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DISSOCIATION VAPOR PRESSURE OF SODIUM ACETATE TRIHYDRATE

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ABSTRACT

The water vapor pressure over solid and liquid sodium acetate trihydrate was measured tensimetrically between about 10 and 80°C. Second law enthalpies and entropies of water vaporization were derived from the data. The results are interpreted on the basis of an existing phase diagram.

INTRODUCTION

Sodium acetate trihydrate ($NaAc \cdot 3H_2O$) has received some attention recently because of its large latent heat of fusion of about 60.3 cal g^{-1}[1,*] which makes it attractive as a heat storage material. Its practical application has been impaired, however, by the tendency of a $NaAc \cdot 3H_2O$-melt to supercool considerably below the melting point. As part of an effort to reinvestigate the system sodium acetate–water, the dissociation water vapor pressure of $NaAc \cdot 3H_2O$ was measured. The pressure measurements by Baxter and Cooper[1] as well as Diesnis[2] were limited to the crystalline state. The former authors used a transpiration method, while the latter applied a static technique similar to the one used in this work.

EXPERIMENTAL

The pressure measurement procedure followed that used by Diesnis[2]. The pressure measuring device consisted of a 200 mm long absolute Hg-manometer to which a 50 cm^3 capacity round Pyrex flask was attached. Sodium acetate trihydrate (Fisher Certified) was halfway filled into the flask through a temporary opening. The device was attached to a high vacuum system via a ground joint, evacuated for about 5 min, and then sealed off. During pump-down, the pressure never quite dropped below a few Torr due to dissociation of the hydrate.

The pressure vessel was immersed in a temperature controlled water-bath that is schematically shown in Fig. 1. Most of the power was supplied by a line-stabilized powerstat, while the remainder was controlled by an on–off contact thermometer. The water temperature was measured to within ±0.05°C from an immersed Hg-thermo-

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[*] Unpublished measurements.

meter which had been calibrated against a standard traceable to NBS. Vapor pressures were read from a cathetometer to within ±0.1 Torr and corrected for the mercury density to 0°C.

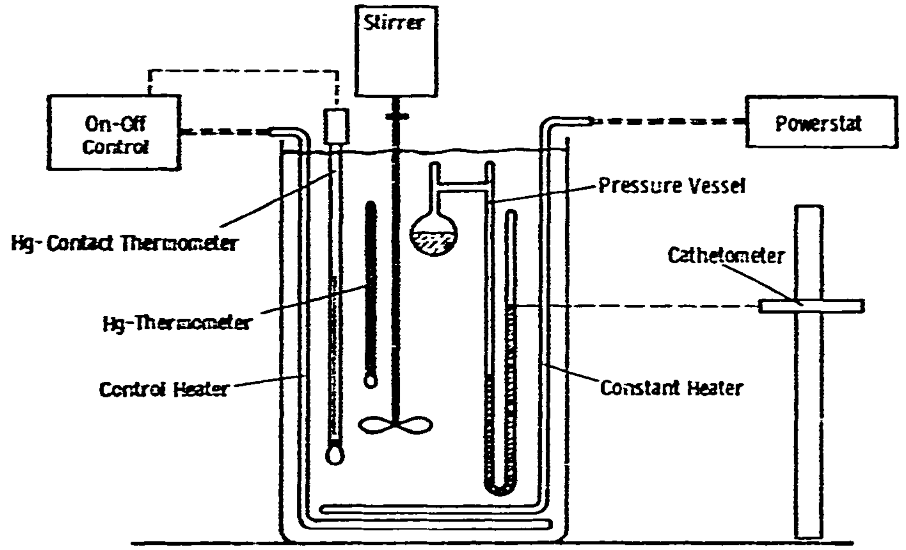

Fig. 1. Experimental set-up for pressure measurement.

RESULTS

Pressures were first measured below the melting point. Equilibration was very sluggish at low temperatures. It was necessary to hold the material at constant temperature for several hours, usually overnight. After crossing the melting point at 58.0°C, pressure readings were initially erratic and not consistent. The temperature was then raised to about 80°C, at which all solid material had dissolved. Pressure equilibrium was attained within minutes at the higher temperature range. The melt did not resolidify when cooled to room temperature. The vapor pressure of the melt was higher than that of the solid hydrate at comparable temperatures.

The melt formed a clear glass after cooling in a dry ice mixture (−78.5°C). Upon returning to ambient temperatures, a smaller portion of the solution had crystallized in the form of a crystal slush at the bottom of the flask. The vapor pressures of this two-phase system were still higher at respective temperatures than those of the supercooled melt.

The vapor pressures that were measured for (A) solid $NaAc \cdot 3H_2O$, (B) the supercooled melt, and (C) the two-phase system are plotted in Fig. 2 as a function of temperature. A slight pressure correction was applied due to the contribution of a small amount of non-condensable gas impurities, which were detected during cooling to −78.5°C.

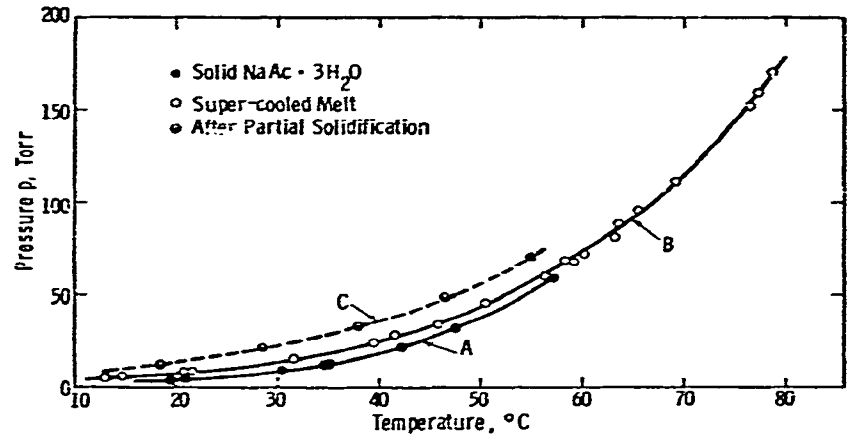

Fig. 2. Dissociation water vapor pressure over sodium acetate trihydrate.

The mixture was left standing for several months without further changes of the water vapor pressure and extent of crystallization. After opening the vessel, samples of crystals and solution were carefully removed for analysis before the remainder spontaneously resolidified during further handling. The liquid portion contained 57.8% NaAc. An X-ray diffraction analysis of the crystalline portion agreed with data given for anhydrous NaAc[5]. The phase which eventually crystallized upon contact with foreign nuclei was identified as the trihydrate by X-ray diffraction[5].

The data of the three vapor pressure curves in Fig. 2 were least square fitted to an empirical equation

$$\log p = a_0 - \frac{a_1}{T}$$

which yielded for the constants* (with p in Torr and T in K):

Curve A $\quad \log p = (10.41 \pm 0.22) - \frac{(2.86_3 \pm 0.00_7)\cdot 10^3}{T}$

Curve B $\quad \log p = (9.01 \pm 0.05) - \frac{(2.38_7 \pm 0.01_5)\cdot 10^3}{T}$

Curve C $\quad \log p = (7.71 \pm 0.08) - \frac{1.92_8 \pm 0.02_3)\ 10^3}{T}$

The equations were plotted in a $\log p - 1/T$ diagram shown in Fig. 3, along with

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*The variance of the constants a_0 and a_1 were obtained from the variance σ^2 of $\log p$ with the relations

$$\mathrm{Var}(a_0) = \frac{\sigma^2 \Sigma x_i^2}{n\Sigma(x_i - \bar{x})^2} \quad \text{and} \quad \mathrm{Var}(a_1) = \frac{\sigma^2}{\Sigma(x_i - \bar{x})^2}$$

where $x = 1/T$ and n is the number of observations.

pressure curves of solid and liquid water. Error limits of the curves are indicated by brackets.

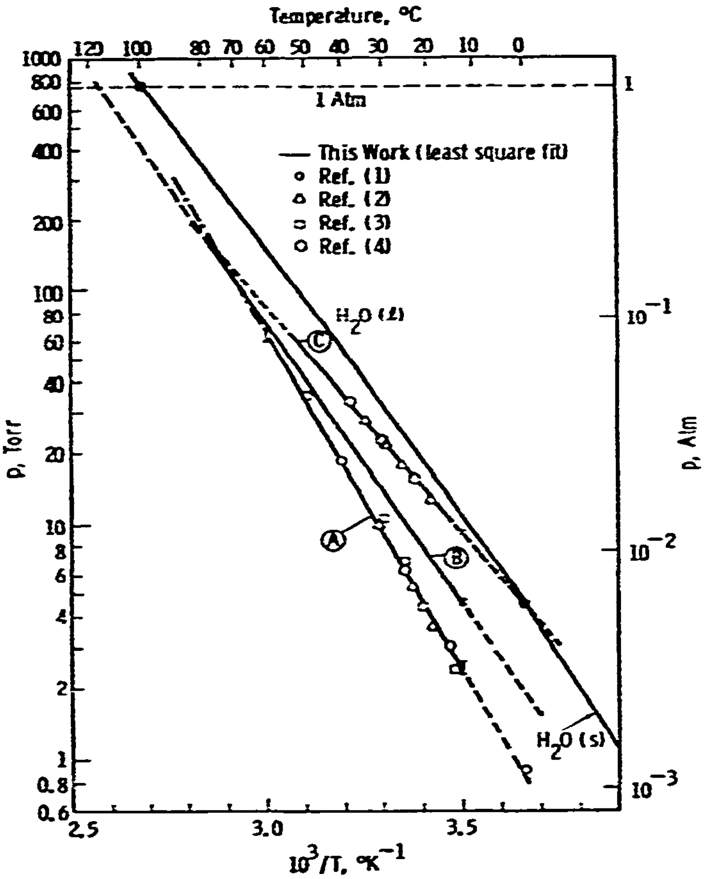

Fig. 3. Vapor pressure over NaAc·3 H_2O and water.

TABLE I

ENTHALPY AND ENTROPY OF EVAPORATION AT MEAN TEMPERATURE $\bar{t}$

System[a]	$\bar{t}$ (°C)	ΔH_{vap} (*kcal* mol^{-1})	ΔS_{vap} (*cal* mol^{-1} °C^{-1})
Solid NaAc·$3H_2O$	38	13.1 ±0.3	44.6±1.0
Supercooled melt	46	10.8_8±0.07	38.2±0.2
NaAc+sat. sol.	40	8.7_9±0.1_1	32.3±0.4

[a] See Discussion.

The second law enthalpies and entropies for the evaporation of water from the various condensed systems at the respective average temperature of measurement were calculated from the constants with

$$\Delta H_{vap} = 2.3\,R\,a_1 \qquad \text{and} \qquad \Delta S_{vap} = 2.3\,R\,a_0 - \log 760$$

and are listed in Table 1. It can be seen that higher dissociation pressures correspond to lower enthalpies and entropy changes, i.e., less stable systems.

The results of the more extensive previous investigations are also plotted in Fig. 3 along with least square fitted vapor pressure curves of this study. The agreement with all sources is excellent.

DISCUSSION

In order to discuss the seemingly complex dissociation vapor pressure data of a system which corresponds to a composition of $NaAc+3H_2O$, it is imperative to refer to existing information for the $NaAc$–H_2O phase diagram. Figure 4 shows the phase diagram based on data from Stephen's[6] and Seidell's[7] compilations.

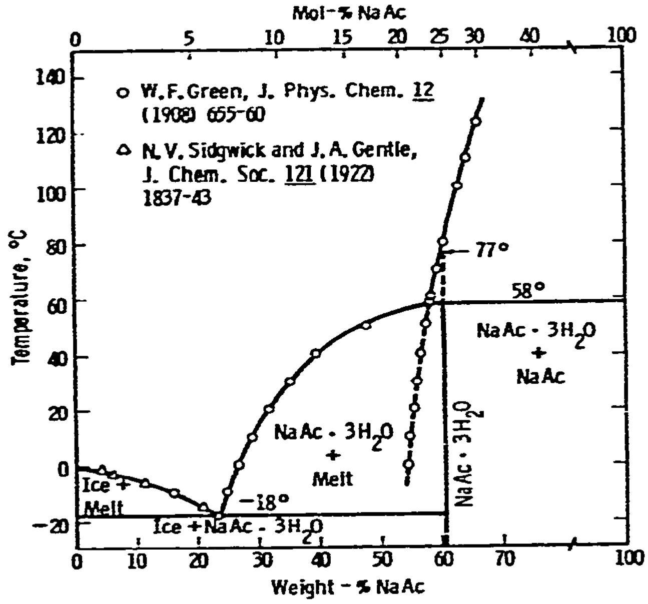

Fig. 4. Phase diagram of $NaAc$–H_2O.

We see that the hydrate melts incongruently to a 58 w/o NaAc solution in equilibrium with the balance of NaAc as solid anhydrate. The vapor pressure of the trihydrate below 58 °C results from dissociation

$$NaAc\cdot 3H_2O(s) \rightleftarrows NaAc(s) + 3H_2O(g)$$

for which the phase rule predicts a univariant equilibrium. The dissociation vapor pressures corresponding to this equilibrium are given by the experimental data that form curve (A) in Fig. 3.

The erratic pressures, that were initially measured just above the peritectic melting point, were apparently due to the fact that equilibrium between melt and residual solid NaAc was not achieved in time. In accordance with the phase diagram, all solids had dissolved after raising the temperature to about 80°C. On cooling the melt, the phase diagram predicts separation of the anhydrate phase followed by complete conversion to the trihydrate below the peritectic temperature. However, we saw that no apparent solidification occurred when the melt was cooled. Hence, the vapor pressures that constitute curve (B) are those of a metastable liquid of the approximate composition $NaAc+3H_2O$. The melt must have a vapor pressure higher than the stable trihydrate phase at the same temperature, which is confirmed by the experiment.

Supercooling of the melt to -78.5°C did not result in homogeneous solidification of the trihydrate but rather in separation of the anhydrous NaAc while leaving a more diluted NaAc solution. The concentration of this metastable solution in contact with anhydrous NaAc was found to be in good agreement with the phase diagram. The high vapor pressures, as given by curve (C), result from the metastable nature of this two-phase system. The pressure measurements agree with several literature data, which evidently must have been obtained on superconcentrated solutions of anhydrous NaAc as well. These solutions form spontaneously the stable trihydrate phase if foreign nuclei are introduced. All three experimental pressure curves intersect at a common point, which is the temperature where a homogeneous melt of composition $NaAc+3H_2O$ is formed, in good agreement with the phase diagram.

The behavior of supersaturated NaAc melts to resist crystallization of the stable trihydrate has been the subject of several investigations[8–10]. A well-founded explanation of the effect is still pending. It appears that the crystal structures of the various quoted forms of NaAc will have to be more closely examined.

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