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THERMAL PROPERTIES OF SODIUM METASILICATE HYDRATES

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ABSTRACT

The heats of fusion and heat capacities at 298.2 K of $Na_2SiO_3 \cdot 5H_2O$, $Na_2SiO_3 \cdot 6H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ have been measured by DSC. The enthalpies and entropies of fusion increase with the water content of the hydrate and the entropy of fusion per mole of water is almost constant. The application of DSC/DTA to the analysis of metasilicate hydrate mixtures is discussed.

INTRODUCTION

Sodium metasilicate forms hydrates with 5, 6, 8 and 9 molecules of water per metasilicate group[1,2]. Their structures have been investigated by X-ray[3–6] and neutron diffraction[7] and it appears that almost all of the hydrogen atoms are involved in hydrogen bonds. All of the hydrates are known[2] to melt below 75 °C but apart from some estimations by McCready[8] there have been few studies of their thermal properties[9], and no direct measurements of their heats of fusion. We now report values for their heat capacities at 25 °C and their heats of fusion obtained by DSC, and we also discuss the use of DSC/DTA for the analysis of their mixtures. Although DTA has been used to investigate hydrated sodium polysilicates[10] its application to metasilicate hydrates has not been previously reported.

EXPERIMENTAL

Sodium metasilicate nonahydrate was prepared by recrystallisation at room temperature from an aqueous solution which contains 30% by weight of Na_2SiO_3 (ref. 2). The crystals were filtered in the absence of CO_2 and dried over $Na_2SiO_3 \cdot 5H_2O$ to give a product with nine moles of water per mole of silicate.

Preparation of the octahydrate by crystallisation from aqueous solution proved to be extremely difficult (cf., ref. 3), and it was never obtained completely free from other hydrates.

The hexahydrate was prepared by isothermal crystallisation at 52 °C from a 45% by weight solution of Na_2SiO_3 after the addition of a small quantity of seed crystals.

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The pentahydrate was prepared by crystallisation of a pure supercooled melt and required approximately 10% of a metasilicate hydrate as seed. Technical grade material (BDH Ltd.) was also used for comparison; its thermal behaviour did not differ significantly from that of the pure material.

All of the materials were carefully analysed by powder X-ray diffraction[3] and weight loss on ignition at 1000 °C.

Measurements were made with a DuPont Instruments Ltd. 990 thermal analyzer used with a cell base Module II and differential scanning calorimeter (DSC) cell. The temperature scale was calibrated with ice, $Ca(NO_3)_2 \cdot 4H_2O$, stearic acid, naphthalene, benzoic acid and indium, and in all cases the onset of fusion (obtained by extrapolation of the leading edge of the endotherms) agreed to within ±1.5 °C with the melting points reported in the literature. The energy calibration was based on the heat capacity of synthetic sapphire[11] and confirmed to within ±1% by the heats of fusion of ice, indium and stearic acid.

The sodium metasilicate hydrates were found to react with the aluminium sample pans normally used with the DSC cell and it was therefore essential to use copper pan bases and lids. Accurate enthalpy and heat capacity measurements could only be obtained when the samples were tightly sealed to prevent the loss of water, but good qualitative analyses could be made with samples in pans with crimped on lids. For quantitative heat measurements water loss was kept below 0.1% of the sample weight; this was particularly difficult to achieve with the pentahydrate which has a relatively high melting point.

RESULTS AND DISCUSSION

Thermodynamic properties

The experimental results and their estimated errors are given in Table 1 along with the values of other workers. The melting points of the three lower hydrates agree within experimental error with the literature values[2] whilst that of the nonahydrate is slightly higher.

The enthalpies of fusion given in Table 1 are in each case the mean of at least 4 observations. The value obtained for the nonahydrate lies between the indirect experimental value of Lange and Stackelberg[9] and the estimated value of McCready[8], whilst that of the pentahydrate is higher than both earlier values[8,9]. The heat of fusion of the hexahydrate has not been previously reported. Our value lies between those of the penta- and nonahydrates, and as might be expected it is somewhat closer to the pentahydrate value.

The entropies of fusion calculated from our ΔH_f values increase with the water content of the salt and the entropy of fusion per mole of water (Table 1) is almost constant. It is thus easy to estimate a value for the entropy of fusion of the octahydrate and hence to obtain an approximate value for its heat of fusion. These estimates, which are the only available values for the octahydrate, are shown in Table 1. The mean value of the entropy of fusion per mole of water based on the results for the 9-, 6- and

TABLE 1

THERMAL PROPERTIES OF SODIUM METASILICATE HYDRATES $Na_2SiO_3 \cdot xH_2O$

Hydrate, x	T_f (°C)	ΔH_f (kJ mol^{-1})	ΔS_f (J mol^{-1} K^{-1})	($\Delta S_f/x$) (J mol^{-1} K^{-1})	$10^2 C_p$ (J mol^{-1} K^{-1}) (solid, 25°C)
9	49.8±1.5 47.8[a]	59.6±2.5 67.6[d] 55.4[e]	184.5	20.48	5.3±0.5 4.75[g]
8	49.5±1.5 48.4[a]	53.1[f]	164.8[f]	20.6[f]	
6	63.2±1.5 62.9[a]	42.0±2.5	124.9	20.82	3.3±0.3 3.53[g]
5	73.0±1.5 72.2[a]	37.3±3.5 30.7[d] 31.5[e]	107.6	21.52	3.1±0.3 3.15[g]
0	1088[b,c]	52.0[c]	38.2[c]	-	1.11±0.05 1.13[g] 1.12[c]

[a] Ref. 2. [b] Ref. 12. [c] JANAF Thermochemical Tables, 2nd ed., 1970. [d] Ref. 8, [e] Ref. 9, obtained indirectly from heats of solution. [f] Estimated, see text. [g] Ref. 8, estimates based on Kopp's law.

5-hydrates (20.9±0.5 J mol^{-1} K^{-1}) is only slightly less than the entropy of fusion of water (22.0 J mol^{-1} K^{-1})[13]. This behaviour is similar to that observed for other inorganic hydrates, many of which have entropies of fusion per mole of water within ±4 J mol^{-1} K^{-1} of the pure water value. The fact that sodium metasilicate solutions contain substantial amounts of polymeric silicates[14] does not appear to have a marked effect on the entropies of fusion of the hydrates.

Within experimental error the heat capacities obtained at 25°C for the solid hydrates agree with those estimated by McCready[8]. Those of the melts were found to be approximately twice as large as those of the solids, but because of the experimental difficulties it was impossible to obtain accurate values[15].

Analytical applications

During this work it was found that DSC/DTA provides an excellent method for the qualitative analysis of metasilicate hydrate mixtures and that in most cases it is much quicker, requires much smaller samples, and is at least as sensitive as the powder X-ray diffraction methods which are usually used. Typical curves obtained with prepared mixtures are shown in Fig. 1 and the operating conditions are given in the caption. The method is particularly suitable for the detection of small quantities of higher hydrates present as impurities in the lower hydrates, thus for example 1% by weight of the nonahydrate in the pentahydrate is detected much more easily than by X-ray diffraction. As can be seen from the figure the method is applicable to a wide range of mixtures. However, it should be noted that the octahydrate and the nona-

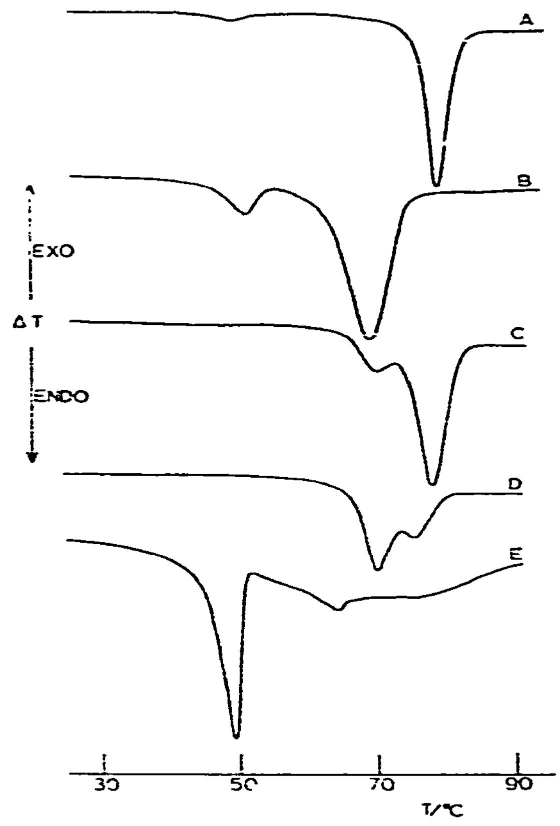

Fig. 1. Typical DSC curves obtained for sodium metasilicate hydrate mixtures. Powdered samples (1–4 mg) in Cu pans with crimped on Cu lids. Heating rate: 10 °C min^{-1} (A–D); 5 °C min^{-1} (E). Approximate molar compositions: (A) 1% 9, 99% 5; (B) 20% 9, 80% 6; (C) 25% 6, 75% 5; (D) 35% 5, 65% 6; (E) 5% 6, 95% 9.

hydrate are indistinguishable. Quantitative measurements have not been made although it is clear that provided the equipment is calibrated with known standards, exact analyses could be obtained more rapidly and easily than by other methods.

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