Phase Diagram for the System Ammonium Oxalate + Hydrogen Peroxide + Water at 283.15 K and 293.15 K

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The solubility of the ternary system $(NH_4)_2C_2O_4 + H_2O_2 + H_2O$ was determined experimentally at 283.15 K and 293.15 K, and the phase diagrams for the system were constructed. In addition, the density of the saturated aqueous solution was measured. The experimental results showed that, at 283.15 K and 293.15 K, two solid phases were formed in the ternary $(NH_4)_2C_2O_4 + H_2O_2 + H_2O$ system which correspond to $(NH_4)_2C_2O_4{\cdot}H_2O$ and $(NH_4)_2C_2O_4{\cdot}H_2O_2$. The compound $(NH_4)_2C_2O_4{\cdot}H_2O_2$ was further confirmed by Schreinemaker's wet residue method. The hydrate $(NH_4)_2C_2O_4{\cdot}H_2O$ has a bigger crystallization field than either $(NH_4)_2C_2O_4{\cdot}H_2O_2$ or the mixture of $(NH_4)_2C_2O_4{\cdot}H_2O$ and $(NH_4)_2C_2O_4{\cdot}H_2O_2$. The solubilities of $(NH_4)_2C_2O_4{\cdot}H_2O$ increased sharply with an increase in the concentration of hydrogen peroxide and increased slightly with increasing temperature.

Introduction

Hydrogen peroxide is capable of forming adducts with both organic and inorganic compounds, e.g., $CO(NH_2)_2{\cdot}H_2O_2$, $Na_2CO_3{\cdot}1.5H_2O_2$, and $4Na_2SO_4{\cdot}2H_2O_2{\cdot}NaCl$. The binding in these adducts is attributed to hydrogen bonding between electron-rich functional groups in the compound and the peroxide hydrogen. The adducts have been used in commercial and industrial applications as bleaching agents, disinfectants, sterilizing agents, oxidizing reagents in organic synthesis, and catalysts for free-radical-induced polymerization reactions. Generally, these types of compound can be prepared by the crystallization of the adduct from an aqueous solution; for example, urea hydrogen peroxide was prepared by Lu et al.[1] in the liquid phase by adding a solution of urea to a solution of hydrogen peroxide and allowing the adduct to crystallize under the proper conditions. Gates et al.[2] prepared a sodium carbonate hydrogen peroxide complex by treating a saturated aqueous solution of sodium carbonate with a solution of hydrogen peroxide. These methods work well for peroxide adducts that form stable, crystalline, free-flowing products from aqueous solution.

Pederson and co-workers[3] synthesized a hydrogen peroxide adduct with ammonium oxalate in 1972, with the formula $(NH_4)_2C_2O_4{\cdot}H_2O_2$ by dissolving ammonium oxalate monohydrate in an aqueous hydrogen peroxide solution (30 % H_2O_2 in water). By slow evaporation at room temperature, colorless, long prismatic crystals of the monoperhydrate were separated. The crystal structure $(NH_4)_2C_2O_4{\cdot}H_2O_2$ was determined from three-dimensional X-ray diffractometer data.[3] Both the oxalate ion and the hydrogen peroxide molecules are situated on 2-fold axes. The interatomic dimensions of the oxalate ion are normal, but the ion is nonplanar. In 1980, Adams and co-workers[4] studied the thermal decomposition of $(NH_4)_2C_2O_4{\cdot}H_2O_2$ under isothermal conditions. Nevertheless, to the best of the present authors' knowledge, further investigation on the adduct, $(NH_4)_2C_2O_4{\cdot}H_2O_2$, has not been described elsewhere in the literature.

It is well-known that solid−liquid phase equilibrium data are important in crystallization processes. Pederson and Pederson[3] and Adams et al.[4] showed that ammonium oxalate can react with a hydrogen peroxide solution of a given concentration and that $(NH_4)_2C_2O_4{\cdot}H_2O_2$ crystallizes from the system. Obviously, the process of preparing $(NH_4)_2C_2O_4{\cdot}H_2O_2$ is based on the phase diagram of the ternary $(NH_4)_2C_2O_4 + H_2O_2 + H_2O$ system. It is very important to study the system and construct the phase diagram of the ternary $(NH_4)_2C_2O_4 + H_2O_2 + H_2O$ system. Although the phase diagram of the systems $(NH_4)_2C_2O_4 + H_2O$,[5−7] $Na_2CO_3 + H_2O_2 + H_2O$,[7] $CO(NH_2)_2 + H_2O_2 + H_2O$,[8] $Na_2SO_4 + H_2O_2 + H_2O$,[9] and $Na_2SO_4 + NaCl + H_2O_2 + H_2O$[10] have been investigated, no data on the solubility or phase diagram for the system $(NH_4)_2C_2O_4 + H_2O_2 + H_2O$ were found in the literature. The objective of this research is to generate and analyze the phase diagrams of the ternary system at 283.15 K and 293.15 K by Schreinemaker's wet residues method[11] and demonstrate the temperature dependence of the ternary phase diagram.

Experimental Section

Materials. The hydrogen peroxide used (not containing stabilizers) was provided by the Jiangsu Yangnong Chemical Group Co. Ltd, with a mass fraction of 75 %. It was of reagent quality. The ammonium oxalate monohydrate, produced by the Shanghai Dafeng Oxalic Acid Co. Ltd., was of reagent quality and used without further purification. The water used to prepare solutions was twice distilled ($< 5\ \mu S{\cdot}cm^{-1}$ conductivity).

Procedure. An external thermostat was used in this experiment, with a device for rotating several bottles at a time. The saturated solution was transferred to a conical flask. The conical flask was covered with rubber caps and placed in a device rotating the flasks at 283.15 K or 293.15 K (± 0.01 K).

The isothermal dissolution method was used during experiments. A known mass of ammonium oxalate monohydrate was dissolved in 25 mL of aqueous hydrogen peroxide with various concentrations (0−75 mass %). To ensure that sampling was performed at 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 experiments were carried out, one starting from a supersaturated solution,

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Table 1. Mass Fraction Solubilities and Densities of the Ternary System $(NH_4)_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) at 283.15 K[a]

liquid phase		moist solids phase		density of liquid phase	
100 w_1	100 w_2	100 w_1	100 w_2	$g \cdot mL^{-1}$	solid phase
3.112	0	72.37	0	1.0152	$(NH_4)_2C_2O_4 \cdot H_2O$
3.78	5.84	70.43	1.47	1.0297	$(NH_4)_2C_2O_4 \cdot H_2O$
6.12	11.39	72.59	2.28	1.0671	$(NH_4)_2C_2O_4 \cdot H_2O$
7.71	17.25	71.32	4.52	1.0951	$(NH_4)_2C_2O_4 \cdot H_2O$
8.61	21.97	73.24	4.16	1.1155	$(NH_4)_2C_2O_4 \cdot H_2O$
11.24	28.19	73.54	4.98	1.1472	$(NH_4)_2C_2O_4 \cdot H_2O$
13.63	33	71.13	5.86	1.1784	$(NH_4)_2C_2O_4 \cdot H_2O$
15.61	37.39	78.47	8.13	1.2069	$(NH_4)_2C_2O_4 \cdot H_2O$
17.17	40.26	68.98	11.75	1.2290	$(NH_4)_2C_2O_4 \cdot H_2O$
19.15	42.68	64.62	21.76	1.2600	$(NH_4)_2C_2O_4 \cdot H_2O + (NH_4)_2C_2O_4 \cdot H_2O_2$
19.33	46.18	69.16	25.12	1.2715	$(NH_4)_2C_2O_4 \cdot H_2O_2$
19.45	49.67	71.32	25.57	1.2821	$(NH_4)_2C_2O_4 \cdot H_2O_2$
19.47	55.39	69.54	26.85	1.2944	$(NH_4)_2C_2O_4 \cdot H_2O_2$

[a] *w*, mass fraction.

Table 2. Mass Fraction Solubilities and Densities of the Ternary System $(NH_4)_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) at 293.15 K[a]

liquid phase		moist solid phase		density of liquid phase	
100 w_1	100 w_2	100 w_1	100 w_2	$g \cdot mL^{-1}$	solid phase
4.259	0	74.47	0	1.0321	$(NH_4)_2C_2O_4 \cdot H_2O$
5.54	6.72	74.85	1.89	1.0566	$(NH_4)_2C_2O_4 \cdot H_2O$
7.32	13.31	77.22	2.34	1.0839	$(NH_4)_2C_2O_4 \cdot H_2O$
9.61	21.91	74.62	4.46	1.1256	$(NH_4)_2C_2O_4 \cdot H_2O$
13.42	27.36	66.95	8.05	1.1605	$(NH_4)_2C_2O_4 \cdot H_2O$
15.95	32.25	67.79	10.16	1.1845	$(NH_4)_2C_2O_4 \cdot H_2O$
20.84	36.2	70.24	10.04	1.2181	$(NH_4)_2C_2O_4 \cdot H_2O$
22.63	40.39	63.08	15.35	1.2473	$(NH_4)_2C_2O_4 \cdot H_2O + (NH_4)_2C_2O_4 \cdot H_2O_2$
22.55	43.51	68.69	24.24	1.2313	$(NH_4)_2C_2O_4 \cdot H_2O_2$
22.62	46.23	66.53	25.19	1.2705	$(NH_4)_2C_2O_4 \cdot H_2O_2$
22.36	53.18	69.15	26.45	1.2899	$(NH_4)_2C_2O_4 \cdot H_2O_2$

[a] *w*, mass fraction.

in which the solid phase precipitated to reach equilibrium and the other starting from a nonsaturated solution, in the which solid dissolved to reach equilibrium. The results showed that for both cases about 5 h was sufficient to reach equilibrium. In our experiments, sampling was performed after a minimum of 7 h. The composition of the solid phase was determined by Schreinemaker's method.[11] In addition, for the invariant points and for at least one point on each saturation curve, the solid phases were identified by X-ray analysis using a PW 1050/70 Philips X-ray diffractometer. After the equilibrium was achieved, the solid and the liquid phases were separated by filtration, and then both phases were analyzed. To avoid appreciable decomposition of hydrogen peroxide, the temperature in this study was selected as 283.15 K or 293.15 K.

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

The hydrogen peroxide concentration was determined by the iodometric method. The total concentrations of the oxalate ion and the hydrogen peroxide were measured by titrating the acidified solution with standard potassium permanganate. The oxalate ion concentration can then be determined by subtracting the hydrogen peroxide concentration from the total concentration of the oxalate ion and hydrogen peroxide.

The densities (ρ) of the aqueous solution were measured by using a pycnometer (11-FY) with an uncertainty of 0.0002 $g \cdot cm^{-3}$, and the reproducibility is ± 0.5 %.

Each analysis was repeated three times, and the average value of the three measurements was considered as the final value of the analysis (uncertainty: ± 0.1 %).

Results and Discussion

The measured solubility and the density of the liquid phase for the ternary system $(NH_4)_2C_2O_4 + H_2O_2 + H_2O$ at 283.15 K and 293.15 K are shown in Tables 1 and 2, respectively. The ternary phase diagrams are plotted in Figures 1 and 2.

In Figures 1 and 2, along C_1T_1 or C_2T_2, linking the component points of the liquid phase and moist solid phase and an extension thereof, the point of intersection of these tie-lines is approximately the solid-phase component for the compound ($(NH_4)_2C_2O_4 \cdot H_2O_2$) on a wet basis. Along S_1C_1 or S_2C_2, linking the component points of the liquid phase and moist solid phase

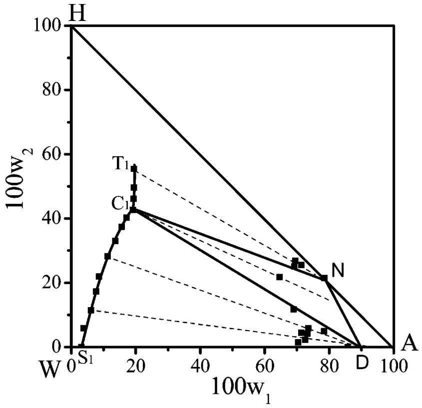

Figure 1. Phase diagram of the ternary $(NH_4)_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) system at 283.15 K: ■, experimental data point; S_1, solubility of $(NH_4)_2C_2O_4$ in water at 283.15 K; C_1, cosaturated point; N, $(NH_4)_2C_2O_4 \cdot H_2O_2$; D, $(NH_4)_2C_2O_4 \cdot H_2O$; A, $(NH_4)_2C_2O_4$; H, H_2O_2; W, H_2O; T_1, experimental data; 100 *w*, mass fraction.

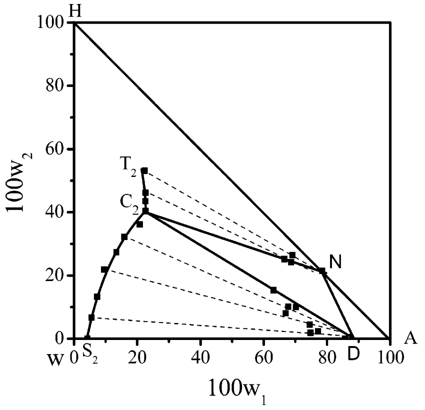

Figure 2. Equilibrium phase diagram of the ternary $(NH_4)_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) system at 293.15 K: ■, experimental data point; S_2, solubility of $(NH_4)_2C_2O_4$ in water at 293.15 K; C_2, cosaturated point; T_2, experimental data; N, D, H, W, and A have the same meaning as described in Figure 1; 100 *w*, mass fraction.

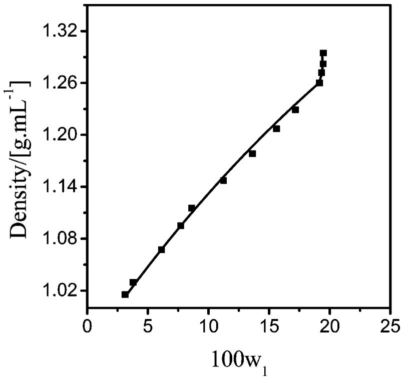

Figure 3. Density value−composition relationship diagram for the ternary $(NH_4)_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) system at 283.15 K: ■, experimental data point; —, experimental relationship diagram.

and an extension thereof, the point of intersection of these tie-lines is approximately the solid-phase component for $(NH_4)_2C_2O_4 \cdot H_2O$. The results indicated that two solids were present in the system: one was $(NH_4)_2C_2O_4 \cdot H_2O$, and the other was an adduct with the formula $(NH_4)_2C_2O_4 \cdot H_2O_2$.

In the phase diagram, as shown in Figures 1 and 2, there are three crystallization fields: $(NH_4)_2C_2O_4 \cdot H_2O_2$ (T_1C_1N and T_2C_2N), $(NH_4)_2C_2O_4 \cdot H_2O$ (S_1C_1D and S_2C_2D), and a mixture of $(NH_4)_2C_2O_4 \cdot H_2O_2$ and $(NH_4)_2C_2O_4 \cdot H_2O$ (C_1ND and C_2ND). The monohydrate $(NH_4)_2C_2O_4 \cdot H_2O$ has a bigger crystallization field than either $(NH_4)_2C_2O_4 \cdot H_2O_2$ or the mixture. The solubility of $(NH_4)_2C_2O_4 \cdot H_2O$ increases sharply with an increase in the concentration of hydrogen peroxide; however, the solubility of $(NH_4)_2C_2O_4 \cdot H_2O_2$ varies little with the concentration of hydrogen peroxide.

The phase diagram has two univariant curves. C_1T_1 and C_2T_2 are saturation curves corresponding to the solid phase $(NH_4)_2C_2O_4 \cdot H_2O_2$ at 283.15 K and 293.15 K, respectively. S_1C_1 and S_2C_2 are saturation curves corresponding to the solid phase $(NH_4)_2C_2O_4 \cdot H_2O$. C_1 and C_2 are invariant points, which represent the equilibrium of the two solid phases $(NH_4)_2C_2O_4 \cdot H_2O$ and $(NH_4)_2C_2O_4 \cdot H_2O_2$.

Figures 1 and 2 further illustrate the temperature dependence of the phase diagram for the ternary $(NH_4)_2C_2O_4$ + H_2O_2 + H_2O system. When the temperature increases from 283.15 K to 293.15 K, the solubility of $(NH_4)_2C_2O_4 \cdot H_2O$ and $(NH_4)_2C_2O_4 \cdot H_2O_2$ increases slightly, and the cosaturated point moves upward. The phase diagrams of the ternary system are similar at different temperatures. The crystalline region of the compound $(NH_4)_2C_2O_4 \cdot H_2O_2$ increases as the temperature decreases. It can also be seen from Figures 1 and 2 that the adduct $(NH_4)_2C_2O_4 \cdot H_2O_2$ is an unsymmetric double salt and can be formed at high concentrations of hydrogen peroxide.

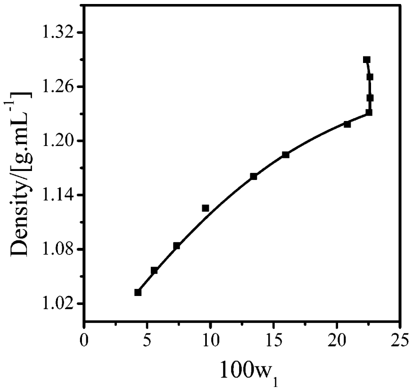

Figure 4. Density value−composition relationship diagram for the ternary system $(NH_4)_2C_2O_4$ (1) + H_2O_2 (2) + H_2O (3) at 293.15 K: ■, experimental data point; —, experimental relationship diagram.

On the basis of data collected in Tables 1 and 2, the relationship between the density of the equilibrium liquid phase and the salt concentration values expressed in mass fractions was plotted in Figures 3 and 4. Results showed that the equilibrium solution density values increased with respect to a rise in the hydrogen peroxide concentration.

Conclusion

The solubility of the ternary ammonium oxalate + hydrogen peroxide + water system was determined experimentally at 283.15 K and 293.15 K. The phase diagram was constructed on the basis of the measured solubility. The densities of the equilibrium liquid phase were obtained. The adduct $(NH_4)_2C_2O_4 \cdot H_2O_2$ was confirmed by Schreinemaker's wet residues method. At the studied temperatures, two solid phases were formed in the ternary system $(NH_4)_2C_2O_4$ + H_2O_2 + H_2O which corresponded to $(NH_4)_2C_2O_4 \cdot H_2O$ and $(NH_4)_2C_2O_4 \cdot H_2O_2$. The phase diagram includes three crystallization fields, $(NH_4)_2C_2O_4 \cdot H_2O_2$, $(NH_4)_2C_2O_4 \cdot H_2O$, and a mixture of $(NH_4)_2C_2O_4 \cdot H_2O_2$ and $(NH_4)_2C_2O_4 \cdot H_2O$, two crystalline curves, and one invariant point at each temperature. The phase diagrams of the ternary system are similar at different temperatures. The monohydrate $(NH_4)_2C_2O_4 \cdot H_2O$ has a bigger crystallization field than either $(NH_4)_2C_2O_4 \cdot H_2O_2$ or the mixture. The solubility of $(NH_4)_2C_2O_4 \cdot H_2O$ increased with an increase in the concentration of hydrogen peroxide, whereas the solubility of $(NH_4)_2C_2O_4 \cdot H_2O_2$ varies little with respect to a rise in the hydrogen peroxide concentration.

The solubility and phase diagram of the systems $K_2C_2O_4$ + H_2O_2 + H_2O[12] and $Na_2C_2O_4$ + H_2O_2 + H_2O[13] have been previously studied by our laboratory. The phase diagram of the system $(NH_4)_2C_2O_4$ + H_2O_2 + H_2O was similar to the systems $K_2C_2O_4$ + H_2O_2 + H_2O and $Na_2C_2O_4$ + H_2O_2 + H_2O at each temperature. However, the crystallization field of $K_2C_2O_4 \cdot H_2O_2$ is larger than that of $Na_2C_2O_4 \cdot H_2O_2$ or $(NH_4)_2C_2O_4 \cdot H_2O_2$ at the same temperature. The $Na_2C_2O_4 \cdot H_2O_2$ or $(NH_4)_2C_2O_4 \cdot H_2O_2$ can only be crystallized in a relatively high concentration of hydrogen peroxide aqueous solutions.

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