# Equilibria in the Aqueous Ternary System Containing $Na^+$, $CH_3CO_2^-$, and $P_2O_7^{4-}$ between 38 and 85 °C

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**Synopsis.** The ternary system $CH_3CO_2Na$-$Na_4P_2O_7$-$H_2O$ was investigated between 38 and 85 °C. No double salt occurs in this temperature range. The saturated $CH_3CO_2Na$ solutions can contain only small amount of $Na_4P_2O_7$. The $CH_3CO_2Na$ solutions have a very strong dehydrating influence on $Na_4P_2O_7 \cdot 10H_2O$. So, the lowest formation temperature of anhydrous $Na_4P_2O_7$ is about 47 °C.

In an earlier paper,[1] we have reported that the addition of a small amount of sodium pyrophosphate decahydrate to sodium acetate solutions is very effective for the crystal nucleation of sodium acetate trihydrate from the solutions. Subsequently, we studied the influence of preheating on crystallization of sodium acetate trihydrate from the aqueous solution with addition of a small amount of sodium pyrophosphate decahydrate and proposed an adsorption model to account for the crystal nucleation catalytic effect.[2] To complete the investigation, knowledge is required of the ternary system sodium acetate–sodium pyrophosphate–water.

The phase diagrams of the binary systems sodium acetate–water and sodium pyrophosphate–water, based on the data from Seidell's compilation[3] are shown in Fig. 1. In this figure, $W_a$ and $W_b$ are the mass fraction of sodium acetate and sodium pyrophosphate respectively.

This paper reports the results from the investigation of sodium pyrophosphate together with sodium acetate aqueous solution.

## Experimental

Sodium acetate trihydrate, anhydrous sodium acetate, and sodium pyrophosphate decahydrate were guaranteed grade reagents. Weighed quantities of reagents and water were placed in a glass vessel equipped with a stirrer bar. The glass vessel was sealed and immersed in a water bath, whose temperature was controlled within ±0.5 °C. After the sample was stirred at a determined temperature for 6 h, the supernatant solution was pipetted off through the filter.

The pyrophosphate ion concentration was measured colorimetrically. Concentrated nitric acid was added in the dilute supernatant solution, and heated at 80 °C for about 1 h in order to decompose a pyrophosphate ion into two orthophosphate ions. Dilute sulfuric acid was further added. When ammonium molybdate aqueous solution was introduced into the solution, a yellow ammonium molybdophosphate precipitate was deposited. The precipitate was extracted with isobutyl methyl ketone. The extract was dried over anhydrous sodium sulfate. The absorbance of the extract was measured at 400 nm.

The supernatant solution was also dried at 120 °C in an oven and the total salt concentration was determined. The sodium acetate concentration was caluculated from the difference in concentration between the total salts and sodium pyrophosphate. The residual solid, which was in equilibrium with the saturated solution was separated and identified by X-ray diffraction. The solution in equilibrium with two solid phases was confirmed by analyzing the solution added by these solids.

## Results

In the ternary system sodium acetate–sodium pyrophosphate–water, five isotherms between 38 and 85 °C are shown in Table 1. The solubilities of the binary systems, sodium acetate–water and sodium pyrophosphate–water, which are determined in the present ex-

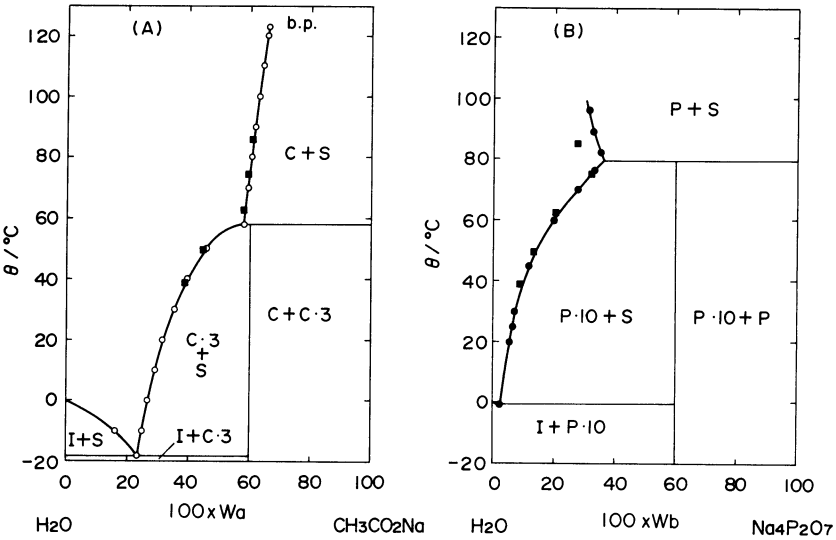

Fig. 1. Phase diagram of the binary systems, $CH_3CO_2Na$-$H_2O$ (A) and $Na_4P_2O_7$-$H_2O$ (B). Symbols: I=ICE, C=$CH_3CO_2Na$, C·3=$CH_3CO_2Na \cdot 3H_2O$, P=$Na_4P_2O_7$, P·10=$Na_4P_2O_7 \cdot 10H_2O$, S=Solution.
○: The data obtained by Green,[4] ●: the data obtained by Menzel and Gabler,[5] and Menzel and Sieg,[6] ■: the data obtained by the present experiment.

Table 1. Isotherms of the ternary system $CH_3CO_2Na$–$Na_4P_2O_7$–$H_2O$ at 38, 50, 62, 75, and 85 °C

| θ | Solution | | Solid[c)] |
|---|---|---|---|
| °C | 100×$W_a$[a)] | 100×$W_b$[b)] | phase |
| 38 | 0 | 8.5 | P·10 |
| | 5.5 | 3.1 | P·10 |
| | 11.1 | 1.1 | P·10 |
| | 16.3 | 0.54 | P·10 |
| | 21.0 | 0.28 | P·10 |
| | 25.6 | 0.18 | P·10 |
| | 29.9 | 0.14 | P·10 |
| | 34.0 | 0.11 | P·10 |
| | 37.9 | 0.10 | P·10 |
| | 37.9 | 0.08 | P·10+C·3 |
| | 38.5 | 0 | C·3 |
| 50 | 0 | 12.9 | P·10 |
| | 6.5 | 4.9 | P·10 |
| | 13.4 | 1.6 | P·10 |
| | 19.2 | 0.73 | P·10 |
| | 25.0 | 0.47 | P·10 |
| | 29.7 | 0.31 | P·10 |
| | 34.0 | 0.24 | P·10 |
| | 37.3 | 0.22 | P·10+P |
| | 41.6 | 0.10 | P |
| | 45.5 | 0.06 | P+0·3 |
| | 45.4 | 0 | C·3 |
| 62 | 0 | 20.4 | P·10 |
| | 9.7 | 6.3 | P·10 |
| | 19.5 | 2.1 | P·10 |
| | 21.4 | 1.3 | P·10+P |
| | 24.7 | 1.1 | P |
| | 29.3 | 0.73 | P |
| | 35.5 | 0.24 | P |
| 62 | 39.9 | 0.10 | P |
| | 46.4 | 0.04 | P |
| | 51.3 | 0.03 | P |
| | 58.0 | 0.02 | P+C |
| | 58.2 | 0 | C |
| 75 | 0 | 31.7 | P·10 |
| | 2.5 | 26.0 | P·10 |
| | 4.8 | 20.6 | P·10+P |
| | 9.4 | 11.1 | P |
| | 20.2 | 2.4 | P |
| | 29.3 | 0.55 | P |
| | 36.9 | 0.13 | P |
| | 44.0 | 0.05 | P |
| | 50.1 | 0.03 | P |
| | 55.9 | 0.03 | P |
| | 59.2 | 0.02 | P+C |
| | 59.6 | 0 | C |
| 85 | 0 | 27.4 | P |
| | 9.3 | 9.3 | P |
| | 18.9 | 1.9 | P |
| | 27.2 | 0.49 | P |
| | 34.2 | 0.18 | P |
| | 40.9 | 0.09 | P |
| | 46.4 | 0.05 | P |
| | 51.9 | 0.02 | P |
| | 56.6 | 0.02 | P |
| | 60.8 | 0.02 | P+C |
| | 60.8 | 0 | C |

a) $W_a$ is the mass fraction of $CH_3CO_2Na$ in the system. b) $W_b$ is the mass fraction of $Na_4P_2O_7$ in the system. c) Symbols: C=$CH_3CO_2Na$, C·3=$CH_3CO_2Na \cdot 3H_2O$, P=$Na_4P_2O_7$, P·10=$Na_4P_2O_7 \cdot 10H_2O$.

periments are plotted in Fig. 1. From these figures, it is clear that the solubilities determined here are in good agreement with the reported data.

The solids which exist in equilibrium with the solution of the system include no double salt in the temperature range investigated. The principal interest is therefore connected with the changes in the isothermally invariant equilibria and the lowest formation temperature of the anhydrous sodium pyrophosphate. The saturated sodium acetate solutions contain only a small amount of sodium pyrophosphate and they have a very strong dehydrating influence on the sodium pyrophosphate decahydrate. Accordingly anhydrous sodium pyrophosphate must be formed at temperatures which are low compared with the corresponding one in the pure aqueous system (79.5 °C). A synopsis of the isothermally invariant equilibria below 85 °C is given in Fig. 2. There it is presumed that the solubility of sodium pyrophosphate in the sodium acetate solutions is insignificant below 0 °C. This figure gives a survey of the formation of the solid.

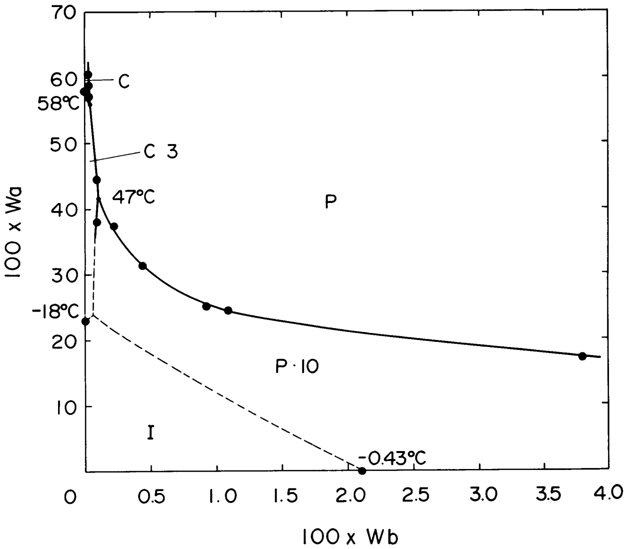

Fig. 2. Synopsis of the composition of the solutions at the invariant and univariant equlibria of the ternary system $CH_3CO_2Na$–$Na_4P_2O_7$–$H_2O$. The symbols in this figure indicate the same phases as those in Fig. 1.

Isothermally invariant points were plotted, with temperature as ordinate and sodium pyrophosphate concentration as abscissa. The lowest formation temperature of anhydrous sodium pyrophosphate is determined from the point of intersection of the curves on which the solution is equilibrium with two solid phases and it is about 47 °C.

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## References

1) T. Wada and R. Yamamoto, *Bull. Chem. Soc. Jpn.*, **55**, 3603 (1982).

2) T. Wada, K. Matsunaga, and Y. Matsuo, *Bull. Chem. Soc. Jpn.*, **57**, 557 (1984).

3) A. Seidell, "Solubility of Inorganic and Metal-Organic Compounds," 4th ed, ACS, Washington, D. C. (1965), Vol. II, pp. 854 and 1106.

4) W. F. Green, *J. Phys. Chem.*, **12**, 655 (1908).

5) H. Menzel and C. Gabler, *Z. Anorg. Allg. Chem.*, **177**, 187 (1929).

6) H. Menzel and L. Sieg, *Z. Elektrochem.*, **38**, 287 (1932).