J. Chem. Eng. Data **2007,** *52,* 1213−1216

Solubility and Phase Diagram of the Quaternary Sodium Carbonate + Ethanol + Hydrogen Peroxide + Water System at T = 293.15 K

Hong-kun Zhao,* Rong-rong Li, Ming-li Su, Cao Tang, Dao-sen Zhang, and Xiao-xing Zhang

College of Chemistry & Chemical Engineering, YangZhou University, Yangzhou, Jiangsu, 225002, People's Republic of China

---

The solubility of the quaternary system sodium carbonate + ethanol + hydrogen peroxide + water was determined at 293.15 K using Schreinemaker's wet residue method. The phase diagram was constructed according to the Jãneck method. There were three solid phases formed in the quaternary system, which corresponded to $Na_2CO_3 \cdot 10H_2O$, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$, and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$. The crystalline region of $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ was larger than that of the other two solids, $Na_2CO_3 \cdot 10H_2O$ and $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$. Adding the ethanol into the $Na_2CO_3 + H_2O_2 + H_2O$ system could promote further crystallization and recover a greater fraction of $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$. The concentrations of sodium carbonate and hydrogen peroxide in the mother liquor after separation from $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ would be lowered as a result of the presence of ethanol. The solubility data and the phase diagram of the quaternary system could provide the fundamental basis and serve as a guide for the preparation of sodium percarbonate.

Introduction

Sodium percarbonate as used herein is the name commonly employed in industry for sodium carbonate peroxyhydrate having the formula $Na_2CO_3 \cdot 1.5H_2O_2$. Although sodium percarbonate has a wide range of uses employing its oxidant[1] and disinfectant qualities,[2] its currently most widespread use is as a bleach in washing compositions and especially in the compact and supercompact compositions that have been promoted by the detergent industry since the 1980s,[3,4] in dishwashing compositions,[5] as a bleach additive,[6] and in hard-surface cleansing compositions.[7] It is characterized by good solubility in water and rapid liberation of hydrogen peroxide, and it is environmentally acceptable because its decomposition products do not pollute the environment.

Sodium percarbonate can be produced by a variety of process routes, normally employing a reaction between hydrogen peroxide and the solution of sodium carbonate. In some variations, often called collectively "wet processes", the process comprises forming an aqueous solution of sodium carbonate and mixing it with an aqueous solution of hydrogen peroxide under reaction conditions including the concentrations of sodium carbonate and hydrogen peroxide and a temperature selected such that sodium percarbonate crystallizes out of solution. To recover a greater fraction of sodium percarbonate from the solution in a wet process, the practice has been commonly adopted of adding ethanol to promote further crystallization before the solid $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ is separated.[8−11] This practice also drives the reaction further toward completion, converting a higher fraction of the reactants into the desired product, and as a further consequence enables greater production to be obtained from a reactor of a given size. It is well-known that the process to obtain $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$ is based on the phase diagram of the quaternary $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ system. It is very important to investigate the phase diagram for designing and optimizing the production of sodium percarbonate.

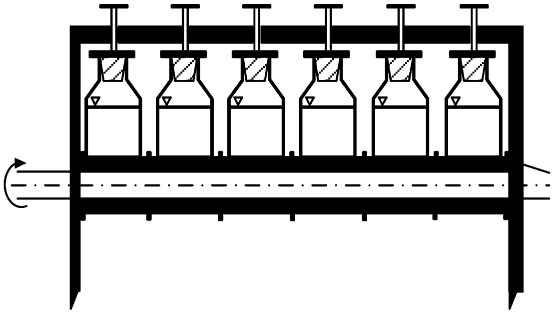

Figure 1. Equipment of the experimental system.

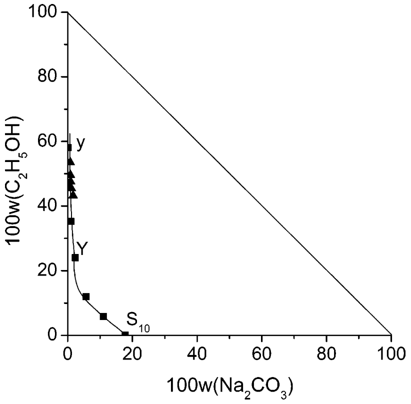

Figure 2. Phase diagram of the ternary $Na_2CO_3 + C_2H_5OH + H_2O$ system at 293.15 K: ▲, taken from the literature (12); ■, this work.

Some studies have been carried out on the phase equilibrium data of the ternary subsystems $Na_2CO_3 + C_2H_5OH + H_2O$[12] and $Na_2CO_3 + H_2O_2 + H_2O$[12−14] of the quaternary $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ system at 293.15 K. However, the solubility data limits in the ternary $Na_2CO_3 + C_2H_5OH + H_2O$ system were insufficient to construct a phase diagram at the temperature studied. The study of the phase equilibrium $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ has not been reported so far. In the present paper, the solubility of the ternary $Na_2CO_3 + C_2H_5OH + H_2O$ system at 293.15 K was measured. This study

---

* To whom correspondence should be addressed. E-mail: hkzhao@zzu.edu.cn. Tel: +(86) 514 7975568. Fax: +(86) 514 7975244.

10.1021/je600523s CCC: $37.00

Table 1. Mass Fraction Solubilities of the Ternary Systems Na_2CO_3 (1) + H_2O_2 (2) + H_2O (3) and Na_2CO_3 (1) + C_2H_5OH (2) + H_2O (3) at T = 293.15 K[a]

Na_2CO_3 (1) + H_2O_2 (2) + H_2O (3)[b]				Na_2CO_3 (1) + C_2H_5OH (2) + H_2O (3)				
liquid phase				liquid phase				
100 w_1	100 w_2	100 w_3	solid phase	100 w_1	100 w_2	100 w_3	solid phase	
18.00	0.00	82.00	N_{10}	17.75	0	82.25	N_{10}	this work
19.36	0.64	80.00	N_{10} + A	11.08	5.83	83.09	N_{10}	this work
25.90	1.02	73.08	N_{10} + A	5.68	11.95	82.37	N_{10}	this work
11.93	2.31	85.76	N_{10} + A	2.32	24.01	73.67	N_{10}	this work
5.14	9.30	85.56	N_{10} + A	0.99	35.12	63.89	N_{10}	this work
6.20	15.11	78.69	N_{10} + A	1.7	43.25	55.05	N_{10}	ref 12
6.04	23.83	70.13	N_{10} + A	1.13	45.48	53.39	N_{10}	ref 12
7.43	29.94	62.63	N_{10} + A	0.19	46.27	53.54	N_{10}	this work
7.80	39.27	52.93	N_{10} + A	0.90	47.57	51.53	N_{10}	ref 12
8.07	43.06	48.87	N_{10} + A	0.84	49.58	49.58	N_{10}	ref 12
7.76	58.00	34.24	A + B	0.80	53.57	45.63	N_{10}	ref 12
				0.091	58.08	41.83	N_{10}	this work

[a] N_{10}, $Na_2CO_3 \cdot 10H_2O$; A, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$; B, $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$; *w*, mass fraction. [b] Taken from ref 12.

Table 2. Mass Fraction Solubilities of the Quaternary System Na_2CO_3 (1) + C_2H_5OH (2) + H_2O_2 (3) + H_2O (4) at T = 293.15 K[a]

	mass fraction/%				Jãneck index/[kg/100 kg of dry salt]				
no.	Na_2CO_3	C_2H_5OH	H_2O_2	H_2O	Na_2CO_3	C_2H_5OH	H_2O_2	H_2O	solid phase
					E_1P_1				
1	13.82	1.67	0.98	83.53	5.95	10.14	83.91	507.16	N_{10} + A
2	9.91	3.36	0.53	86.20	3.84	24.34	71.82	624.38	N_{10} + A
3	8.65	4.50	0.36	86.49	2.64	33.35	64.01	640.36	N_{10} + A
4	7.65	6.02	0.32	86.01	2.31	43.00	54.69	614.56	N_{10} + A
5	7.04	7.96	0.61	84.38	3.92	51.00	45.08	540.37	N_{10} + A
6	5.33	15.07	0.99	78.61	4.61	70.46	24.93	367.60	N_{10} + A
7	3.74	22.33	0.94	72.99	3.48	82.68	13.84	270.21	N_{10} + A
8	3.68	27.85	1.31	67.15	4.00	84.79	11.21	204.43	N_{10} + A
9	2.58	41.98	3.68	51.76	7.63	87.02	5.35	107.30	N_{10} + A
10	1.72	62.89	11.80	23.59	15.44	82.31	2.25	30.87	N_{10} + A
11	1.41	53.77	13.45	31.37	19.60	78.35	2.05	45.71	N_{10} + A
12	1.67	44.26	19.59	34.48	29.90	67.55	2.55	52.63	N_{10} + A
13	1.07	34.63	22.89	41.40	39.07	59.10	1.83	70.65	N_{10} + A
14	2.53	26.37	28.10	42.99	49.30	46.26	4.44	75.42	N_{10} + A
15	1.94	18.71	31.11	48.23	60.10	36.15	3.75	93.18	N_{10} + A
16	2.75	11.46	31.11	54.68	68.65	25.28	6.07	120.67	N_{10} + A
17	2.76	7.93	29.30	60.01	73.27	19.83	6.90	150.06	N_{10} + A
					E_2P_1				
18	0.09	0.05	0.49	99.37	78.04	8.02	14.04	158.17	A + B

[a] N_{10}, $Na_2CO_3 \cdot 10H_2O$; A, $Na_2CO_3 \cdot 1.5H_2O_2 \cdot H_2O$; B, $Na_2CO_3 \cdot 2H_2O_2 \cdot H_2O$; *w*, mass fraction.

aims to provide accurate solubility data and a phase diagram for the solution of $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ at 293.15 K, as an aid toward the determination of crystallization parameters in the process of preparing sodium percarbonate.

Experimental Section

Materials and Instruments. The hydrogen peroxide used (not containing stabilizers) in this work was produced by the Jiangsu Yangnong Chemical Group Co. Ltd., with a mass fraction of 75 %. Na_2CO_3 (purity of 99.98 %), provided by the Guangzhou Chemical Reagent Factory, and C_2H_5OH (purity of 99.96 %), provided by the Jiangyin Chemical Reagent Factory, were of reagent quality. The water used to prepare the solutions was twice distilled (conductivity < 5 μS/cm). A thermostat was used in this experiment, with a device for rotating several bottles at a time. The accuracy of the thermostat temperature was ± 0.1 K. The schematic of the experimental system is shown in Figure 1. The glass stoppers of the bottles were covered with rubber caps while in the thermostat. A Rigaku D/max-2400 X-ray diffraction analyzer was used for solid-phase X-ray analysis.

Experiments. The solubility was determined by employing the method of isothermal solution saturation, and the solid phase was determined by Schreinmaker's wet residue method. The experiments were performed according to the following procedures. The experimental system, prepared according to a specified component ratio, was placed in the corresponding shaking bath. The experiments were performed at atmospheric pressure, and the temperature was fixed at 293.15 K. Sampling was performed at 2 h intervals until equilibrium was attained. If two analyses gave identical results, it was assumed that the equilibrium had been achieved. The samples were always shaken for at least 10 h and then allowed to stand for at least 5 h, which enabled the suspended crystals to fully settle. After equilibrium, the liquid phase and solid phase with a little saturated liquid were taken out and then quantitatively analyzed. X-ray diffraction was also employed to determine whether the solid phase was pure or a mixture.

Analysis. The moist solid samples were dissolved in water, and aliquot portions of the solutions so obtained were used for the analysis.

The hydrogen peroxide concentration was determined by titration using the iodometric method (uncertainty of 0.01 %). The sodium carbonate concentration was determined by titration using standard hydrochloric acid (uncertainty of 0.01 %). The total concentrations of ethanol and hydrogen peroxide were determined by oxidation using a potassium dichromate solution

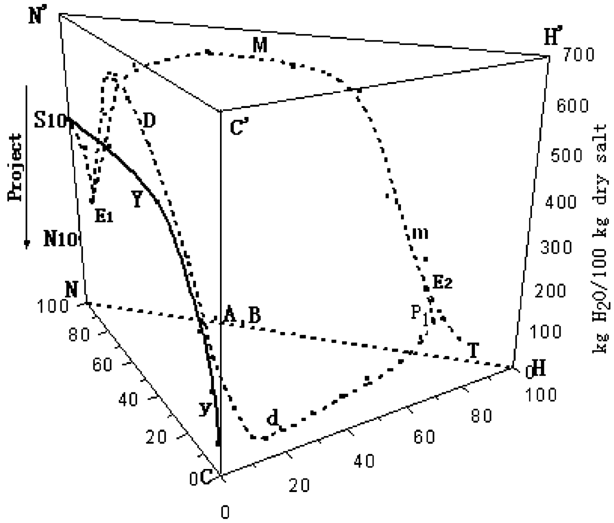

Figure 3. Phase diagram of the quaternary $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ system at 293.15 K: E_1, cosaturated point of a solution with solid phases $Na_2CO_3{\cdot}10H_2O$ and $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$; E_2, cosaturated point of a solution with solid phases $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$ and $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$; P_1, cosaturated point of a solution with solid phases $Na_2CO_3{\cdot}10H_2O$, $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$, and $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$; S_{10}, the solubility of Na_2CO_3 in water at 293.15 K; N, Na_2CO_3; H, H_2O_2; C, C_2H_5OH; A, $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$; B, $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$.

(uncertainty of 0.01 %). The ethanol concentration could then be calculated by subtracting the hydrogen peroxide concentration from the total concentration of ethanol and hydrogen peroxide. Each analysis was repeated three times, and the average value of three measurements was considered as the final value of the analysis (precision: ± 0.1 %).

Results and Discussion

The solubilities of the ternary system $Na_2CO_3 + C_2H_5OH + H_2O$ and the quaternary system $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ at 293.15 K are tabulated in Tables 1 and 2, respectively. To construct the phase diagram of the quaternary system $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$, the solubility data of the system $Na_2CO_3 + H_2O_2 + H_2O$ at 293.15 K are also presented in Table 1 (taken from ref 12). On the basis of the solubility data in Table 1, the phase diagram of the ternary system $Na_2CO_3 + C_2H_5OH + H_2O$ is plotted in Figure 2. According to the Jãneck index, the phase diagram of the quaternary system $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ is plotted in Figures 3 and 4.

It can be seen from Figure 2 that the measured solubility data of the system $Na_2CO_3 + C_2H_5OH + H_2O$ agree well with those in the literature.[12] Figure 2 further illustrates that only one solid is formed in the ternary system $Na_2CO_3 + C_2H_5OH + H_2O$ at the studied temperature. Analytical results show that the solid phase is $Na_2CO_3{\cdot}10H_2O$. Curve S_{10}Yy represents the crystallization line of the solid-phase $Na_2CO_3{\cdot}10H_2O$.

In Figure 3, curve $S_{10}E_1MmE_2T$ in the surface NN′HH′ is the solubility curve of the ternary system $Na_2CO_3 + H_2O_2 + H_2O$ at 293.15 K. Curves $S_{10}E_1$, E_1ME_2, and E_2T correspond to the crystallization line of the solid phases $Na_2CO_3{\cdot}10H_2O$, $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$, and $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$, respectively; E_1 is the cosaturated point with solid phases $Na_2CO_3{\cdot}10H_2O$ and $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$; and E_2 is another cosaturated point with solid phases $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$ and $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$. Curve S_{10}Yy in the surface NN′C′C is the solubility curve of the ternary system $Na_2CO_3 + C_2H_5OH + H_2O$.

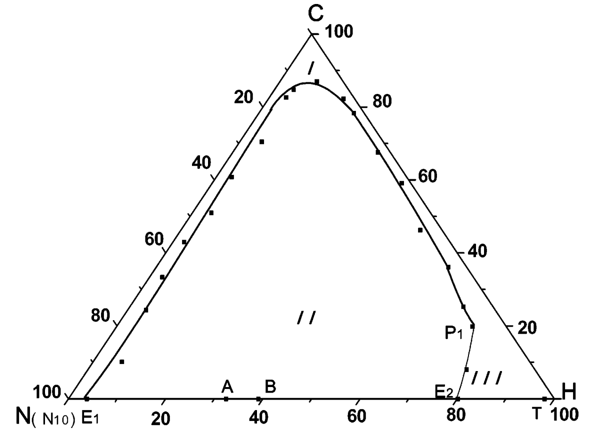

Figure 4. Jãneck projection of the quaternary $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ system at 293.15 K: I, $Na_2CO_3{\cdot}10H_2O$ crystallization zone; II, $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$ crystallization zone; III, $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$ crystallization zone; N, Na_2CO_3; H, H_2O_2; C, C_2H_5OH; E_1, E_2, and P_1 have the same meaning as those described in Figure 3.

Figure 3 is the stereoscopic phase diagram, and Figure 4 is the projective phase diagram of the quaternary system $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$. Figures 3 and 4 show that there are three solid phases formed in solution which correspond to $Na_2CO_3{\cdot}10H_2O$, $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$, and $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$, respectively. The region I in Figure 4, embraced by curve $E_2P_1dDE_1S_{10}Yy$ in Figure 3, corresponds to the crystallization field of the solid-phase $Na_2CO_3{\cdot}10H_2O$; similarly, the region II in Figure 4, embraced by curve $P_1dDE_1MmE_2$ in Figure 3, corresponds to the crystallization field of the solid-phase $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$; and the region III in Figure 4, embraced by curve P_1E_2T in Figure 3, corresponds to the crystallization field of the solid-phase $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$. $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$ has a bigger crystallization field than that of the other two solids, $Na_2CO_3{\cdot}10H_2O$ and $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$. The large crystallization region in the phase diagram indicates that $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$ is of low solubility. Therefore, adding ethanol to the system $Na_2CO_3 + H_2O_2 + H_2O$ can promote further crystallization of $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$ from the solution. This practice drives the reaction further toward completion, converting a higher fraction of the reactants, Na_2CO_3 and H_2O_2, into the desired product $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$.

The phase diagram of the quaternary system $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ has two univariant curves, $E_1 \rightarrow P_1$ and $E_2 \rightarrow P_1$, and one isothermal invariant point, P_1. The point P_1 is represented by the solution composition being in equilibrium with solid phases $Na_2CO_3{\cdot}10H_2O$, $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$, and $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$.

Conclusion

The phase equilibrium of the quaternary system $Na_2CO_3 + C_2H_5OH + H_2O_2 + H_2O$ at 293.15 K was studied by Schreinemaker's wet residue method. The solubility data were determined by experiment. The phase diagram of the quaternary system was constructed according to the experimental data. There are three solid-phase crystallizations, $Na_2CO_3{\cdot}10H_2O$, $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$, and $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$, in the equilibrium phase diagram at 293.15 K. The $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$ system has a bigger crystallization field than that of the other two solids, $Na_2CO_3{\cdot}10H_2O$ and $Na_2CO_3{\cdot}2H_2O_2{\cdot}H_2O$, which indicates that $Na_2CO_3{\cdot}1.5H_2O_2{\cdot}H_2O$ is of low solubility. Adding ethanol to the system $Na_2CO_3 + H_2O_2 + H_2O$ drives the reaction further toward completion, converting a higher fraction of the reactants, Na_2CO_3 and H_2O_2, into the desired product $Na_2CO_3{\cdot}$

$1.5H_2O_2 \cdot H_2O$. The data and the phase diagram of the quaternary system can provide the fundamental basis for the preparation of the sodium percarbonate.

Acknowledgment

The authors would like to express their sincere thanks to the editors and anonymous reviewers for their constructive suggestions.

Literature Cited

(1) McKillop, A.; Sanderson, W. R. Sodium Perborate and Sodium Percarbonate: Cheap, Safe and Versatile Oxidising Agents for Organic Synthesis. *Tetrahedron* **1995**, *51*, 6145−6166.

(2) Kazutoyo, U. Therapeutic Agent for Dermatosis due to Trichophyton and Eczema and Skin Germicidal/Activating Agent. JP Patent 2,001,354,574, December 25, 2001.

(3) Dixon. S.; Oakes. J. Laundry Detergent Compositions. WO Patent 03,014,283, February 2, 2003.

(4) Thomas, H. G. Detergent. U.S. Patent 2,003,040,453, February 27, 2003.

(5) Speckmann, H. D.; Poethkow, J.; Heike, S. D.; Middelhauve, B. Bleach-containing Washing or Cleaning Agents. WO Patent 2,004,058,931, July 15, 2004.

(6) Kwang, H.; Ki-Hwan, K.; Chang-Hyun, J.; Seon-Ho, S.; Moon-Jeong, R.; Kyu-Yeol, C.; Jong-Ho, K. Bleaching activator. U.S. Patent 6,528,470, March 4, 2003.

(7) Koji, S.; Hiroyuki, Y.; Kazukuni, T. Detergent Composition For Hard Surface. JP Patent 2,000,026,892, January 25, 2000.

(8) Ge, G. H.; Jiang, Z. L.; Wang, J. Y. New Technology for Promoting the Yield of Sodium Percarbonate. *Inorg. Chem. Ind.* (*Chin.*) **1997**, *29*, 23−24.

(9) Huang, M. K.; Huang, S. X. Method for Producing Stable Sodium Percarbonate. CN Patent 1,131,123, September 18, 1996.

(10) Qu, J.; Zhu, J. Y.; Chen, Y.; Tao, L. Study on the Production of Sodium Percarbonate by Two-State Technology. *Chem. Ind. Times* (*Chin.*) **2000**, *14*, 35−37.

(11) Zhang, K. S.; Zeng, F. C. The production and research progress of sodium percarbonate. *Inorg. Chem. Ind.* (*Chin.*) **2005**, *37*, 18−20.

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

(13) Drozdetskii, A. G.; Ostapkevicn, N. N.; Trefilov, P. A.; Alieva, I. A. Sodium carbonate−Hydrogen peroxide−Water System at 20°. *Zh. Neorg. Khim.* **1983**, *28*, 793−794.

(14) Vol'nov, I. I.; Latysheva, E. I. Study of the Sodium carbonate−Hydrogen peroxide−Water System by Isothermal Solubility. *Zh. Neorg. Khim.* **1984**, *29*, 2672−2677.

Received for review November 17, 2006. Accepted April 1, 2007. We gratefully acknowledge the High Education Natural Science Foundation of Jiangsu Province (Grant No. HK051087) and the Open Project Program of the Key Laboratory of Physical Chemistry, Yangzhou University, China for their support.

JE600523S