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Studies on Salt Hydrates for Latent Heat Storge. VI. Preheating Effect on Crystallization of Sodium Acetate Trihydrate from Aqueous Solution with a Small Amount of Disodium Hydrogenphosphate

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With particular reference to the use of Na_2HPO_4 as nucleation catalyst for crystallization of $CH_3CO_2Na \cdot 3H_2O$, influences of preheating temperature and time were studied on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from three kinds of CH_3CO_2Na aqueous solutions, whose concentrations were 58.0, 60.3, and 62.8 wt%. In 60.3 wt% aqueous solution ($CH_3CO_2Na \cdot 3H_2O$), the nucleation catalyst begins to get deactivated by preheating at 81 °C. The temperature at which the catalyst begins to get deactivated is slightly raised with increasing CH_3CO_2Na concentration of the solution. The results obtained are compared with those previously reported on the use of $Na_4P_2O_7 \cdot 10H_2O$ as nucleation catalyst, and are discussed on the basis of the crystalline adsorption model.

Sodium Acetate Trihydrate ($CH_3CO_2Na \cdot 3H_2O$) has recently attracted attention as a useful heat storage material because of its large latent heat of fusion (264 J/g).[1,2] Pure $CH_3CO_2Na \cdot 3H_2O$ melt supercools at condiserably lower temperatures than its melting point (58.4 °C).[3,4] Its practical application has been impaired by this supercooling phenomenon.[5] Wada and Yamamoto[6] found that addition of $Na_4P_2O_7 \cdot 10H_2O$ is very effective for preventing the supercooling. Afterward, Kimura[7] found that addition of a mixture of Na_2HPO_4 and anhydrous CH_3CO_2Na is also effective for the prevention.

Ternary system CH_3CO_2Na–Na_2HPO_4–H_2O has been investigated between 38 and 75 °C.[8] No double salt formation occurs in this temperature range. The saturation concentrations of Na_2HPO_4 in saturated CH_3CO_2Na solutions are 1.5 wt% at 50 °C, 0.7 wt% at 62 °C, and 0.6 wt% at 75 °C. The lowest formation temperature of anhydrous Na_2HPO_4 is about 57 °C.

Recently, Wada *et al.*[9] studied the influence of preheating on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from aqueous solutions containing $Na_4P_2O_7 \cdot 10H_2O$ as nucleation catalyst and obtained results that the nucleation catalyst $Na_4P_2O_7 \cdot 10H_2O$ begins to get degraded in its nucleation ability by preheating at about 81 °C and that the temperature (T_c) at which the catalyst begins to get degraded in its nucleation ability is raised with increasing CH_3CO_2Na concentration of the solution. Such results have been explained in detail on the basis of the crystaline adsorption model[9] proposed by Richards.[10] This model is illustrated in Fig. 1.

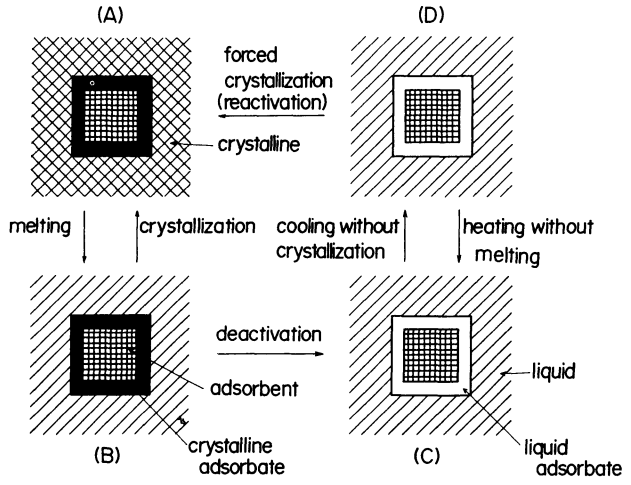

Fig. 1. The crystalline adsorption model for crystal nucleation.
(A): Crystalline state, (B): melting state with crystalline adsorbate, (C): melting state with liquid adsorbate, (D): supercooled state.

It can be seen from Fig. 1 that the crystalline $CH_3CO_2Na \cdot 3H_2O$ adsorbed on the adsorbent ($Na_4P_2O_7$) is not allowed to fuse at its ordinary melting point, preserving its crystal nucleation ability even above its melting point. The heat of adsorption of crystalline $CH_3CO_2Na \cdot 3H_2O$ onto the adsorbet is higher than that of liquid adsorbate. When crystalline $CH_3CO_2Na \cdot 3H_2O$ adsorbate has been fused entirely at an elevated temperature, $CH_3CO_2Na \cdot 3H_2O$ hardly crystallizes from the solution. However, even if the crystalline adsorbate has entirely been fused, it will again be formed during the cooling process becsuse of forced crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the solution containing the nucleation catalyst.

This paper reports influences of preheating temperature and time on the crystal nucleation of $CH_3CO_2Na \cdot 3H_2O$ from sodium acetate solutions containing a small amount of Na_2HPO_4 added. Results obtained are compared with those in the case of solutions containing $Na_4P_2O_7 \cdot 10H_2O$ as nucleation catalyst and subjected to a discussion on the basis of the crystalline adsorpton model.

Experimental

$CH_3CO_2Na \cdot 3H_2O$, CH_3CO_2Na, and Na_2HPO_4 were guaranteed grade reagents from Wako Pure Chemical Industries, Ltd. Experimental procedures are similar to those reported in the preceding paper.[9] Eight grams of CH_3CO_2Na aqueous solution and 0.16 g of Na_2HPO_4 were placed in a tube, which was afterwards sealed. The sealed tubes were put into a water bath equipped with a gently-vibrating rack. Before subsequent steps, all aqueous solutions with a small amount of Na_2HPO_4 added were heated at 70 °C for 1 h and then cooled to room temperature in order to force $CH_3CO_2Na \cdot$

$3H_2O$ to crystallize. Then, the tubes were shaked if necessary.

Experiment 1. One hundred sealed tubes, each containing a CH_3CO_2Na aqueous solution at a concentration of 58.0, 60.3, or 62.8 wt% and a small amount of nucleation catalyst added, were heated to a predetermined temperature, kept there for 3 h and then cooled to 40 °C at a rate of 5 °C/h. This process was repeated with the preheating temperature raised stepwise. In some of the 100 tubes preheated at a certain temperature, $CH_3CO_2Na \cdot 3H_2O$ failed to crystallize on cooling to 40 °C. Such tubes were excluded because the nucleation catalyst in the tube must have been deactivated or degraded in its nucleation ability. This deactivation possibility was supported by the observation that $CH_3CO_2Na \cdot 3H_2O$ scarcely crystallized in the excluded tubes during similar heating and cooling tests as mentioned above. The percentage of the tubes having deactivated nucleation catalysts over the total tubes was plotted against the temperature difference between the preheating temperature and the melting point (58.4 °C) to get Fig. 2.

Experiment 2. One hundred tubes, each containing a 58 wt% aqueous solution and a small amount of nucleation catalyst added, were heated to a constant preheating temperature, kept there for 3 h, and then cooled to 40 °C at a rate of 5 °C/h. This procedure was applied to several preheating temperatures. In some of the 100 tubes preheated for a certain time, $CH_3CO_2Na \cdot 3H_2O$ failed to crystallize on cooling to 40 °C. Such tubes were excluded for the same reason as in *Experiment 1.* The percentage of the tubes in which the nucleation catalyst was deactivated over the total tubes was plotted against the preheating time to get Fig. 3.

Experiment 3. Experimental procedures were similar to those in *Experiment 2* except that those tubes in which $CH_3CO_2Na \cdot 3H_2O$ had failed to crystallize on cooling to 40 °C were not excluded but cooled to room temperature to force $CH_3CO_2Na \cdot 3H_2O$ to crystallize; they were then subjected to sequentially succeeding heating and cooling tests. The percentage of the tubes in which the nucleation catalyst was deactivated over the total tubes was plotted against the preheatng time to get Fig. 4.

Results and Discussion

It is clear from Fig. 2 that, under the conditions of *Experiment 1,* the nucleation catalysts in the 60.3 wt% CH_3CO_2Na aqueous solutions begin to get deactivated at 81 °C, higher by 23 °C than the melting point of $CH_3CO_2Na \cdot 3H_2O$ until all of them were deactivated at about 88 °C. These temperatures are in good agreement with the data obtained when $Na_4P_2O_7 \cdot 10H_2O$ was used as nucleation catalyst. In 58.0 and 62.8 wt% solutios, the nucleation catalysts begin to get deactivated at 81 and 82 °C, until all were deactivated at 88 and 89 °C, respectively. In 100 tubes each containing 8 g of 60.3 wt% aqueous solution with no nucleation catalyst, the cooling to 40 °C preceded by preheating at 60 °C for 3 h caused no $CH_3CO_2Na \cdot 3H_2O$ to crystallize. It is evident that the addition of Na_2HPO_4 is very effective for preserving the crystal nucleation ability above the melting point of $CH_3CO_2Na \cdot 3H_2O$. It is understood from Fig. 2 that T_c is slightly raised with increasing CH_3CO_2Na concentration of the solution. Such a phenomenon is qualitatively similar to one observed in the case of solutions with $Na_4P_2O_7 \cdot 10H_2O$ added as nucleation catalyst; the degree of concentration dependence of T_c is appreciably lower than in the previous case.

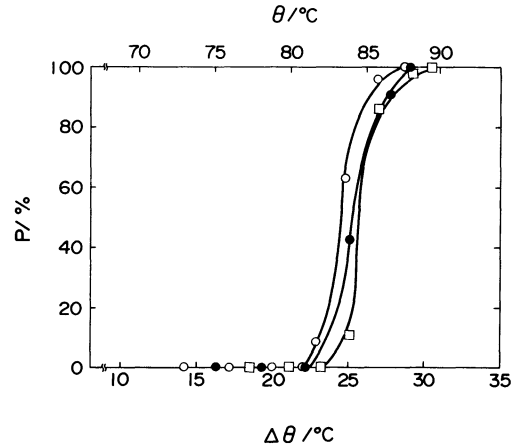

Fig. 2. The influence of preheating temperature on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the three aqueous solutions in use of a small amount of Na_2HPO_4 as a nucleation catalyst.
○: 58.0 wt% CH_3CO_2Na aqueous solution, ●: 60.3 wt% CH_3CO_2Na aqueous solution, □: 62.8 wt% CH_3CO_2Na aqueous solution.

It can be seen from Fig. 3 that under the conditions of *Experiment 2,* in the 100 tubes each containing 8 g of 58.0 wt% CH_3CO_2Na aqueous solution and 0.16 g of

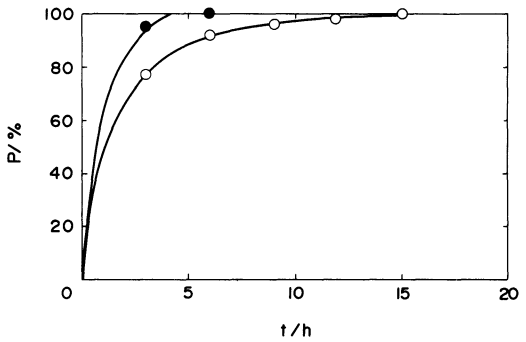

Fig. 3. The influence of preheating time on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the 58.0 wt% aqueous solution in use of Na_2HPO_4 as a nucleation catalyst under the conditions of *Experiment 2.*
○: Preheated at 84 °C, ●: preheated at 85 °C.

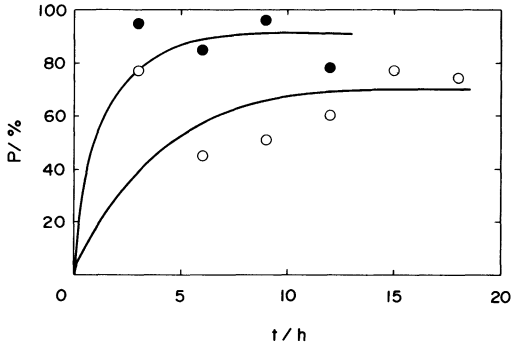

Fig. 4. The influence of preheating time on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the 58.0 wt% aqueous solution in use of Na_2HPO_4 as a nucleation catalyst under the conditions of *Experiment 3.*
○: Preheated at 84 °C, ●: preheated at 85 °C.

Na_2HPO_4, $CH_3CO_2Na \cdot 3H_2O$ did not crystallize at all after the tubes had been preheated at 84 °C for 15 h and at 85 °C for 6 h. The preheating time that results in deactivation of all the catalysts is shortened with increasing preheating temperature. This result is similar to the case of $Na_4P_2O_7 \cdot 10H_2O$.

It is seen from Fig. 4 that under the conditions of *Experiment 3*, in some of the 100 pieces of tubes each containing 8 g of 58.0 wt% CH_3CO_2Na aqueous solution and 0.16 g of Na_2HPO_4, $CH_3CO_2Na \cdot 3H_2O$ crystallized even after they had been preheated at 84 °C for 15 h and at 85 °C for 6 h. The percentages of the tubes with deactivated nucleation catalysts seem to approach constant values with increasing preheating time, though with a wide variation; the preheating at 84 or 85 °C corresponds to about 70 or 90%, respectively. Compared with Fig. 3, it is evident that deactivated nucleation catalysts may be reactivated by forced crystallization of $CH_3CO_2Na \cdot 3H_2O$ from solutions containing the crystal nucleation catalyst. The same phenomenon was observed in the case of CH_3CO_2Na aqueous solution with $Na_4P_2O_7 \cdot 10H_2O$ added.

In 20 pieces of tubes each containing 8 g of 58 wt% CH_3CO_2Na aqueous solution with 0.001, 0.01 or 0.04 g Na_2HPO_4 added, $CH_3CO_2Na \cdot 3H_2O$ hardly crystallized on cooling after the Na_2HPO_4 had been dissolved entirely in the CH_3CO_2Na solution by the preheating at 70 °C. It is understood from this experiment and the phase equilibria of ternary system CH_3CO_2Na–Na_2HPO_4–H_2O that the anhydrous Na_2HPO_4 solid in the solution is required for the crystallization of $CH_3CO_2Na \cdot 3H_2O$ to occur from the solution near the transition temperature. A similar conclusion was drawn in our preceding investigation using $Na_4P_2O_7 \cdot 10H_2O$ as crystal nucleation catalyst.

The results obtained from the present experiments will be discussed on the basis of the crystalline adsorption model proposed by Richards, which is illustrated in Fig. 1. According to this model, the Na_2HPO_4 added to a CH_3CO_2Na aqueous solution offers an adsorbent for which the heat of adsorption of crystalline $CH_3CO_2Na \cdot 3H_2O$ is higher than that of liquid adsorbate. From the phase equilibria of ternary system CH_3CO_2Na–Na_2HPO_4–H_2O the adsorbent is considered to be anhydrous Na_2HPO_4.

It is understood on the basis of the concept of adsorption that the melting temperature of crystalline $CH_3CO_2Na \cdot 3H_2O$ adsorbed on the adsorbent is raised with increasing CH_3CO_2Na concentration of the solution. Therefore, T_c is expected to be raised with increasing CH_3CO_2Na concentration. This expectation is compatible with the result shown in Fig. 2.

It is also plausible that the crystalline $CH_3CO_2Na \cdot 3H_2O$ adsorbate melts faster at higher temperatures than T_c. Therefore, the preheating time which results in complete catalyst deactivation is expected to be shortened with increasing preheating temperature. This expectation is also compatible with the result shown in Fig. 3.

According to the crystalline adsorption model a satisfactory, though qualitative, explanation has been given the reactivation of a deactivated nucleation catalyst which is effected by forced crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the solution containing that nucleation catalyst; some quantitative explanation of these crystal nucleation catalytic actions remains to be given.

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