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Studies on Salt Hydrate for Latent Heat Storage. III. Pseudo-binary System, $CH_3CO_2Na\cdot3H_2O$–$HCONH_2$

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Synopsis. A pseudo-binary system $CH_3CO_2Na\cdot3H_2O$–$HCONH_2$ has been studied by differential scanning calorimetry. In this system, a one to one addition compound $CH_3CO_2Na\cdot HCONH_2\cdot3H_2O$ is formed. This addition compound melts congruently at 40.5 °C and its heat of fusion is 255 J/g. So, it is hopeful for solar energy storage.

Salt hydrates have received attention recently, because of their large heat of fusion.[1] A few salt hydrates were used for solar energy storage.[2,3] Materials with melting points within the range 40—45 °C are suitable for solar energy storage.

In order to develop a latent heat storage material with melting point within the range 40—45 °C, the pseudo-binary system $CH_3CO_2Na\cdot3H_2O$–$HCONH_2$ was studied by differential scanning calorimetry (DSC). From this measurement, the partial phase-diagram of the ternary system CH_3CO_2Na–$HCONH_2$–H_2O at ambient pressure was constructed. In this system, a one to one addition compound of the two components, $CH_3CO_2Na\cdot3H_2O$ and $HCONH_2$ was formed. The heat of fusion of this addition compound was determined.

Experimental

$CH_3CO_2Na\cdot3H_2O$, CH_3CO_2Na, and $HCONH_2$ were of guaranteed grade reagent supplied from Wako Pure Chemical Industries Ltd.

Differential scanning calorimetry (DSC) was performed using SSC 56OU DSC (DAINISEIKOSHA CO. Ltd.), which was heat-flux DSC. Weighed quantities of $CH_3CO_2Na\cdot3H_2O$, $HCONH_2$, and other chemicals were heated and mixed to form a homogeneous melt. One drop of this melt was placed in a 15 μl silver crucible and was solidified. After the crucible was closed, the sample was heated at the rate of 0.5 °C/min from 10 °C to 90 °C. The melting temperature of the sample was obtained from the sample temperature curve at time corresponding to endothermal peak. This DSC system was calibrated by using ice (t_m: 0.0 °C, ΔH_m: 335 J/g), sodium sulfate decahydrate (t_m: 32.4 °C) and sodium acetate trihydrate (t_m: 58.4 °C) as standards.

Results and Discussion

The phase diagram of the binary system CH_3CO_2Na–H_2O based on W. F. Greem's data[4] is shown in Fig. 1. In this figure, W_a shows mass fraction of CH_3CO_2Na and W_b shows mass fraction of H_2O. We see that $CH_3CO_2Na\cdot3H_2O$ melts incongruently to an aqueous solution containing 58 percent CH_3CO_2Na by weight in equilibrium with the balance of CH_3CO_2Na and that the balance of CH_3CO_2Na dissolves entirely in its water of crystallization at 78 °C.

The DSC curves of some mixtures of the pseudo-binary system $CH_3CO_2Na\cdot3H_2O$–$HCONH_2$ are illus-

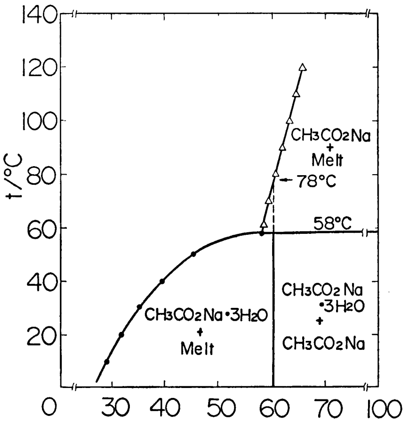

Fig. 1. Phase diagram of the binary system CH_3CO_2Na–H_2O.
●: Melting point of $CH_3CO_2Na\cdot3H_2O$, △: melting point of CH_3CO_2Na.

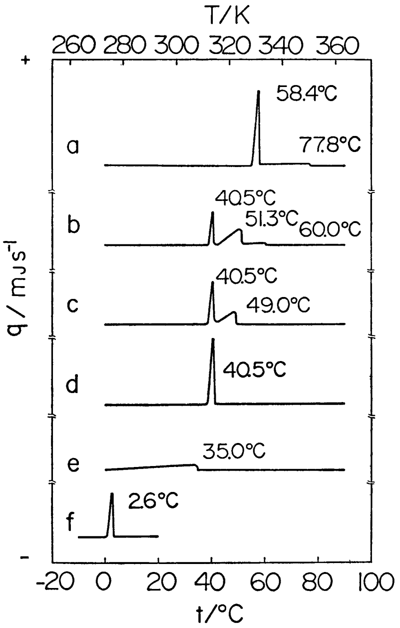

Fig. 2. DSC curves of mixtures of the pseudo-binary system $CH_3CO_2Na\cdot3H_2O$–$HCONH_2$. a: $CH_3CO_2Na\cdot3H_2O$, b: 0.10 mass fraction of $HCONH_2$, c: 0.15 mass fraction of $HCONH_2$, d: 0.25 mass fraction of $HCONH_2$, e: 0.50 mass fraction of $HCONH_2$, f: $HCONH_2$.

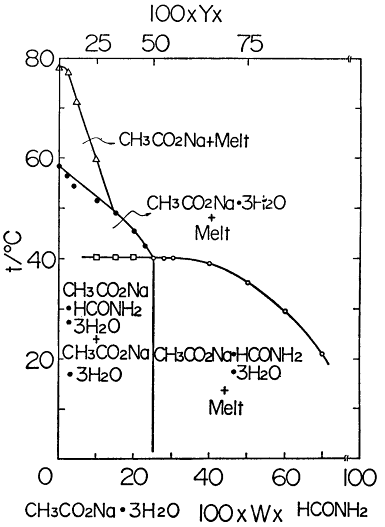

Fig. 3. Pseudo-binary section in the ternary system CH_3CO_2Na–$HCONH_2$–H_2O at ambient pressure.
●: Melting point of $CH_3CO_2Na\cdot3H_2O$, ○: melting point of $CH_3CO_2Na\cdot HCONH_2\cdot3H_2O$, △: melting point of CH_3CO_2Na, □: eutectic point.

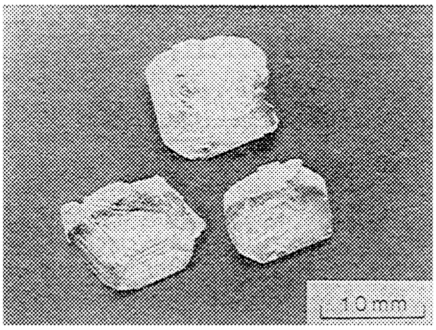

Fig. 4. Photograph of crystals of the addition compound, $CH_3CO_2Na \cdot HCONH_2 \cdot 3H_2O$.

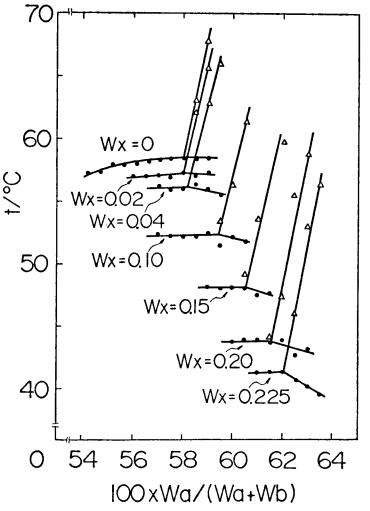

Fig. 5. Melting-point diagram of the ternary system CH_3CO_2Na–$HCONH_2$–H_2O, at ambient pressure in which the mass fraction of $HCONH_2$ is kept constant in each system. ●: Melting point of $CH_3CO_2Na \cdot 3H_2O$, △: melting point of CH_3CO_2Na.

trated in Fig. 2. In this figure, the numbers on the ordinate, q indicates heat flux. The heat absorption accompanying the dissolving of CH_3CO_2Na in its water of crystallization is much smaller than that accompanying the melting of $CH_3CO_2Na \cdot 3H_2O$ but it is illustrated in magnified scale. Considering the phase diagram of the system CH_3CO_2Na–H_2O shown in Fig. 1, we understand that the peak at 58.4 °C of DSC curve of $CH_3CO_2Na \cdot 3H_2O$ corresponds to the melting of $CH_3CO_2Na \cdot 3H_2O$ and the change at 77.8 °C corresponds to the entire dissolution of CH_3CO_2Na in its water of crystallization.

The pseudo-binary section in a ternary system CH_3CO_2Na–$HCONH_2$–H_2O at ambient pressure, which is constructed from such DSC curves, is shown in Fig. 3. In this figure, W_x shows mass fraction of $HCONH_2$, while Y_x shows mole fraction of $HCONH_2$. From this figure, it is clear that in the pseudo-binary system $CH_3CO_2Na \cdot 3H_2O$–$HCONH_2$, a one to one addition compound of the two components forms, and this addition compound $CH_3CO_2Na \cdot HCONH_2 \cdot 3H_2O$ melts congruently at 40.5 °C. The photograph of crystals of this addition compound is shown in Fig. 4. These crystals are colorless and transparent. The specific gravity of this crystal at room temperature is 1.404 g/cm³.

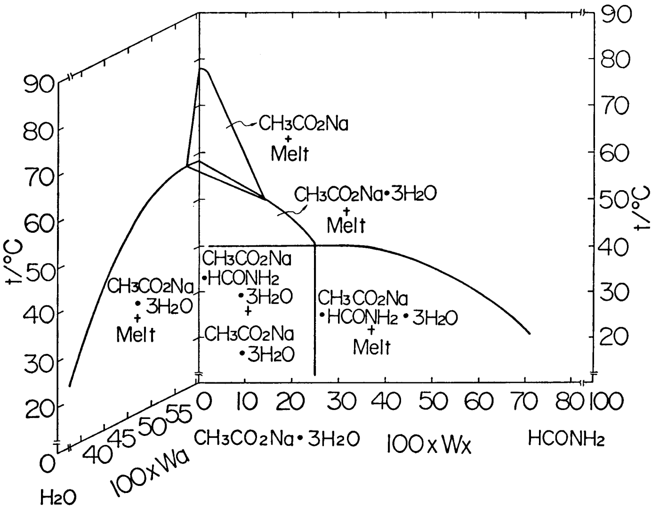

Fig. 6. Partial phase diagram of the ternary system CH_3CO_2Na–$HCONH_2$–H_2O at ambient pressure.

The melting-point diagrams for the system CH_3CO_2Na–$HCONH_2$–H_2O at ambient pressure, in which the mass fraction of $HCONH_2$ is kept constant in each system are plotted in Fig. 5 by using DSC caves such as the curve (c) in Fig. 2. In this figure, the numbers on the abscissa, $100 \times W_a/(W_a+W_b)$ is weight percent of CH_3CO_2Na in the system without $HCONH_2$ content. The melting-point diagram for the system CH_3CO_2Na–H_2O which does not contain $HCONH_2$ is in good agreement with reported data.[4] It is apparent that as mass fraction of $HCONH_2$, W_x increases, the liquidus line on $CH_3CO_2Na \cdot 3H_2O$ side shifts to lower temperature and the liquidus line on CH_3CO_2Na side shifts to higher concentration of CH_3CO_2Na.

The partial phase diagram of the ternary system CH_3CO_2Na–$HCONH_2$–H_2O at ambient pressure is constructed by using the results of Figs. 1, 3, 5, and it is shown in Fig. 6.

The heat of fusion of the addition compound $CH_3CO_2Na \cdot HCONH_2 \cdot 3H_2O$ is found to be 255 J/g by DSC. This value is much larger than the heat of fusion of $Ca(NO_3)_2 \cdot 4H_2O$ (t_m: 43 °C), 142 J/g. The melting point of this addition compound, 40.5 °C is suitable for solar energy storage and its heat of fusion is very large. So, this addition compound $CH_3CO_2Na \cdot HCONH_2 \cdot 3H_2O$ is, hopeful for solar energy storate use.

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References

1) M. Telkes, "Solar Materials Science," ed by L. E. Murr, Academic Press (1980), Chap. 11.
2) K. W. Böer, J. H. Higgins, and J. K. O'connor, *IECEC '75 Record*, **1975**, 7.
3) R. Stepler, *Popular Science*, **1980-3**, 49.
4) W. F. Green, *J. Phys. Chem.*, **12**, 655 (1908).