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Studies on Salt Hydrates for Latent Heat Storage. V. Preheating Effect on Crystallization of Sodium Acetate Trihydrate from Aqueous Solution with a Small Amount of Sodium Pyrophosphate Decahydrate

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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% and which contained a small amount of crystal nucleation catalyst, $Na_4P_2O_7 \cdot 10H_2O$. In 60.3 wt% aqueous solution ($CH_3CO_2Na \cdot 3H_2O$), the nucleation catalyst begins to get deactivated by preheating at about 81 °C, higher by 23 °C than the melting point of $CH_3CO_2Na \cdot 3H_2O$. The temperature at which the catalyst begins to get deactivated is raised with increasing CH_3CO_2Na concentration of the solution; thus, in 62.8 wt% CH_3CO_2Na aqueous solution, the catalyst begins to get deactivated at 85 °C. One hundred samples, each consisting of 8 g of 60.3 wt% CH_3CO_2Na aqueous solution and 0.16 g of $Na_4P_2O_7 \cdot 10H_2O$, all crystallized on cooling to 40 °C, even after they had been preheated at 80 °C for 39 h. These results are explained on the basis of the crystalline adsorption model proposed by Richards.

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] $CH_3CO_2Na \cdot 3H_2O$ melt tends to supercool even if cooled considerably below its melting point (58.4 °C).[3,4] Its practical application has been impaired by this supercooling phenomenon.[5] Wada and Yamamoto,[6] in search for a crystal nucleation catalyst, have found that addition of $Na_4P_2O_7 \cdot 10H_2O$ is very effective for preventing the supercooling.

A phase diagram of binary system CH_3CO_2Na–H_2O, based on data from Seidell's compilation,[7] is shown in Fig. 1. The dashed line is the liquidus line for metastable CH_3CO_2Na. It is clear that $CH_3CO_2Na \cdot 3H_2O$ melts incongruently to a 58.0 wt% CH_3CO_2Na aqueous solution in equilibrium with the residual solid, anhydrous CH_3CO_2Na, and that anhydrous CH_3CO_2Na dissolves entirely in its water of crystallization at about 78 °C.

Ternary system CH_3CO_2Na–$Na_4P_2O_7$–H_2O has been investigated between 38 and 85 °C.[9] No double salt formation occurs in this temperature range. Saturation concentrations of $Na_4P_2O_7$ in saturated CH_3CO_2Na solutions are 0.08 wt% at 38 °C, 0.06 wt% at 50 °C, 0.02 wt% at 62 °C, 0.02 wt% at 75 °C, and 0.02 wt% at 85 °C. The lowest formation temperature of anhydrous $Na_4P_2O_7$ is about 47 °C.

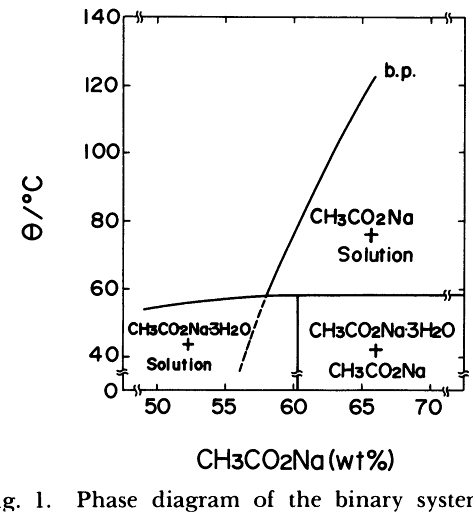

Fig. 1. Phase diagram of the binary system CH_3CO_2Na–H_2O.[8]

The crystallization tendency of the liquid is diminished with increasing preheating temperature.[10,11] Richards[12] studied the preheating effect on crystallization of $CH_3CO_2Na \cdot 3H_2O$ from aqueous solution. He used 20 sealed tubes each containing 3 g of 12 M (1 M= 1 mol dm^{-3}), about 50 wt%, CH_3CO_2Na aqueous solution and kept them at room temperature during intervals between preheating treatments. He reported that $CH_3CO_2Na \cdot 3H_2O$, when preheated at a temperature 2, 3.5, or 7 °C above its melting point, was allowed to crystallize in 100, 35, or 5% of the sample tubes, respectively.

A number of explanations are applicable to the above behavior. Richards[12] proposed the crystalline adsorption model that a crystal form may persist above its melting point if some adsorbent present in a sample binds the crystalline adsorbate more strongly than the liquid adsorbate, that is, if the heat of adsorption of the crystalline adsorbate onto the adsorbent is higher than that of the liquid adsorbate. This crystalline adsorption model is illustrated in Fig. 6. This model is characteristically capable of explaining the fact that reactivation of a deactivated nucleation catalyst can be effected by forced crystallization of the liquid containing that catalyst.

This paper reports influences of preheating temperature and time on crystallization of $CH_3CO_2Na \cdot 3H_2O$ from three kinds of CH_3CO_2Na aqueous solutions, whose concentrations are 58.0, 60.3, and 62.8 wt% and which have a small amount of $Na_4P_2O_7 \cdot 10H_2O$ added. For the system to be useful as a latent heat storage material, the temperature at which the crystal nucleation catalyst begins to get deactivated is very important. Results obtained are explained on the basis of the crystalline adsorption model.

Experimental

$CH_3CO_2Na \cdot 3H_2O$, CH_3CO_2Na, and $Na_4P_2O_7 \cdot 10H_2O$ were guaranteed grade reagents from Wako Pure Chemical Industries, Ltd. Eight grams of CH_3CO_2Na aqueous solution and 0.16 g of $Na_4P_2O_7 \cdot 10H_2O$ were placed in a tube, which was afterwards sealed. The concentration of the CH_3CO_2Na aqueous solution prepared was 58.0 wt% (peritectic composition), 60.3 wt% ($CH_3CO_2Na \cdot 3H_2O$), or 62.8 wt%. The sealed tubes were put into a water bath equipped with a gently-vibrating rack. Before subsequent steps, all aqueous solutions with a smal amount of $Na_4P_2O_7 \cdot 10H_2O$ 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, with shaking if necessary.

Experiment 1. One hundred sealed tubes each containing a 60.3 wt% CH_3CO_2Na aqueous solution were heated to a predetermined temperature above the melting point of $CH_3CO_2Na \cdot 3H_2O$, 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 heen deactivatd. 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 other two aqueous solutions were examined in the same manner as above. Thus, the influence of preheating temperature on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from aqueous solution was studied. The percentage of the tubes in which the nucleation catalyst was deactivated was plotted against the temperature difference between the preheating temperature and the melting point to get Fig. 2.

Experiment 2. Experimental procedures were similar to those in *Experiment 1* except that the preheating temperature was kept constant. One hundred tubes were heated to a preheating temperature, kept there for 3 h, and then cooled to 40 °C at a rate of 5 °C/h. 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.* Similar experiments were conducted with a variation of preheating temperature. The influence of preheating time on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from 60.3 and 58.0 wt% CH_3CO_2Na aqueous solutions was studied by finally plotting the percentage of the tubes in which the catalyst was deactivated against the preheating time to get Figs. 3 and 4, respectively.

Experiment 3. Experimental procedures were similar to those adopted in *Experiment 2* except that, when in some tubes $CH_3CO_2Na \cdot 3H_2O$ failed to crystallize on cooling to 40 °C, these tubes were cooled to room temperature to force $CH_3CO_2Na \cdot 3H_2O$ to crystallize, with shaking if necessary, and returned to subsequent steps. This experiment was conducted on the 58.0 wt% CH_3CO_2Na aqueous solution. The percentage of the tubes in which the catalyst was deactivated was plotted against the preheating time to get Fig. 5.

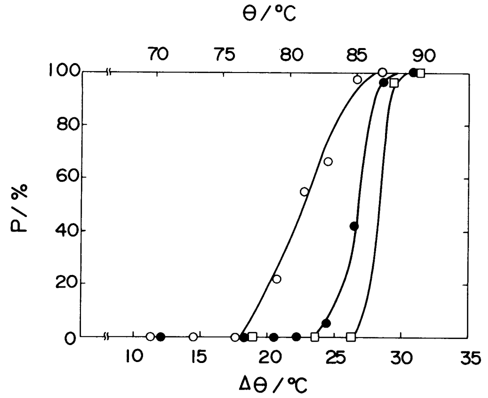

Fig. 2. The influence of preheating temperature on the crystallizaion of $CH_3CO_2Na \cdot 3H_2O$ from the three kinds of aqueous solution with a small amount of $Na_4P_2O_7 \cdot 10H_2O$.
○: 58.0 wt% CH_3CO_2Na aqueous solution, ●: 60.3 wt% CH_3CO_2Na squeous solution, □: 62.8 wt% CH_3CO_2Na aqueous solution.

Results

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 89 °C and that those in the 58.0 and 62.8 wt% solutions begin to get deactivated at 77 and 85 °C until all were deactivated at 85 and 89 °C, respectively. In the 100 tubes each containing 8 g of 60.3 wt% CH_3CO_2Na aqueous solution with no nucleation catalyst added, the cooling to 40 °C preceded by the preheating at 60 °C for 3 h caused no $CH_3CO_2Na \cdot 3H_2O$ to crystallize at all. The present CH_3CO_2Na aqueous solutions with no nucleation catalyst begin to get deactivated at a temperature lower than in the Richards experiment. This may be caused not only by differences in the CH_3CO_2Na concentration and experimental conditions but also by the difference in purity of reagents used. It is evident that the addition of $Na_4P_2O_7 \cdot 10H_2O$ to the CH_3CO_2Na aqueous solution 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 the temperature at which the catalyst begins to get deactivated is raised with increasing CH_3CO_2Na concentration of the solution containing that catalyst. The amount of the $Na_4P_2O_7 \cdot 10H_2O$ added is so small and the solubility of $Na_4P_2O_7$ in the $CH_3CO_2Na \cdot 3H_2O$ melt is so low[9] that the liquidus lines for $CH_3CO_2Na \cdot 3H_2O$ and CH_3CO_2Na may be considered to be scarcely influenced by the addition of $Na_4P_2O_7 \cdot 10H_2O$ to the CH_3CO_2Na aqueous solution. Figure indicates that the anhydrous CH_3CO_2Na in the 58 wt% aqueous solution is unstable above 58.4 °C, the one in the 60.3 wt% solution is unstable above 78 °C, and that the one in the 62.8 wt% solution is unstable above 97 °C. The deactivation of the nucleation catalyst depends on the CH_3CO_2Na concentration of the solution containing that catalyst, but is not directly related to the existence of anhydrous CH_3CO_2Na in the solution, although Kimura[13] has pointed out that the existence of anhydrous CH_3CO_2Na plays an important role in the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the solution.

It can be seen from Fig. 3 that in the 100 tubes each containing 8 g of 60.3 wt% CH_3CO_2Na aqueous solution with 0.16 g $Na_4P_2O_7 \cdot 10H_2O$ added, the nucleation catalysts were all caused to deactivate by preheating at 85 °C for 10 h, at 86 °C for 8 h or at 87 °C for 4 h. The preheating time that results in deactivation of all the catalysts is shortened with incressing preheating temperature. As is also seen from Fig. 3, even the preheating of the solutions at 80 °C for 39 h leads in any cases to crystallization on cooling to

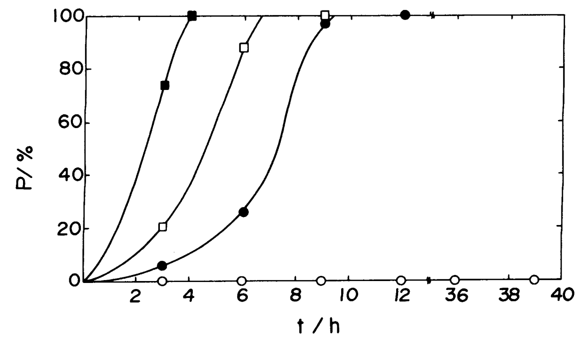

Fig. 3. The influence of preheating time on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the 60.3 wt% CH_3CO_2Na aqueous solution.
○: Preheated at 80 °C, ●: preheated at 85 °C, □: preheated at 86 °C, ■: preheated at 87 °C.

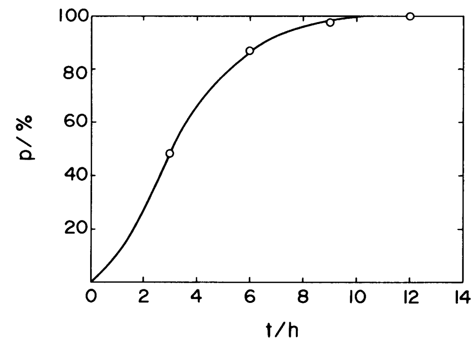

Fig. 4. The influence of preheating time on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the 58.0 wt% CH_3CO_2Na aqueous solution preheated at 83 °C.

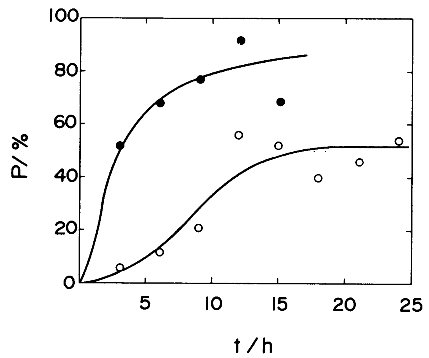

Fig. 5. The influence of preheating time on the crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the 58.0 wt% CH_3CO_2Na aqueous solution under the *Experiment 3* conditions.
○: Preheated at 80 °C, ●: preheated at 83 °C.

40 °C. Thus it is deduced that the nucleation catalysts will not be caused to deactivate at all, no matter how long the solutions containing them are preheated below 80 °C. This is a very important finding from the standpoint of practical application.

It is seen from Fig. 4 that in the 100 tubes each containing a 58.0 wt% CH_3CO_2Na aqueous solution with the catalyst added, the catalysts were all deactivated when preheated at 83 °C for 10 h. The curve in Fig. 4 is similar to those in Fig. 3, so that the preheating time at which the catalysts were all caused to deactivate is supposed to be shorter than 10 h when the preheating temperature is above 83 °C.

In Fig. 5, the percentage of the tubes containing deactivated catalysts seems to approach a constant value, not 100%, with increasing preheating time. When 58.0 wt% CH_3CO_2Na aqueous solutions are preheated at 80 °C under the conditions of *Experiment 3,* the constant value is about 50%, and when they are preheated at 83 °C, it is about 90%. Compared with Fig. 3, it is evident that deactivated catalysts may be reactivated by forced crystallization of $CH_3CO_2Na \cdot 3H_2O$ from solutions containing them.

In 20 tubes each containing 8 g of 58 wt% CH_3CO_2Na aqueous solution with 0.0001, 0.0005, or 0.001 g $Na_4P_2O_7 \cdot 10H_2O$ added, $CH_3CO_2Na \cdot 3H_2O$ hardly crystallized on cooling to 40 °C after the $Na_4P_2O_7 \cdot 10H_2O$ had been dissolved entirely in the CH_3CO_2Na solution by preheating at 70 °C. It is understood from this experiment and the phase equilibria of ternary system CH_3CO_2Na–$Na_4P_2O_7$–H_2O that anhydrous $Na_4P_2O_7$ solid is required for the crystallization of $CH_3CO_2Na \cdot 3H_2O$ to occur from the solution near the transition temperature.

Discussion

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. 6. According to this model, the $Na_4P_2O_7 \cdot 10H_2O$ 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. The adsorbent is considered to be anhydrous $Na_4P_2O_7$ from the phase equilibria of ternary system CH_3CO_2Na–$Na_4P_2O_7$–H_2O,[9] although Wada and Yamamoto[6] discussed the crystal nucleation catalytic effect from the similarity of crystallographic data between $CH_3CO_2Na \cdot 3H_2O$ and $Na_4P_2O_7 \cdot 10H_2O$. The crystalline $CH_3CO_2Na \cdot 3H_2O$ adsorbed on the adsorbent is not allowed to fuse at its ordinary melting

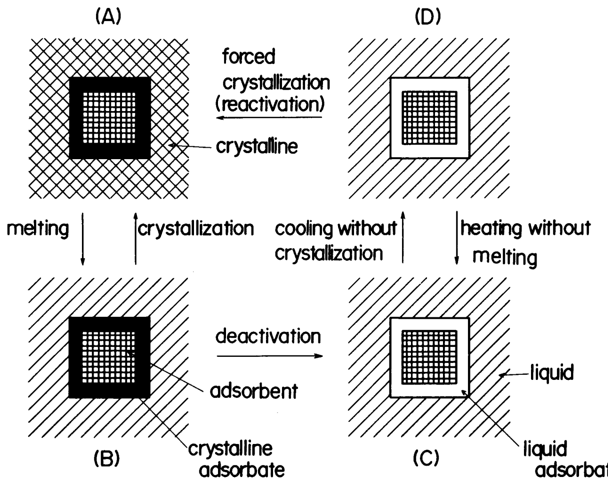

Fig. 6. The crystalline adsorption model proposed by Richards.[11]
(A): Crystalline state, (B): melting state with crystalline adsorbate, (C): melting state with liquid adsorbate, (D): supercooled state.

point but preserves its crystal nucleation ability above its melting point. This condition is shown in Figs. 6(A) snd (B). When the crystalline $CH_3CO_2Na \cdot 3H_2O$ adsorbate is fused entirely at an elevated temperature, $CH_3CO_2Na \cdot 3H_2O$ hardly crystallizes from the solution. This is also shown in Figs. 6(C) and (D). However, even if the crystalline adsorbate has been fused entirely, it is again formed by a forced crystallization of $CH_3CO_2Na \cdot 3H_2O$ from the solution containing the adsorbent. This is shown in Figs. 6(D) and (A). This expectation is compatible with the result obtained from *Experiment 3.*

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 depends not only on the difference in the heat of adsorption for the adsorbent between the crystalline $CH_3CO_2Na \cdot 3H_2O$ and the CH_3CO_2Na aqueous solution but also on the CH_3CO_2Na concentration of the solution. The temperatre is lowered with decreasing CH_3CO_2Na concentration of the slution. This is compatible with the result obtained from *Experiment 1.*

It is also plausible that the crystalline $CH_3CO_2Na \cdot 3H_2O$ adsorbate melts faster at higher temperatures. Therefore, the preheating time which results in complete catalyst deactivaion is expected to be shortened with increasing preheatig temperature. This expectation is also compatible with the result obtained in *Experiment 2.*

It is also found that when a small amount of glycine ($H_2NCH_2CO_2H$) or calcium tartrate tetrahydrate ($C_4H_4O_6Ca \cdot 4H_2O$) is added to a CH_3CO_2Na aqueous solution containing with a small amount of $Na_4P_2O_7 \cdot 10H_2O$ the crystal nucleation catalyst is caused to deactivate by heating and cooling cycles, even if the heating is conducted at 75 °C. That is to say, $H_2NCH_2CO_2H$ or $C_4H_4O_6Ca \cdot 4H_2O$ acts as a catalytic poison for the nucleation catalyst $Na_4P_2O_7 \cdot 10H_2O$. This fact is also explained satisfactorily on the basis of the crystalline adsorption model. If these compounds adsorb on the surface of adsorbent more strongly than the crystalline $CH_3CO_2Na \cdot 3H_2O$ adsorbate, that is, the heats of adsorption of these compounds for the adsorbent are higher than that of the crystalline adsorbate, these compounds will adsorb on the surface of adsorbent through displacement of the crystalline $CH_3CO_2Na \cdot 3H_2O$ adsorbate during heating and cooling cycles. Therefore, the crystal nucleation catalysts are caused to deactivate by the thermal cycling.

Thus, the results obtained have all been explained satisfactorily on the basis of the crystalline adsorption model. However, these explanations are qualitative and the existence of crystalline adsorbate above its ordinary melting point has not yet been confirmed. Therefore, quantitative explanations of these behavior are future problems.

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