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An investigation into the use of the eutectic mixture sodium acetate trihydrate–tartaric acid for latent heat storage

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Abstract

In this paper, the study of the pseudo-binary system $CH_3COONa \cdot 3H_2O–C_4H_6O_6$ by means of differential scanning calorimetry is reported. Its eutectic mixture melts congruently at 50 °C and its heat of fusion was found to be 209.3 J g^{-1}. Considering the temperature of the phase change and its heat storage capacity, this eutectic mixture is a most suitable material for latent heat storage of solar energy.

INTRODUCTION

As fossil fuel decreases with each passing day, energy has become one of the major issues attracting worldwide attention in the past few years. Every country is now conducting research into new energy resources. Because solar energy is non-polluting, inexhaustible and clean, it will play an important role as an alternative energy source in the future.

Solar energy, however, has its shortcomings: intermittence and dispersion. Only when an effective energy storage is developed so as to gather the energy by day for night use, on sunny days for rainy-day use and at random for concentrated use, can the use of solar energy become a reality on a large scale. So far there have been three ways of storing the heat of solar energy: sensible heat storage, latent heat storage and reversible reaction storage.

In recent years, mixtures containing salt hydrates have been widely studied in the search for suitable materials for the storage of latent heat. Böer et al. [1] used the eutectic mixture of the system $Na_2SO_4 \cdot 10H_2O–NH_4Cl–NaCl$ as a heat storage material in passive solar houses. Yoneda and Takanashi [2] investigated the $Mg(NO_3) \cdot 6H_2O–MgCl_2 \cdot 6H_2O$ system and found that its eutectic mixture fused at 51.1 °C and that the heat of fusion was 144 J g^{-1}. In China, the Gansu (Provincial) Natural Energy Research Institute, the Hebei Energy Research Institute and the Central China Normal University have all made an extensive study of the system $Na_2SO_4 \cdot 10\ H_2O$.

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However, mixtures of salt hydrates and organic compounds have not been studied extensively. Sodium acetate trihydrate is another salt hydrate which merits our attention. In an earlier paper [4], we investigated the $CH_3COONa \cdot 3H_2O–CH_3CONH_2$ system; in this paper, the system $CH_3COONa–C_4H_6O_6$ is studied using differential scanning calorimetry. In addition, part of the phase diagram of the ternary system $CH_3COONa–C_4H_6O_6–H_2O$ is drawn, and the melting point and heat of fusion are determined. The experiment indicated that the melting point of the eutectic mixture of the system is 50 °C and that the heat of fusion is 209.3 J g^{-1}. Thus, the eutectic mixture of this sodium acetate trihydrate system is suitable for latent heat storage of solar energy.

EXPERIMENTAL

Chemicals

Of the chemicals used, $CH_3COONa \cdot 3H_2O$, $C_4H_6O_6$ and $Na_2SO_4 \cdot 10H_2O$ were analytical reagents, $Na_2S_2O_3$ was a high-class reagent and KNO_3 and Al_2O_3 were specpure reagents.

Instruments

A differential scanning calorimeter (DSC), Model CDR-1 differential thermal analyser (Shanghai Balancing Instruments Factory) was used with a Model TG–332A microanalytical balance, accurate to 0.01 mg.

Experimental

Sodium acetate trihydrate and tartaric acid were weighed accurately in different proportions, and were finely ground with a pestle and mortar and thoroughly mixed. About 10 mg of the mixture was weighed out and placed in a 5 mm × 4 mm aluminium crucible covered with an aluminium lid. As a reference, 10 mg of Al_2O_3 was placed in a similar crucible. The two crucibles were placed on the specimen supports and heated from 20 to 200 °C at a rate of 2 °C min^{-1}, the paper speed of the chart recorder being 5 mm min^{-1}. The melting point of the specimen can be read from the DSC curve and the fusion heat calculated according to the area of the endothermic peak.

Before use, the instruments were calibrated according to the melting points of $Na_2SO_4 \cdot 10H_2O$ (32.4 °C) and $CH_3COONa \cdot 3H_2O$ (58.4 °C) and the fusion heat of specpure KNO_3.

RESULTS AND DISCUSSION

According to the phase diagram of the binary system $CH_3COONa–H_2O$, drawn on the basis of Greem's [5] data (Fig. 1), where W_a represents the

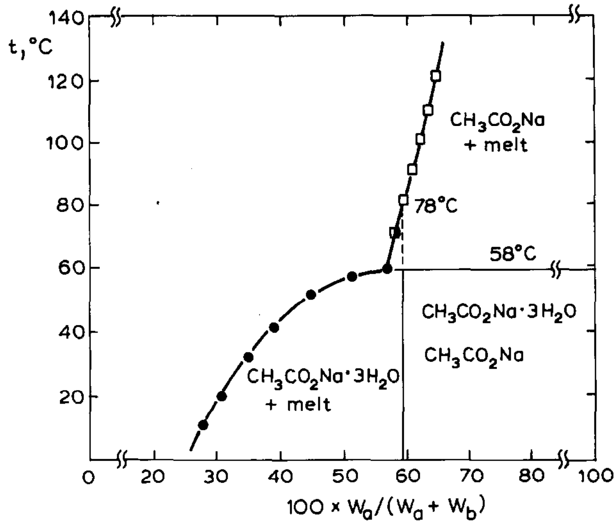

Fig. 1. Phase diagram of the binary system $CH_3COONa–H_2O$ showing: ●, the melting point of $CH_3CO_2Na \cdot 3\,H_2O$; □, the melting point of CH_3CO_2Na.

mass fraction of CH_3COONa, W_b is the mass fraction of H_2O and the scale on the abscissa $100 \times W_a/(W_a + W_b)$, represents percent content of CH_3COONa, it can been seen that sodium acetate trihydrate melts incongruently into an aqueous solution containing 58% CH_3COONa by mass at 58.4° C. This solution and the anhydrous solid-state CH_3COONa are in a state of balance; the anhydrous salt dissolves completely in the water of crystallisation at 78° C.

During steady-state cooling, not all of the molten trihydrate can form the crystalline trihydrate salt because 1 mole of sodium acetate trihydrate contains 82 g of anhydrous sodium acetate, and 54 g of crystallised water. At 58.4° C, 54 g of crystallised water can dissolve about 36 g of sodium acetate. The remaining 46 g of anhydrous sodium acetate will sink to the bottom, resulting in a phase separation.

When the melt cools in a steady state, the stored energy is released according to the following two steps:

$$\text{solution (58\% } CH_3COONa) \rightarrow CH_3COONa + \text{weaker solution} \quad (1)$$

$$\text{weaker solution} + CH_3COONa \rightarrow CH_3COONa \cdot 3H_2O \quad (2)$$

In process (1), crystals of $CH_3COONa \cdot 3H_2O$ are formed from the saturated solution at a much faster rate than in process (2), because process (2) is one of diffusion. Therefore, CH_3COONa is crystallised according to process (1), thus causing the coagulation heat to be lower than the fusion heat. Many cycles of fusion and coagulation will greatly decrease the heat storage capacity.

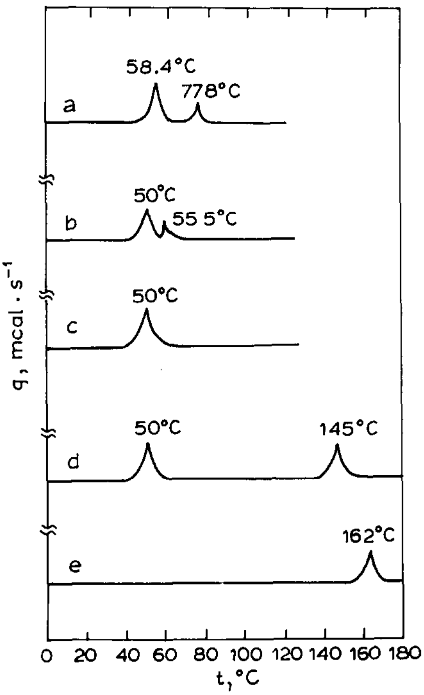

Fig. 2. DSC curves of the pseudo-binary system $CH_3COONa \cdot 3H_2O–C_4H_6O_6$: a, $CH_3COONa \cdot 3H_2O$; b, 0.3 (mass fraction) $C_4H_6O_6$; c, 0.55 (mass fraction) $C_4H_6O_6$; d, 0.6 (mass fraction) $C_4H_6O_6$; e, $C_4H_6O_6$.

A eutectic mixture of tartaric acid and sodium acetate trihydrate can melt congruently at its lowest congruent point. This can overcome effectively the phase separation.

The DSC curves of some mixtures of the pseudo-binary system $CH_3COONa \cdot 3H_2O–C_4H_6O_6$ are shown in Fig. 2.

From the discussion above on the phase diagram of the system $CH_3COONa–H_2O$ (Fig. 1), it can be seen that in Fig. 2, the endothermic peak at 58.4° C on the DSC curve of $CH_3COONa \cdot 3H_2O$ corresponds to the incongruent melting of $CH_3COONa \cdot 3H_2O$; the change at 77.8° C corresponds to the solid anhydrous sodium acetate dissolving completely in the water of crystallisation; on curve e, the endothermic peak at 162° C represents the fusion of pure $C_4H_6O_6$. Curves b and d show the incongruent melting of the pseudo-binary $CH_3COONa \cdot 3H_2O–C_4H_6O_6$ system; however, an endothermic peak occurs on both of them at 50° C. Curve c represents the DSC curve of the pseudo-binary system containing 45% $CH_3COONa \cdot 3H_2O$ and 55% $C_4H_6O_6$ (by mass). There is only the single endothermic peak at 50° C on this curve which indicates that the pseudo-binary system forms a eutectic mixture and that congruent melting occurs at 50° C.

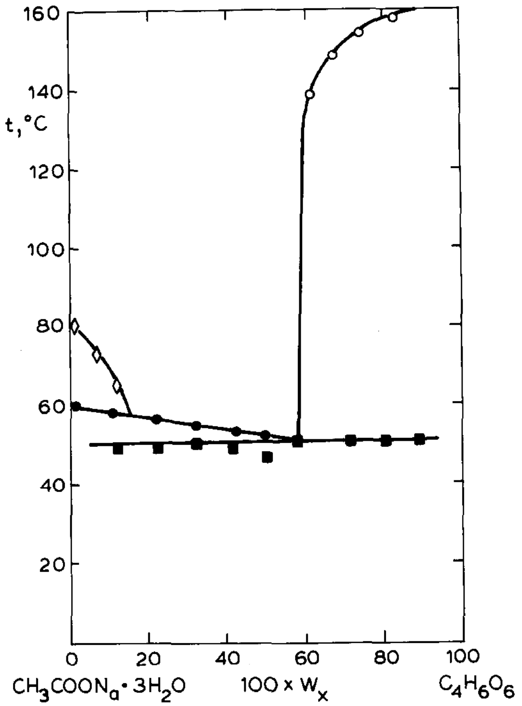

Fig. 3. Temperature–composition diagram of the $CH_3COONa \cdot 3H_2O$–$C_4H_6O_6$ system under normal pressure, showing: ●, the melting point of $CH_3COONa \cdot 3H_2O$; ○, the melting point of $C_4H_6O_6$; □, the melting point of CH_3COONa; ■, the melting point of the eutectic mixture.

From these DSC curves, a melting point–composition diagram can be drawn of the pseudo-binary system $CH_3COONa \cdot 3H_2O$–$C_4H_6O_6$, as shown in Fig. 3, where W_x represents the mass fraction of $C_4H_6O_6$ and $100 \times W_x$ is the mass percentage of $C_4H_6O_6$ in the system. It is clear from the diagram that a eutectic mixture is formed from the pseudo-binary system $CH_3COONa \cdot 3H_2O$–$C_4H_6O_6$ which contains 0.45 (mass fraction) of sodium acetate trihydrate and 0.55 (mass fraction) of $C_4H_6O_6$; congruent melting occurs at 50 ° C.

From Figs. 1–3, part of the phase diagram of the ternary system CH_3COONa–$C_4H_6O_6$–H_2O under normal pressure can be drawn (Fig. 4).

Figure 4 shows that provided sufficient $C_4H_6O_6$ or H_2O is added, congruent melting can occur in $CH_3COONa \cdot 3H_2O$ and the liquidus descends on the side of $CH_3COONa \cdot 3H_2O$ with the addition of $C_4H_6O_6$ or H_2O. The effect of adding $C_4H_6O_6$ to $CH_3COONa \cdot 3H_2O$ is similar to that of adding water. However, the lowest congruent point of the pseudo-binary system $CH_3COONa \cdot 3H_2O$–$C_4H_6O_6$ is 50 ° C, which is most suitable for heat storage of solar energy, and, together with solar energy heaters, it can be used for active heating in houses and buildings.

In comparison, the lowest congruent point of the $CH_3COONa \cdot 3H_2O$–H_2O system is −18 ° C, which is too low.

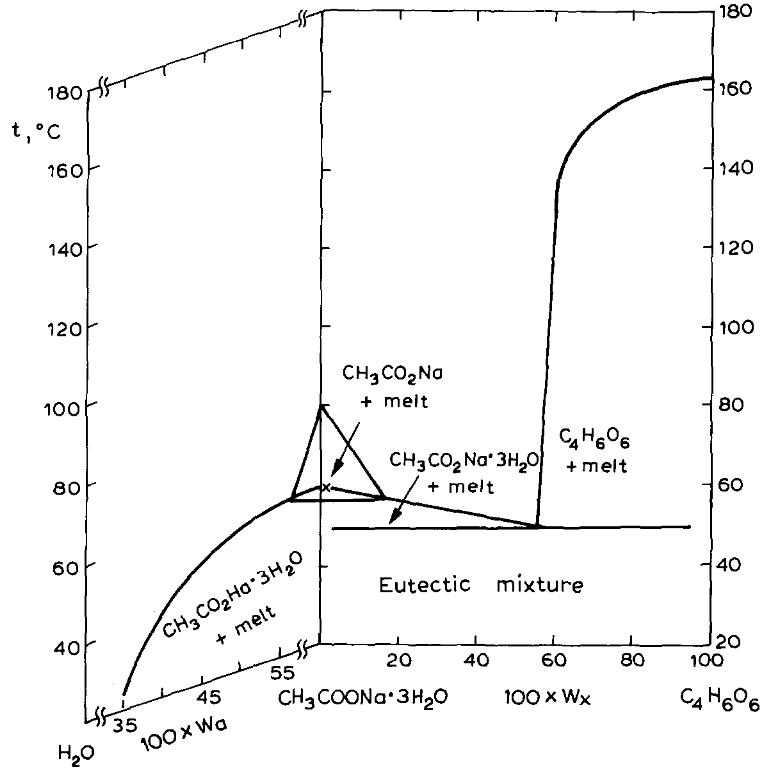

Fig. 4. Part of the phase diagram of the CH_3COONa–$C_4H_6O_6$–H_2O system under normal pressure.

The DSC results indicate that the fusion heat of the eutectic mixture of the pseudo-binary system $CH_3COONa \cdot 3H_2O$–$C_4H_6O_6$ is about 209.3 J g^{-1}.

If the fusion heats of the pure constituents are known, the fusion heat of a binary eutectic mixture can be calculated according to the formula

$$\Delta H_m^{eu} = T_m^{eu}\left\{W^A\left(\frac{\Delta H_m^A}{T_m^A}\right) + W^B\left(\frac{\Delta H_m^B}{T_m^B}\right)\right\} \tag{3}$$

where W^A and W^B are mass fractions of constituents A and B, respectively, T_m^A, T_m^B and T_m^{eu} (K) are the melting points of constituents A, B and the eutectic mixture, respectively, and ΔH_m^A and ΔH_m^B (J g^{-1}) are the fusion heats of constituents A and B, respectively.

In this pseudo-binary system, constituent A represents sodium acetate trihydrate and constituent B is tartaric acid. The data for $CH_3COONa \cdot 3H_2O$) are: melting point, 58.4° C; fusion heat, 264.3 J g^{-1} (literature value 264 J g^{-1}); and for $C_4H_6O_6$: melting point, 162° C; fusion heat, 228.7 J g^{-1}. From the above data, $T_m^A = 331.4$ K, $T_m^B = 434$ K, $T_m^{eu} = 323$ K, $\Delta H_m^A =$ 264.3 J g^{-1}, $\Delta H_m^B = 228.7$ J g^{-1}, $W^A = 0.45$ and $W^B = 0.55$. Substituting into eqn. (3) yields $\Delta H_m^{eu} = 209.5$ J g^{-1}.

Hence, it can be seen that the experimental value for the fusion heat of the eutectic mixture agrees with the computed value.

CONCLUSION

The melting point-composition diagram of the pseudo-binary system $CH_3COONa \cdot 3H_2O$–$C_4H_6O_6$ and part of the phase diagram of the ternary system CH_3COONa–$C_4H_6O_6$–H_2O have been drawn on the basis of the investigation by differential scanning calorimetry. Experiment shows that the pseudo-binary system composed of 45% $CH_3COONa \cdot 3H_2O$ and 55% $C_4H_6O_6$ (by mass) forms a eutectic mixture at 50 °C, and congruent melting occurs, its heat of fusion being 209.3 J g^{-1}. If the temperature of the phase change and the heat storage capacity are considered, this eutectic mixture provides a most suitable material for latent heat storage of solar energy.

REFERENCES

1 K.W. Böer, J.H. Higgins and J.K. O'Connor, Intersoc. Energy Convers. Eng. Conf. 75 Record 7 (1975).
2 N. Yoneda and S. Takanashi, Sol. Energy, 21 (1978) 61.
3 T. Wada, F. Kimura and R. Yamamoto, Bull. Chem. Soc. Jpn., 56 (1983) 1223–1226.
4 J.-H. Li, D. Li, J.-C. Zhang and Y.-W. Zhang, Selected Papers from the Annual Conference of the China Solar-Energy Association, 1987, pp. 144–145.
5 W.F. Greem, J. Phys. Chem., 12 (1980) 655.
6 M. Telkes, in L.E. Murr (Ed.), Solar Materials Science, Academic Press, New York, 1980, Chap. 11.
7 S. Cantor, Thermochim. Acta, 26 (1978) 39–47.