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PHASE CHANGES IN ACETAMIDE–SALT SYSTEMS: MELTING POINTS AND LATENT HEAT OF FUSION OF PURE ACETAMIDE AND ACETAMIDE–AMMONIUM CHLORIDE

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ABSTRACT

Pure acetamide has been shown by DSC to have a melting point of 80.9 ± 1.2 °C and an enthalpy of fusion of 15.5 ± 0.65 kJ mol^{-1} (263 ± 11 kJ kg^{-1}) in the stable trigonal crystalline form (as obtained by recrystallization from solvents), but in the metastable orthorhombic form in which it solidifies from the molten state, the values fall to 70.1 ± 1.6 °C and 13.1 kJ mol^{-1} (222 kJ kg^{-1}) respectively.

In the binary system (CH_3CONH_2–NH_4Cl), the eutectic with trigonal acetamide is at 70.8 °C (5.6 mol% NH_4Cl) and with the orthorhombic form at 56.8 °C (5.5 mol% NH_4Cl). The enthalpies of fusion were 13.5 and 11.1 kJ mol^{-1} (230 and 189 kJ kg^{-1}) respectively. Cooling curves determined on larger samples (30–50 g of 5.5 mol% NH_4Cl) showed little supercooling (1–2 °C in > 96% of the curves). Exceptionally the lower melting (metastable) form crystallized but usually converted to the stable form before crystallization was complete.

INTRODUCTION

Acetamide has a valuable combination of properties which are only beginning to be recognized. Besides low cost and many convenient physical properties, it is also highly polar and has an enthalpy of fusion comparable to that of many inorganic salts which makes it a potential phase change heat storage material. Moreover, in the molten phase it is an excellent solvent for both organics and, particularly, for many inorganic salts [1]. Thus there are a considerable range of binary and ternary acetamide–salt mixtures which would be expected to yield almost any desired melting point below 80 °C and also a high enthalpy phase change.

However, relatively few of these eutectics have yet been defined. For example, of the many ammonium salts, only the binary eutectic of

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acetamide–ammonium nitrate has so far been reported (as 64 : 36 mol%, m.p. 38° C [2], 65 : 35 mol%, m.p. 38° C [3] and, earlier, as 67 : 33 mol%, m.p. 37.5° C [4]). Thus, the binary eutectic with ammonium chloride was chosen for study in order to define its eutectic point and to measure the enthalpy of the phase change by DSC.

A complication is that acetamide has a little-known metastable crystalline form in addition to the well-known stable trigonal form. The latter is the crystal form normally obtained on recrystallization from organic solvents (e.g. the X-ray structure determination was carried out on crystals obtained from ethyl acetate solution [5,6]) and has a melting point usually quoted as 80, 81 or 82.3° C [7]. The unstable orthorhombic crystals have been obtained by crystallization of a pure acetamide melt, and have a slightly different crystal structure [8], with a melting point given as 69–73° C. Thus, formation of the less stable modification is at least a possibility on solidification of both pure acetamide and molten binary mixtures [7].

EXPERIMENTAL

Materials

Acetamide from several sources (BDH reagent grade, Fluka, Koch-Light, Merck and Ventron) was washed twice with ethanol/ether (1 : 10), recrystallized from ethyl acetate and dried under vacuum at 60° C for four hours.

Ammonium chloride (Fluka reagent grade) was dried at 105° C for six hours. Both compounds were stored in desiccators.

Apparatus

DSC measurements were carried out with a Perkin–Elmer microcalorimeter DSC-2, connected to a Perkin–Elmer multi-range strip chart recorder, Model 56, and sometimes to an APPLE IIe computer.

Cooling curves were obtained on 30–50 g samples heated to 80° C, and placed in a water jacket whose temperature was varied to give an average cooling rate of 0.2° C min^{-1}, recorded on a chromel–alumel thermocouple immersed in the melt sample.

Procedure

For DSC measurements, dry recrystallized acetamide was used, as well as recrystallized acetamide, premelted twice. 30–50 g portions of acetamide–ammonium chloride mixtures were weighed into dry, stoppered flasks, premelted at 80–90° C and mixed well, before samples for DSC measurements were taken. For comparison, one mixture was cycled between 80 °C and room temperature 15 times before samples were taken.

DSC samples of 0.8–8 mg were weighed on a Perkin–Elmer Auto microbalance AD-2 and quickly sealed into aluminium pans. DSC measurements were made over 30–100 °C for acetamide and 20–90 °C for acetamide–ammonium chloride mixtures, at rates between 1.25 and 5 °C min^{-1}. Most endothermic curves were obtained using a 5 °C min^{-1} heating rate, but exothermic curves were scanned at cooling rates of 1.25 or 2.5 °C min^{-1} because crystallization from supercooled melts occurred suddenly and was very fast.

Enthalpies of fusion and crystallization were obtained from the curves using a computer program developed by Dr. V. Markovic, Boris Kidric Institute. Surface area measurements were computed using a HIPAD digitizer (Houston Instruments) connected to an Ohio Scientific computer (Televideo TVI-912C). Melting and crystallization temperatures were taken as the maxima of the endo- and exothermic peaks respectively [9]. With the DSC output fed into the APPLE IIe computer, another program developed by Dr. Markovic calculated the enthalpies and temperatures of maxima directly. Enthalpies of fusion calculated by the two methods agreed to within 0.5%. However, because of the very fast crystallization, the APPLE IIe did not respond with sufficient accuracy and, therefore, enthalpies of crystallization are only reported from surface area measurements.

RESULTS AND DISCUSSION

Recrystallized pure acetamide was found to melt at 80.9 ± 1.2°C (18 determinations) with an enthalpy change of 15.5 ± 0.65 kJ mol^{-1} (263 ± 11 kJ kg^{-1}) which indicates the presence of the stable trigonal form. Moreover, the value of ΔH_m is close to the values of 15.6 [10,11], 14.9 [12] and 14.7 [13] kJ mol^{-1} (265 [10], 264 [11], 252 [12] and 249 kJ kg^{-1} [13]) recently determined, and compares with the value (16.4 kJ mol^{-1}, 278 kJ kg^{-1}) reported in 1914 [14]. All these determinations suggest that the value of 13.3 kJ mol^{-1} (225 kJ kg^{-1}) reported by Dunn and co-workers [15,16] is too low.

On continuing the thermal cycle, the molten acetamide proved difficult to crystallize, undercooling considerably with a crystallization temperature of 38.5 ± 3.8°C (ΔH (cryst.) 11.6 ± 0.65 kJ mol^{-1}, 197 ± 6 kJ kg^{-1}). However, this solid had a melting point (70.1 ± 1.6 °C) much lower than the original, suggesting formation of the alternative less stable orthorhombic crystal form, for which melting points of 69–73 °C have been reported [7,8,11].

Further thermal cycling did not cause further change, the averaged melting points being, for the second cycle 70.1 ± 1.6 °C, for the third cycle 70.1 ± 0.9 °C, for the fourth cycle 69.8 ± 0.7 °C, and for the fifth and further cycles 71.2 ± 0.9 °C, indicating that the lowered melting point is not due to continuing thermal decompositions. Similarly, the average enthalpy of fusion for each cycle was constant within half a standard deviation, the average value for all cycles, except the first, being 13.1 ± 0.65 kJ mol^{-1} (222 ± 11 kJ kg^{-1}). Again considerable but no greater supercooling occurred, the average crystallization temperature being 36.5 ± 3° C. Factors contributing to lower values for the enthalpy of crystallization (11.5 ± 0.30 kJ mol^{-1}, 195 ± 5 kJ kg^{-1}) were the undercooling and thus the extended times before crystallization occurred, together with the reduced accuracy inherent in the very rapid process.

The formation of metastable orthorhombic crystals on cooling acetamide had earlier been noted by Dunn et al. [16] in the course of repeated DSC cycles, but in this case the change in melting point occurred "after a few cycles", and the change in enthalpy of fusion to 10.3 kJ mol^{-1} (175 kJ kg^{-1}) took place almost linearly over 100 cycles. The reason for this discrepancy is not clear, but it may be noted that the enthalpy of fusion reported earlier for untreated reagent grade acetamide [15] is identical to that found for this acetamide which was twice recrystallized from ethyl acetate [16]. In our work, small (0.8–8 mg) samples recrystallized in the lower melting (metastable) form through at least 15 cycles. No reversion to the higher melting point (stable) form was observed even after keeping for 21 months at room temperature. However, change in the enthalpy of fusion for the third and subsequent cycles was observed, together with lowered melting points, when samples absorbed moisture due to defective sealing. Such samples were discarded.

Interestingly, samples from a twice-premelted 30 g batch gave the higher melting (stable) form on the first DSC curve and the metastable form in subsequent cycles, thus illustrating the important effect of sample size as well as showing that the stable form of acetamide can be obtained from the melt, in addition to recrystallization from ethyl acetate or methanol.

The acetamide–ammonium chloride binary system showed rather similar effects at compositions close to the eutectic (earlier determined by the cooling curve method on 20 g samples as being near 5.5 mol% NH_4Cl) in as much as the melting points and enthalpies of fusion on the first cycle (listed in Table 1) were significantly higher than for the second and subsequent cycles (Table 2). Again there was no change after the second cycle. The two maxima in the DSC trace correlate with the solidus and liquidus of the binary phase diagrams. That from the first melting cycle, corresponding to trigonal acetamide–ammonium chloride, indicated a eutectic of 71° C (at 5.6 mol% NH_4Cl), and those from second and subsequent cycles corresponded to a eutectic of 57° C (at 5.5 mol% NH_4Cl) with orthorhombic acetamide. Some support is also given from the relative size of the two maxima: with 4.9 and 5.3 mol% ammonium chloride, the second, higher temperature peak (i.e. the liquidus) was larger indicating that relatively less of the eutectic was present than with the 5.5 mol% mixture where the first maximum was larger

TABLE 1

Melting point and enthalpy changes from first DSC cycles for acetamide–ammonium chloride mixtures

Composition (mol% NH_4Cl)	Number of mixtures	Melting point maxima (°C)		Enthalpy of fusion		Crystallization temperature (°C)	Enthalpy of crystallization	
		Lower	Higher	(kJ mol^{-1})	(kJ kg^{-1})		(kJ mol^{-1})	(kJ kg^{-1})
4.9	2	68.3 ± 0.1	74.7 ± 0.4	13.05 ± 0.23	226.5 ± 4.6	24.8	10.34 ± 0.07	176.8 ± 1.2
5.3	5	68.9 ± 1.9	73.5 ± 1.2	12.93 ± 0.39	220.0 ± 6.7	27.6 ± 1.2	10.66 ± 0.12	181.4 ± 2.1
5.5	11	69.9 ± 2.3	72.1 ± 1.9	12.93 ± 1.33	220.3 ± 22.6	25.1 ± 1.2	10.50 ± 0.46	178.9 ± 7.9
5.7	5	72.1 ± 2.0	74.1 ± 1.7	14.20 ± 0.62	242.0 ± 10.5	28.2 ± 3.3	10.79 ± 0.46	183.9 ± 7.9
6.0	2	70.3 ± 0.4	74.8 ± 3.6	13.20 ± 0.56	224.9 ± 9.6	25.9 ± 0.6		

TABLE 2

Melting point and enthalpy change from second and subsequent DSC cycles for acetamide–ammonium chloride mixtures

Composition (mol% NH_4Cl)	Number of mixtures	Number of determinations	Melting point maxima (°C)		Enthalpy of fusion		Crystallization temperature (°C)	Enthalpy of crystallization	
			Lower	Higher	(kJ mol^{-1})	(kJ kg^{-1})		(kJ mol^{-1})	(kJ kg^{-1})
4.9	2	5	56.8 ± 0.3	62.3 ± 0.4	11.02 ± 0.37	188.3 ± 6.3	25.9 ± 2.0	10.45 ± 0.06	178.6 ± 2.5
5.3	5	48	56.8 ± 0.8	62.3 ± 0.6	10.64 ± 0.39	188.1 ± 6.7	27.8 ± 3.0	11.13 ± 0.22	189.3 ± 3.8
5.5	11	53	57.0 ± 2.3	62.4 ± 2.3	11.19 ± 1.03	190.6 ± 17.5	25.1 ± 1.2	10.50 ± 0.62	178.9 ± 10.5
5.7	5	18	58.0 ± 1.4	61.9 ± 1.7	11.23 ± 0.29	191.4 ± 5.0	27.4 ± 2.9	10.48 ± 0.19	178.5 ± 3.3
6.0	2	5	57.1 ± 0.2	61.7 ± 2.0	10.96 ± 0.81	186.8 ± 13.8	27.7 ± 2.3	10.57	180.1

with the second frequently appearing only as a shoulder. For the 5.7 and 6.0 mol% mixtures, the relative sizes of the peaks were somewhat variable.

The metastable acetamide in the binary system, as in pure acetamide, appeared to be stable at room temperature; samples left standing for eleven months had almost identical melting points and enthalpies of fusion as samples remeasured within an hour. Yet this reversion to the stable form of acetamide was again a function of sample size, for in each binary mixture the components were initially premelted in 10–30 g batches though the first DSC curve showed stable (trigonal) acetamide. This remained true even when the batch was cycled 15 times (over 20 days).

The enthalpy of fusion from the first cycles was virtually constant (Table 1) and averaged 13.3 kJ mol^{-1} (227 kJ kg^{-1}). The enthalpy change on crystallization was lower (average 10.6 kJ mol^{-1}, 180 kJ kg^{-1}) and closer to the enthalpy of fusion obtained from the second and subsequent cycles (average 11.0 kJ mol^{-1}, 189 kJ kg^{-1}) which again was almost unaffected by change in composition, as was the enthalpy of crystallization for these cycles (average 10.6 kJ mol^{-1}, 180 kJ kg^{-1}).

Thus it may be concluded that after the first melting cycle had occurred, the crystalline form of the acetamide did not change further, nor did measurable thermal decomposition take place over 16 cycles (29 months). The size of the enthalpy change, though lowered from the value for acetamide (and almost certainly from the undetermined value for ammonium chloride, which is probably close to 21.4 kJ mol^{-1}, 400 kJ kg^{-1}) remained relatively high, and in fact larger than that for several organic compounds suggested as phase change heat storage materials (e.g. diphenyl 140 and palmitic acid 165 kJ kg^{-1}) and even than that for some inorganic salts (e.g. sodium nitrate 174, potassium hydroxide 168 and calcium bromide 146 kJ kg^{-1}).

Supercooling is one of the limiting factors for use of acetamide in practical storage units and, therefore, more than 100 cooling curves were determined (with 30–50 g samples of 5.5 mol% NH_4Cl and an average cooling rate of 0.2–0.6 ° C min^{-1}). Characteristically, very little supercooling occurred (Fig. 1, curve a) and the higher melting point (stable trigonal acetamide) crystals were formed, in contrast to results with milligram sized samples. In only one case (Fig. 1, curve c) was the lower melting (metastable) form crystallized alone, but in three other cases (Fig. 1, curve b) the metastable form crystallized initially and then transformed to the higher melting (stable) form during crystallization. These results did not vary with the source of the acetamide, provided that in each case it was suitably purified and dried. The average maxima of the cooling curves were, respectively, 72 and 58 ° C which were in good agreement with the melting points obtained from DSC measurements. The small amount of supercooling from 30–50 g samples (1–2 ° C) is in agreement with the findings of Dunn et al. [16] for similar sized samples, and illustrates again the much greater probability of suitable nuclei in larger samples. Nevertheless the effect of added

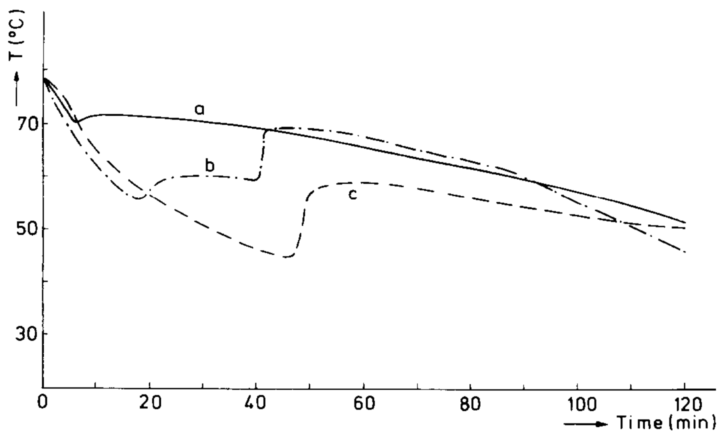

Fig. 1. Cooling curves for 30 g portions acetamide–ammonium chloride (94.5 : 5.5 mol%): curve a, ——— 0.20 °C min^{-1}; curve b, — · — · — 0.28 °C min^{-1}; curve c, — — — 0.20 °C min^{-1}.

nucleants to reduce supercooling still further and to completely eliminate the crystallization of the metastable form is being investigated further.

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REFERENCES

1 O.F. Stafford, J. Am. Chem. Soc., 55 (1933) 3987.
2 L.S. Bleshchinskaya, K. Suliamankulov and M.D. Davranov, Zh. Neorg. Khim., 28 (1983) 1068.
3 I.M. Boklovkin and E.D. Vikman, Zh. Obshch. Khim., 35 (1965) 949.
4 O.K. Khaishbashev, Bull. Acad. Sci. URSS Classe. Sci. Chim., (1945) 587.
5 F. Senti and D. Harker, J. Am. Chem. Soc., 62 (1940) 2008.
6 W.A. Denne and R.W.H. Small, Acta Crystallogr. Sect. B, 27 (1971) 1094.
7 S.S. Urazovskii and O.A. Gunder, Dokl. Akad. Nauk SSSR, 91 (1953) 885.
8 W.C. Hamilton, Acta Crystallogr., 18 (1965) 866.
9 M. Ziet, Purification of Inorganic and Organic Materials, M. Dekker, New York, 1969.
10 H.G.M. De Wit, C.G. De Kruif and J.C. Van Miltenburg, J. Chem. Thermodyn., 15 (1983) 891.
11 H.H. Emons, R. Naumann and K. Jahn, Thermochim. Acta, 104 (1986) 127.

12 K. Hrynakowski and A. Smoczkiewiczowa, Rocz. Chem., 17 (1937) 165.
13 L. Vogel and H. Schuberth, Wiss. Z. Martin Luther Univ. Halle-Wittenberg, Math-Naturwiss Reike, 34 (1985) 79.
14 A.H.R. Muller, Z. Phys. Chem., 86 (1914) 177.
15 P.E. Arndt, J.G. Dunn and R.L.S. Willix, Thermochim. Acta, 79 (1984) 55.
16 J.G. Dunn, H.G. Smith and R.L.S. Willix, Thermochim. Acta, 80 (1984) 343.