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Solubility and Phase Diagram for the Ternary Sodium Oxalate + Hydrogen Peroxide + Water System at (283.15 and 293.15) K

Hong-Kun Zhao,* Dao-Sen Zhang, Cao Tang, Rong-Rong Li, Ming-Li Su, Wen-Lin Xu, and Ya-Qiong Wang

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

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In this investigation, the mutual solubilities for the ternary $Na_2C_2O_4 + H_2O_2 + H_2O$ system were determined at (283.15 and 293.15) K. The phase diagrams of the system were constructed based on the measured solubility. The compound $Na_2C_2O_4 \cdot H_2O_2$ was confirmed by Schreinemaker's wet residue method. In addition, the density of the system was obtained. At (283.15 and 293.15) K, two solid phases were formed in the ternary $Na_2C_2O_4 + H_2O_2 + H_2O$ system, which corresponded to $Na_2C_2O_4$ and $Na_2C_2O_4 \cdot H_2O_2$. The phase diagrams of the ternary system were similar at different temperatures; the solubilities of $Na_2C_2O_4$ and $Na_2C_2O_4 \cdot H_2O_2$ in water increased slightly with increasing temperature. The crystalline region of the compound $Na_2C_2O_4 \cdot H_2O_2$ decreased as the temperature increased, the temperature having little effect on the yield of $Na_2C_2O_4 \cdot H_2O_2$.

Introduction

Perhydrates are of considerable technical importance as carriers of hydrogen peroxide. Several perhydrates such as $Na_2CO_3 \cdot 1.5H_2O_2$, $CO(NH_2)_2 \cdot H_2O_2$, $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, etc. have been produced and used in industry. Pederson[1] synthesized a new hydrogen peroxide adduct with sodium oxalate, with the formula $Na_2C_2O_4 \cdot H_2O_2$ by the following approach: sodium oxalate was dissolved in perhydrol (30 % H_2O_2). By slow evaporation, the crystals of $Na_2C_2O_4 \cdot H_2O_2$ were formed as needles along the α axis. The crystal structure was determined from three-dimensional X-ray data.[2] The composition of the crystal corresponded very closely to sodium oxalate monoperhydrate ($Na_2C_2O_4 \cdot H_2O_2$). The oxalate ion and the hydrogen peroxide molecule are centrosymmetric. The structure is built up of endless chains of alternating hydrogen peroxide molecules and oxalates ions linked together by hydrogen bonds. In 1980, Adams et al. studied the thermal decomposition of $Na_2C_2O_4 \cdot H_2O_2$ under isothermal conditions.[3] Nevertheless, to the best of our present knowledge, further investigations on the compound $Na_2C_2O_4 \cdot H_2O_2$ have not been reported in the literature.

It is well-known that solid−liquid phase equilibrium data are important in crystallization processes. As described by Pederson and Pederson[2] and Adams et al.,[3] sodium oxalate reacted with hydrogen peroxide solution, and $Na_2C_2O_4 \cdot H_2O_2$ crystallized from the system. Obviously, the preparing process of $Na_2C_2O_4 \cdot H_2O_2$ was based on the phase diagram of the ternary $Na_2C_2O_4 + H_2O_2 + H_2O$ system. It is important to study the system and construct the phase diagram of the ternary $Na_2C_2O_4 + H_2O_2 + H_2O$ system. Although the phase diagrams of the systems $Na_2CO_3 + H_2O_2 + H_2O$,[4] $CO(NH_2)_2 + H_2O_2 + H_2O$,[5] $Na_2SO_4 + H_2O_2 + H_2O$,[6] and $Na_2SO_4 + NaCl + H_2O_2 + H_2O$[7] have been investigated, we have found no data on the solubility or phase diagram for the $Na_2C_2O_4 + H_2O_2 + H_2O$ system in the literature. The objectives of this research are to generate and analyze the phase diagrams of the ternary system at (283.15 and 293.15) K by Schreinemaker's wet residue method[8] and demonstrate the temperature dependence of the ternary phase diagram.

Experimental Section

Materials and Apparatus. The mass fraction purity of sodium oxalate is no less than 99.6 %. The hydrogen peroxide (not containing stabilizers) was purchased from the Jiangsu Yangnong Chemical Group Co. Ltd., with a mass fraction of 75 %. A thermostat water bath was used for controlling measurements at (283.15 ± 0.01) K or (293.15 ± 0.01) K. A RigakuD/max-2400 X-ray diffraction analyzer was used for solid-phase X-ray analysis.

Procedure. Schreinmaker's wet residue method was used in this experiment. The system was prepared by mixing amounts of the three components to give convenient quantities of solution and solid phase after establishing the equilibrium condition. The components were taken in such proportions that the composition of the resulting saturated solution fell in the desired portion of the solubility curve. All mixtures were stirred in flasks in a thermostat bath, in which the temperature was controlled at (283.15 ± 0.01) K or (293.15 ± 0.01) K. A sample was prepared and placed in a thermostat, and chemical titration was used to analyze the liquid phase of the sample at 2 h intervals. If the result became constant, it indicated that equilibrium was achieved. Results indicated that it took about 15 h to reach equilibrium. After equilibrium was accomplished, the solid and the liquid were separated by filtration.

The equilibrium liquid phase and the wet residue were dissolved in water and analyzed by titration. The hydrogen peroxide concentration was determined by the iodometric method. The total concentration of the oxalate ion ($C_2O_4^{2-}$) and the hydrogen peroxide concentration were determined by titrating the acidified solution with standard potassium permanganate. Then the oxalate ion ($C_2O_4^{2-}$) concentration can be determined by subtracting the hydrogen peroxide concentration from the total concentration of the oxalate ion and hydrogen peroxide. The densities (ρ) were measured with a specific weighing bottle calibrated by the floating force of air with a precision of ± 0.2 mg. Each analysis was repeated three times, and the average value of the three measurements was considered as the final value of the analysis. The average relative error of the measurement was estimated to be 0.1 %.

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* Corresponding author. E-mail: hkzhao@zzu.edu.cn. Tel: +86 514 7975568. Fax: +86 514 7975244.

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Results and Discussion

The measured solubility and the density of the liquid phase for the ternary $Na_2C_2O_4 + H_2O_2 + H_2O$ system at (283.15 and 293.15) K are shown in Tables 1 and 2, respectively. The ternary phase diagrams are given in Figures 1 and 2.

In the phase diagrams as shown in Figures 1 and 2, T_1M_1 and T_2M_2 are saturation curves corresponding to the solid-phase $Na_2C_2O_4 \cdot H_2O_2$ at (283.15 and 293.15) K, respectively; E_1T_1 and E_2T_2 are saturation curves corresponding to the solid-phase $Na_2C_2O_4$. T_1 and T_2 are invariant points, which represent the saturated solution of the solid phases $Na_2C_2O_4$ and $Na_2C_2O_4 \cdot H_2O_2$. The phase diagram is divided into four regions by the two solubility curves. The regions in the phase diagram are denoted as follows: I (WE_1M_1 and WE_2M_2), unsaturated solution; II (E_1T_1A and E_2T_2A), region corresponding to the coexistence of $Na_2C_2O_4$ and the saturated solution; III (AT_1D and AT_2D), region corresponding to the coexistence of $Na_2C_2O_4$, $Na_2C_2O_4 \cdot H_2O_2$, and the saturated solution; IV (DT_1M_1 and DT_2M_2), region corresponding to the coexistence of $Na_2C_2O_4 \cdot H_2O_2$ and the saturated solution. It is also indicated in Figures 1 and 2 that $Na_2C_2O_4 \cdot H_2O_2$ is an asymmetric compound at (283.15 and 293.15) K.

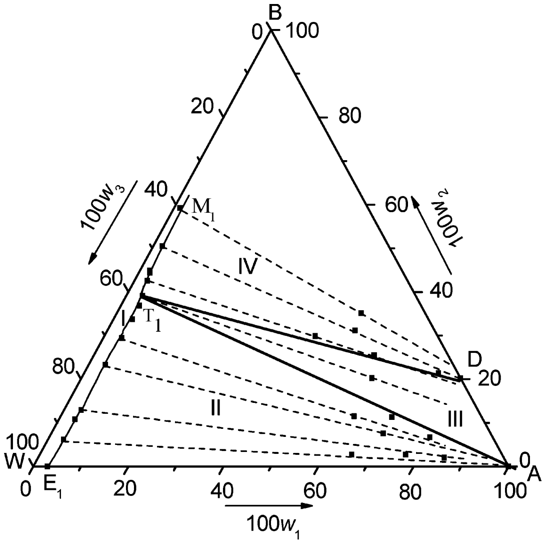

Figure 1. Phase diagram of the ternary $Na_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) system at 283.15 K; T_1, cosaturated point; E_1, solubility of $Na_2C_2O_4$ in water; A, $Na_2C_2O_4$; B, H_2O_2; W, H_2O; M_1, experimental data; D, $Na_2C_2O_4 \cdot H_2O_2$; I, unsaturated region; II, crystalline region of solid $Na_2C_2O_4$; III, crystalline region of solids $Na_2C_2O_4$ and $Na_2C_2O_4 \cdot H_2O_2$; IV, crystalline region of solid $Na_2C_2O_4 \cdot H_2O_2$.

In Figures 1 and 2, along the solubility curve T_1M_1 or T_2M_2, linking the component points of the liquid phase and wet solid phase and extended, the point of intersection of these tie-lines is the approximate solid-phase component for the compound $Na_2C_2O_4 \cdot H_2O_2$ on a wet basis. Similarly, along the solubility curve E_1T_1or E_2T_2, linking the component points of the liquid

Table 1. Mass Fraction Solubilities of the Ternary $Na_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) System at 283.15 K[a]

liquid phase		wet solid phase			
100 w_1	100 w_2	100 w_1	100 w_2	density of liquid phase (g·mL^{-1})	solid phase
2.95	0			1.0434	$Na_2C_2O_4$
3.22	6.23	65.67	2.72	1.0559	$Na_2C_2O_4$
3.37	10.83	77.01	2.72	1.0697	$Na_2C_2O_4$
3.62	12.98	85.50	2.03	1.0824	$Na_2C_2O_4$
3.54	23.32	69.89	7.55	1.0930	$Na_2C_2O_4$
3.89	29.43	61.79	11.5	1.1185	$Na_2C_2O_4$
3.96	33.78	80.08	6.70	1.1398	$Na_2C_2O_4$
3.96	36.84	69.85	11.31	1.1849	$Na_2C_2O_4$
3.45	39.09	61.15	20.25	1.2018	$Na_2C_2O_4 + Na_2C_2O_4 \cdot H_2O_2$
2.73	42.49	44.41	29.83	1.2139	$Na_2C_2O_4 \cdot H_2O_2$
2.34	44.44	58.98	25.53	1.2221	$Na_2C_2O_4 \cdot H_2O_2$
2.11	44.86	74.56	21.40	1.2269	$Na_2C_2O_4 \cdot H_2O_2$
1.93	50.47	52.09	31.19	1.2373	$Na_2C_2O_4 \cdot H_2O_2$
1.28	59.22	51.44	35.14	1.2478	$Na_2C_2O_4 \cdot H_2O_2$

[a] *w*, mass fraction.

Table 2. Mass Fraction Solubilities of the Ternary $Na_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) System at 293.15 K[a]

liquid phase		wet solid phase			
100 w_1	100 w_2	100 w_1	100 w_2	density of liquid phase (g·mL^{-1})	solid phase
3.4	0			1.0239	$Na_2C_2O_4$
3.48	4.41	79.84	1.09	1.0371	$Na_2C_2O_4$
3.60	9.88	94.23	0.96	1.0656	$Na_2C_2O_4$
3.40	13.22	77.60	4.32	1.0827	$Na_2C_2O_4$
3.75	17.82	81.06	3.82	1.0978	$Na_2C_2O_4$
3.49	22.08	87.51	2.72	1.1198	$Na_2C_2O_4$
3.83	25.39	83.32	4.32	1.1383	$Na_2C_2O_4$
3.51	31.27	83.47	5.09	1.1699	$Na_2C_2O_4$
2.89	38.43	58.16	16.48	1.2017	$Na_2C_2O_4$
2.83	41.19	73.91	12.31	1.2179	$Na_2C_2O_4$
2.76	42.24	75.81	10.77	1.2251	$Na_2C_2O_4$
2.32	43.55	73.49	16.61	1.2307	$Na_2C_2O_4 + Na_2C_2O_4 \cdot H_2O_2$
2.01	44.97	54.64	27.79	1.2418	$Na_2C_2O_4 \cdot H_2O_2$
1.78	50.73	62.69	26.41	1.2534	$Na_2C_2O_4 \cdot H_2O_2$
1.52	57.64	58.73	29.67	1.2614	$Na_2C_2O_4 \cdot H_2O_2$
1.48	65.86	58.83	33.22	1.2651	$Na_2C_2O_4 \cdot H_2O_2$

[a] *w*, mass fraction.

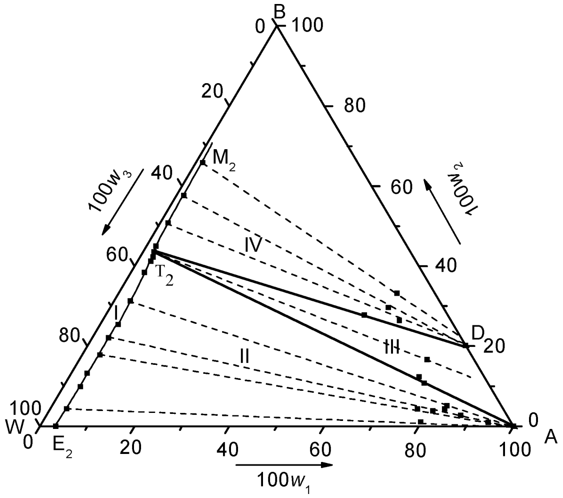

Figure 2. Phase diagram of the ternary $Na_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) system at 293.15 K; T_2, cosaturated point; E_2, solubility of $Na_2C_2O_4$ in water; M_2, experimental data; A, B, W, D, I, II, III, and IV have the same meaning as described in Figure 1.

phase and wet solid phase and extended, the point of intersection of these tie-lines is the approximate solid-phase component for $Na_2C_2O_4$. The results indicate that two solids are present in the system: one is $Na_2C_2O_4$, and the other is a compound with formula $Na_2C_2O_4{\cdot}H_2O_2$. It is also found that for solutions up to 39.09 % (283.15 K) or 43.55 % (293.15 K) with respect to hydrogen peroxide (saturated with sodium oxalate) the solid phase in equilibrium is sodium oxalate, and above the corresponding concentration with respect to hydrogen peroxide the solid phase in equilibrium is $Na_2C_2O_4{\cdot}H_2O_2$. The results are in agreement with the phase diagram and from direct analysis obtained by crystallization after drying of the compound.

Figures 1 and 2 further illustrate the temperature dependence of the phase diagram for the ternary $Na_2C_2O_4$ + H_2O_2 + H_2O system. When the temperature increases from (283.15 to 293.15) K, the solubilities of $Na_2C_2O_4$ and $Na_2C_2O_4{\cdot}H_2O_2$ in water increase slightly, and the invariant point moves upward. However, the phase diagrams of the ternary system are similar at different temperatures. With an increase in temperature, the crystalline region of the compound $Na_2C_2O_4{\cdot}H_2O_2$ decreases. The temperature has little effect on the yield of $Na_2C_2O_4{\cdot}H_2O_2$.

Conclusion

In this work, solubility data and the density of the liquid phase for the ternary $Na_2C_2O_4$ + H_2O_2 + H_2O system at (283.15 and 293.15) K were measured. The solid phase was determined by Schreinmaker's wet residue method. The phase diagrams of the ternary system were constructed. There were two solid phases formed in the ternary system that corresponded to $Na_2C_2O_4$ and $Na_2C_2O_4{\cdot}H_2O_2$. The phase diagrams of the ternary system were similar at the different temperatures. The crystalline region of the compound $Na_2C_2O_4{\cdot}H_2O_2$ decreased with increasing temperature. The temperature has little effect on the yield of $Na_2C_2O_4{\cdot}H_2O_2$. The solubility data and the phase diagram of the ternary system can provide the basis and serve as a guide for the preparation of sodium oxalate monoperhydrate.

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