2.9	1.3272	1.3838	N_{10}
9	22.34	12.97	41.11	1.96	1.2600	1.3759	N_{10}
10	28.66	16.58	39.67	2.34	1.3382	1.3892	N_{10}
11	19.98	11.32	40.13	2.01	1.2249	1.3726	N_{10}
12	17.3	8.85	40.8	1.56	1.1982	1.3666	N_{10}
13	15.12	4.96	40.82	0.83	1.1234	1.3543	N_{10}
14	11.4	0.00	40.82	0.00	1.0687	1.3422	N_{10}

[a] N_{10}, $Na_2SO_4 \cdot 10H_2O$; C, $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$.

Table 3. Mass Fraction Solubilities *w* of the System Sodium Sulfate (1) + Sodium Chloride (2) + Water (3) at 288.15 K

	liquid phase		moist solid phase				
no.	$100w_1$	$100w_2$	$100w_1$	$100w_2$	density of liq phase/ $g \cdot mL^{-1}$	refractive index	solid phase[a]
1	0	26.5	0.18	91.65	1.1984	1.3814	NaCl
2	2.66	25.38	0.22	91.38	1.2116	1.3820	NaCl
3	3.82	24.69	0.19	90.97	1.2199	1.3832	NaCl
4	5.82	23.54	0.16	91.33	1.2317	1.3838	NaCl
5	5.83	23.54	13.61	63.54	1.2300	1.3846	NaCl + N_{10}
6	5.85	23.52	28.74	29.45	1.2297	1.3842	NaCl + N_{10}
7	5.65	18.33	39.26	1.89	1.1834	1.3732	N_{10}
8	6.08	11.34	39.41	1.47	1.1356	1.3621	N_{10}
9	8.22	5.82	40.08	1.06	1.1124	1.3556	N_{10}
10	12.66	0	40.21	0	1.1984	1.3510	N_{10}

Ternary System $Na_2SO_4 + H_2O_2 + H_2O$. It is shown in Figure 2 that two double salts were presented in the system $Na_2SO_4 + H_2O_2 + H_2O$ when the concentration of H_2O_2 was less than 50 mass %. The results of chemical analysis, X-ray power diffusion, and infrared absorption spectroscopy indicated that one double salt was $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ and the other was $Na_2SO_4 \cdot 10H_2O$. No double salt like $Na_2SO_4 \cdot 2H_2O_2$ was found in the system. Those observations were in good agreement with the results reported by Pani.[1] In the phase diagram as shown in Figure 2, E_1 is a cosaturated point, which indicates a solution saturated with $Na_2SO_4 \cdot 10H_2O$ and $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$. The regions in the diagram are denoted as follows: 21, unsaturated solution; 22, region corresponding to the coexistence of $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ and the saturated solution; 23, region corresponding to the coexistence of $Na_2SO_4 \cdot 10H_2O$ and the saturated solution; 24, region corresponding to the coexistence of $Na_2SO_4 \cdot 10H_2O$, $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$, and the saturated solution. E_1M is a single-saturation curve corresponding to the solid-phase $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$, and E_1S_N is a single-saturation curve corresponding to the solid-phase $Na_2SO_4 \cdot 10H_2O$. It is also indicated in Figure 2 that $Na_2SO_4 \cdot 0.5H_2O_2 \cdot H_2O$ is an asymmetric double salt.

Ternary System $Na_2SO_4 + NaCl + H_2O$. Figure 3 is phase diagram of the system $Na_2SO_4 + NaCl + H_2O$ at 288.15 K. The diagram given in Figure 3 is similar to the phase diagram at 290.65 K but different from the phase diagram at 298 K. There are three crystallization regions in Figure 3: 32, region corresponding to the coexistence of NaCl and the saturated solution; 33, region corresponding to the coexistence of $Na_2SO_4 \cdot 10\ H_2O$ and the saturated solution; 34, region corresponding to the coexistence of $Na_2SO_4 \cdot 10\ H_2O$, NaCl, and the saturated solution; 31, unsaturated solution. E_2 is a cosaturated point, which indicates a solution saturated with $Na_2SO_4 \cdot 10\ H_2O$ and NaCl. There

Table 4. Mass Fraction Solubilities *w* of the Quaternary System Sodium Sulfate (1) + Sodium Chloride (2) + Hydrogen Peroxide (3) + Water (4) at 288.15 K[a]

	mass fraction								Jãneck index/[kg/100 kg of dry salt]										
	liquid phase				moist solid phase				liquid phase				moist solid phase						
no.	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$	Na_2SO_4	NaCl	H_2O_2	H_2O	Na_2SO_4	NaCl	H_2O_2	H_2O	density/ $g{\cdot}mL^{-1}$	n_D	solid phase
1	4.32	19.43	36.56	39.69	40.63	51.02	5.85	2.50	7.16	32.22	66.62	65.81	41.67	52.33	6.00	2.56	1.3280	1.4003	B + A
2	2.79	21.24	22.34	53.63	36.23	52.42	6.08	5.27	6.02	45.8	48.18	115.66	38.25	55.34	6.42	5.56	1.2839	1.3918	B + A
3	2.99	22.40	15.49	59.12	17.50	76.21	3.26	3.02	7.32	54.8	37.88	144.61	18.14	78.59	3.36	3.12	1.4570	1.3902	B + A
4	2.77	21.88	14.02	61.36	9.91	86.37	1.90	1.83	7.18	56.52	36.29	153.83	12.39	87.97	1.94	1.85	1.2528	1.3889	B + A
5	3.30	22.72	11.45	62.53	79.30	8.01	7.20	5.49	8.81	60.64	30.56	166.88	83.91	8.48	7.62	5.81	1.2484	1.3877	B + A
6	3.46	22.87	9.14	64.53	76.01	10.26	7.73	6.01	9.75	64.48	25.77	181.93	80.86	10.91	8.22	6.38	1.2418	1.3862	B + A
7	4.49	22.84	7.14	65.53	79.54	10.18	8.80	1.48	13.03	66.26	20.21	190.11	80.73	10.33	8.93	1.50	1.2784	1.3851	B + A
8	4.91	23.23	5.08	66.78	67.73	21.05	7.39	3.83	14.78	69.93	15.29	201.02	70.43	21.89	7.68	3.98	1.2398	1.3850	B + A
9	5.32	23.01	4.02	67.65	73.24	15.45	7.86	3.46	16.45	71.13	12.43	209.12	75.86	16.00	8.14	3.57	1.2465	1.3838	B + A
10	6.75	22.83	3.23	22.83	63.46	29.60	6.28	0.66	20.57	69.58	9.84	204.79	63.88	29.80	6.32	0.66	1.2420	1.3852	B + A
11	7.58	22.61	2.55	67.26	23.86	64.09	1.31	10.74	23.15	69.06	7.79	205.44	30.75	71.80	1.47	12.03	1.2458	1.3849	N_{10} + A
12	8.83	21.81	1.83	67.53	30.83	56.63	0.23	12.31	27.19	67.17	5.64	207.98	35.16	64.58	0.26	14.04	1.2503	1.3851	N_{10} + A
13	8.28	22.21	1.60	67.91	26.79	60.65		12.56	25.80	69.21	4.97	211.62	30.64	69.36		14.36	1.2460	1.3859	N_{10} + A
14	7.28	22.76	0.84	69.12	26.28	48.94		24.78	23.58	7.3.70	2.72	223.83	34.94	65.06		32.94	1.2406	1.3850	N_{10} + A
15	6.96	23.06	0.33	9.65	31.00	52.75		16.25	22.93	75.98	1.09	229.49	37.01	62.99		19.40	1.2350	1.3848	N_{10} + A
16	7.89	21.28	2.96	67.87	48.12	3.36	1.65	46.87	24.56	66.23	9.21	211.24	90.57	6.32	3.11	88.22	1.2377	1.3840	N_{10} + B
17	9.50	17.44	5.98	67.08	56.02	5.69	4.79	33.50	28.86	52.98	18.17	203.77	84.4	8.56	7.20	50.38	1.2357	1.3803	N_{10} + B
18	11.52	14.06	8.45	65.97	68.37	8.12	7.41	16.10	33.85	41.32	24.83	193.86	81.49	9.68	8.83	19.19	1.2393	1.3802	N_{10} + B
19	12.93	12.79	9.59	64.69	57.75	5.38	5.72	31.34	36.62	36.22	27.16	183.21	83.88	7.81	8.31	45.24	1.2354	1.3791	N_{10} + B
20	15.10	11.21	10.08	63.61	52.89	4.16	4.49	38.47	41.49	30.81	27.70	174.80	85.94	6.76	7.30	62.50	1.2359	1.3800	N_{10} + B
21	15.50	8.83	11.79	63.88	49.73	3.71	4.18	42.39	42.91	24.45	32.64	176.85	86.31	6.44	7.25	73.55	1.2527	1.3800	N_{10} + B
22	18.81	6.53	13.56	61.10	48.19	2.80	3.81	45.21	48.35	16.79	34.86	157.07	87.94	5.11	6.95	82.48	1.2545	1.3809	N_{10} + B
23	22.20	2.64	27.16	48.00	71.44	3.84	12.08	12.64	42.69	5.08	52.23	92.31	81.78	4.40	13.83	14.47	1.3321	1.3884	B + C
24	23.29	2.67	21.51	52.53	73.07	2.39	10.03	14.51	85.47	2.80	11.73	16.97	49.06	5.62	45.31	110.66	1.3379	1.3868	B + C
25	24.16	3.09	17.64	55.11	71.91	3.07	10.53	14.49	53.82	6.88	39.3	122.77	84.10	3.59	12.31	16.95	1.3044	1.3846	B + C
26	23.02	1.35	31.90	43.73	73.91	3.63	11.67	10.79	40.91	2.10	56.69	77.71	82.85	4.07	13.08	12.10	1.3493	1.3905	B + C
27	22.32	3.97	14.02	59.69	66.60	6.79	9.68	16.90	55.37	9.85	34.78	148.08	80.17	8.17	11.65	20.38	1.2917	1.3839	B + C
28	25.32	1.55	15.24	57.89	103.7	0.58	7.23	−11.5	60.13	3.68	36.19	137.47	93.00	0.52	6.48	10.32	1.3802	1.3850	N_{10} + C
29	24.10	2.79	14.37	58.74	69.80	0.68	8.65	20.90	58.41	6.76	34.83	142.37	88.21	0.86	10.93	26.37	1.3099	1.3852	N_{10} + C
30	27.48	1.05	14.50	56.97	71.54	0.20	7.45	20.81	63.86	2.44	33.7	132.4	90.34	0.25	9.41	26.28	1.3369	1.3840	N_{10} + C
31	26.53	1.18	14.58	57.71	68.05	0.039	7.31	24.60	62.73	2.79	34.48	136.46	90.25	0.05	9.70	32.63	1.3272	1.3840	N_{10} + C
32	26.08	2.12	14.53	57.27	70.65	1.37	8.08	19.90	61.03	4.96	34.00	134.03	88.20	1.71	10.09	24.84	1.3264	1.3839	N_{10} + C

[a] A, NaCl; C, $Na_2SO_4{\cdot}0.5H_2O_2{\cdot}H_2O$; B, $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$; N_{10}, $Na_2SO_4{\cdot}10H_2O$.

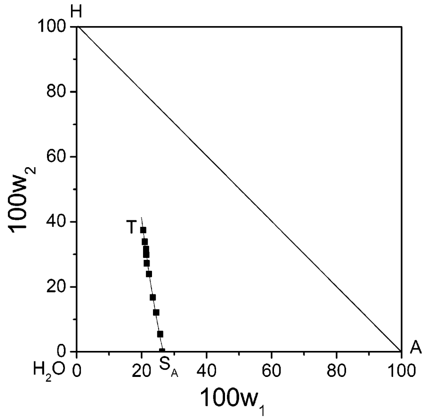

Figure 1. Measured solubility and isothermal phase diagram of the system sodium chloride (1) + hydrogen peroxide (2) + water (3) at 288.15 K: S_A, solubility of NaCl in water at 288.15 K.

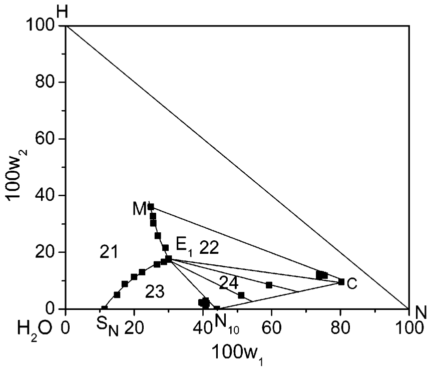

Figure 2. Measured solubility and isothermal phase diagram of the system sodium sulfate (1) + hydrogen peroxide (2) + water (3) at 288.15 K: N_{10}, $Na_2SO_4{\cdot}10H_2O$; C, $Na_2SO_4{\cdot}0.5H_2O_2{\cdot}H_2O$; E_1, cosaturated point; S_N, solubility of Na_2SO_4 in water at 288 0.15 K.

was no crystallization region of anhydrous sodium sulfate in the system 288.15 K, as shown in Figure 3.

Quaternary System Na_2SO_4 + NaCl + H_2O_2 + H_2O. The phase diagram of the quaternary system Na_2SO_4 + NaCl + H_2O_2 + H_2O at 288.15 K was given in Figures 4 and 5. There were four solid phases formed in the system, which 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. There are five *cosaturation* curves of two components: curve 1, corresponding to the coexistence of crystals $Na_2SO_4{\cdot}10\ H_2O$ 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 $Na_2SO_4{\cdot}0.5\ H_2O_2{\cdot}H_2O$ with saturated solution; IV, corresponding to the equilibrium of crystal $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ with saturated solution.

As shown in Figure 4, there are two invariant points E_3 and E_4. E_3 corresponds to coexistence of crystals NaCl, $Na_2SO_4{\cdot}10H_2O$, and $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$; E_4 corresponds to

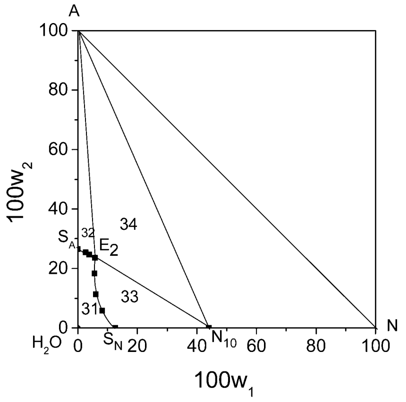

Figure 3. Measured solubility and isothermal phase diagram of the system sodium sulfate (1) + sodium chloride (2) + water (3) at 288.15 K: N_{10}, $Na_2SO_4{\cdot}10H_2O$; E_2, cosaturated point; S_N, solubility of Na_2SO_4 in water at 288 0.15 K.

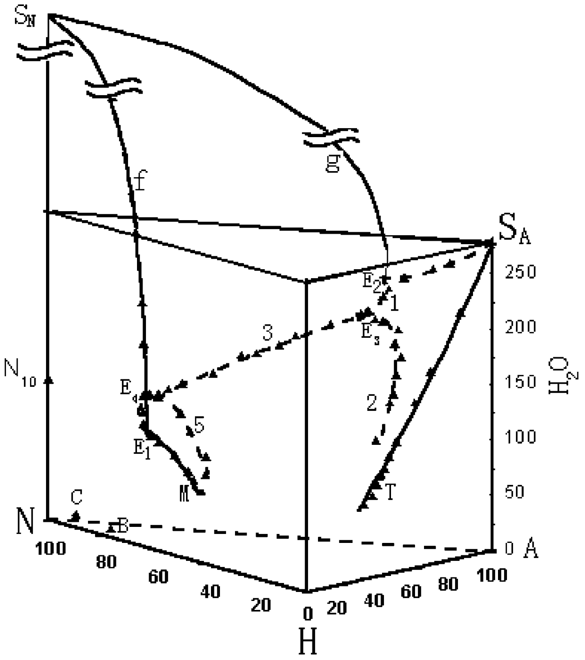

Figure 4. Measured solubility and isothermal phase diagram of the quaternary system sodium sulfate (1) + sodium chloride (2) + hydrogen peroxide (3) + water (4) at 288.15 K: C, $Na_2SO_4{\cdot}0.5H_2O_2{\cdot}H_2O$; B, $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$; E_3, cosaturated point of a solution with solid 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 $Na_2SO_4{\cdot}0.5H_2O_2{\cdot}H_2O$; S_A, N_{10}, A, and S_N have the same meanings as those described in Figures 1 and 2.

coexistence of crystals $Na_2SO_4{\cdot}10H_2O$, $Na_2SO_4{\cdot}0.5H_2O_2{\cdot}H_2O$, and $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$.

Figures 4 and 5 indicate that the adduct $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ is an asymmetric double salt.

It should be noted that the concentration of hydrogen peroxide employed in the experiments is below 50 mass %. For high concentration of hydrogen peroxide (i.e., higher than 50 mass %), the research will be carried out in the future.

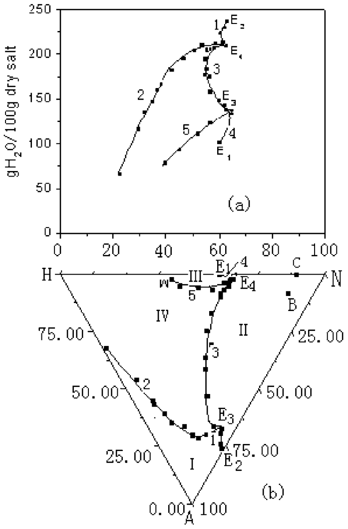

Figure 5. Jãneck projection of the quaternary system sodium sulfate (1) + sodium chloride (2) + hydrogen peroxide (3) + water (4) at 288.15 K: a, aqueous phase diagram; b, dry salt phase diagram. I, NaCl crystallization zone; II, $Na_2SO_4{\cdot}10H_2O$ crystallization zone; III, $Na_2SO_4{\cdot}0.5H_2O_2{\cdot}H_2O$ crystallization zone; IV, $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$ crystallization zone.

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