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THERMAL PROPERTIES OF ACETAMIDE IN THE TEMPERATURE RANGE FROM 298 K TO 400 K

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ABSTRACT

The thermal properties of acetamide were investigated by the DTA and DSC methods. It was shown that the stable and unstable modifications of acetamide can be formed from the subcooled melts. The melting enthalpy of the stable hexagonal compound is 264 ± 2 kJ kg^{-1} and is therefore approximately 50 kJ kg^{-1} above that of the unstable modification. From the determined thermal capacities a storage density of 310 kJ kg^{-1} for the temperature range 343.5 to 363.5 is obtained which favours its use as a latent heat storage material. In spite of the high storage density value the application of acetamide for static latent heat storage is not very promising owing to its unfavourable crystallization behaviour.

INTRODUCTION

The thermal properties of acetamide near the melting point of approximately 353 K are of great interest, especially with the application of this compound as a latent heat storage material [1–5]. Unlike other organic compounds such as paraffins, carboxylic acids and polyethylene glycols which have volume-related melting enthalpies (storage densities) of at the most 150–180 MJ m^{-3}, the storage density of acetamide of nearly 250 MJ m^{-3} (Table 1) is in the range of the group of inorganic salt hydrates generally considered promising. Moreover, acetamide shows a congruent melting behaviour, a high thermal stability and chemical resistance, is commercially available and is only slightly corrosive to metallic container materials [1,2,4,6]. However, the subcooling of the melt and the formation of an unstable modification from the subcooled state are disadvantages [1,6–11].

In spite of numerous publications a definitive evaluation of the compound as a latent heat storage material is not possible. The results from the literature are given in Table 1. The high scattering of the melting enthalpies is very evident. In many cases detailed information on sample preparation and the method of measurement used is not available. Furthermore, measurements of the specific heat near the melting point are not reported. We

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TABLE 1

Physical properties of acetamide

ϑ_F (°C)		$\Delta_F H_{SP}$ (kJ kg^{-1})		$\Delta_F H_{SP}$, (MJ m^{-3})		ρ_l (kg m^{-3})	ρ_s (kg m^{-3})	References
Stable form	Unstable form	Stable form	Unstable form	Stable form	Unstable form			
82.3	71.1	276.74	238.64	276.18 *	238.16 *			9
79.2	69.1							15
81.54								11
78.85		207.67 ± 1.42		207.25 *				19
		251.75		251.25 *				17
77–81	67–77	225	175	224.5 *	174.6 *			6
80		252		251.49 *				16
70–82		225		224.55 *				20
81		241		240.52 *		998_{85}	1159_{20}	2
83		237.9		241.0		1010		21
80		252		251.49 *				4
82								1
							1155 (stable) 1119 (unstable)	14
						967_{105} 980_{120}		22
80.5	69	264.2	212–218	263.7 *	211–217 *			own values (DSC)

* Calculated with $\rho_l = 998$ kg m^{-3}.

have therefore measured the melting enthalpy and thermal capacities of acetamide. These results allow an exact determination of the theoretical storage capacity of the compound and conclusions to be drawn regarding the behaviour under static storage conditions.

EXPERIMENTAL

Sample material and characterization

Reagent grade acetamide (manufacturer: Poland, m.p. 77°C) was twice recrystallized from water-free ethyl acetate, dried for 70 h in the drying cupboard at 50°C to remove adhesive solvent and then vacuum-dried in a desiccator with KOH. Characterization of the product gave the following results: (i) elementary analysis, C, 40.72% (theoretical 40.67%), H, 8.45% (theoretical 8.53%), N, 23.63% (theoretical 23.71%); (ii) water content according to Karl Fischer [12], 0.07 mol H_2O/mol acetamide; (iii) no chloride impurities.

X-ray investigations were carried out with a powder diffractometer using the HZG4 goniometer (VEB Carl Zeiss Jena, BT Präzisionsmechanik Freiberg) with CuK_α radiation ($\lambda = 1.5418$ Å) in the glancing angle range (2θ) 0–90° with intervals of 0.1°. Sample preparation was carried out under N_2 and protection by a thin polyethylene film on the sample holder. The X-ray diffraction pattern agrees with the values of the ASTM specification for all primary and secondary reflections (position and intensity) [13].

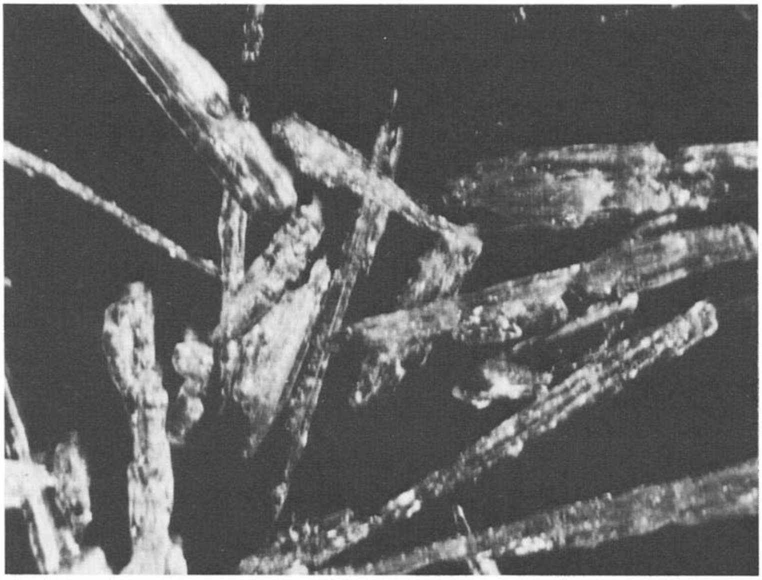

Fig. 1. Micrograph of acetamide (stable form), magnification, 7.5 : 1.

According to the calculation of the reflections for the unstable modification on the basis of the lattice data given by Hamilton [14] additionally-occurring reflections of low intensity (maximally 2%) with d values (Å) of 9.31, 4.67 and 3.11 cannot be attributed to this form. Consequently, the applied sample material is clearly the stable hexagonal form of acetamide. It crystallizes in the form of partly intergrown thin hexagonal needles with a length of about 5 to 20 mm (Fig. 1).

DTA investigations

DTA measurements in the closed system using gas-tight crucibles (material EMO Ti-Pd 0.2) to characterize the melting and solidification behaviour of acetamide were carried out. The investigations were performed with the thermal analyser (SETARAM, France) in a cryostat (−200 to +500°C) equipped with a crucible holder using platinel thermocouples. In each case the thermal spectra were taken between 40 and 130°C at heating and cooling rates of 2 K min^{-1}. The extrapolated onset temperature (T_{ON}) was used to give the melting and solidification temperatures. The difference between T_{ON} of the solidification and the melting point of 80.4°C was taken as a measure of the subcooling effect. All error indications in this work refer to a confidence interval of 0.95.

DSC investigations

Determination of the melting enthalpy ($\Delta_F H_{SP}$) and the specific thermal capacities (C_p) of acetamide were carried out by means of the differential scanning calorimeter DSC-2C (Perkin-Elmer, U.S.A.) with a scanning rate of 5 K min^{-1} using closed (gas-tight) aluminium crucibles. Calibration of the equipment was carried out with indium and lead. The peak evaluation was carried out according to the peak routine of the TADS.

RESULTS AND DISCUSSION

Melting and solidification behaviour

Figure 2 shows 10 DTA spectra of an acetamide sample in the closed system. During the first melting the melting temperature is consistently 79°C. Crystallization occurs at 48°C, 31 K below this temperature (Table 2). In the next 3 thermal spectra melting temperatures can then be observed which in each case are 10 K lower than in the first cycle, whereas in the following cycles the sample melts similarly to the first spectrum at 80–81°C. The solidification temperatures, on the contrary, are constant in all spectra at 50.3 ± 0.8°C. A constant subcooling of 30 ± 0.8 K confirms the high subcooling tendency of acetamide which, according to Körber [8], is 30–40

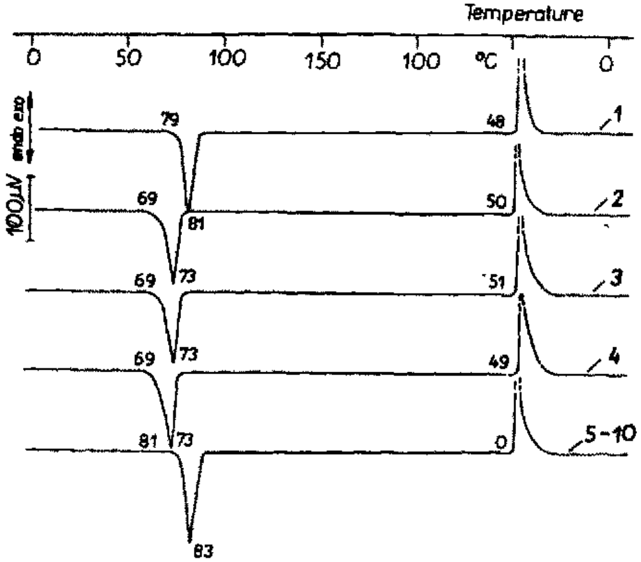

Fig. 2. DTA spectra of acetamide, $m = 0.012$ g, 1–10 cycle number.

K for small samples. The melting points at 80.4 ± 0.9°C and 69.0°C agree well with the data given in Table 1 [2,4,11,15,16].

The results show that acetamide crystallizes from the melt both in the stable and unstable forms, thus confirming the observations of Hamilton [14] and Dunn [6]. It is interesting that in the the present study of 4 thermal spectra the stable form crystallizes again in spite of high subcooling. Formally, this opposes the theory of Schaeling [10] which implies that acetamide is a typical representative of a category of substances where the unstable

TABLE 2

DTA results for the melting and solidification behaviour of acetamide

Spectrum no.	Sample weight (mg)	Heating (T_{ON}) (°C)	Cooling (T_{ON}) (°C)	Subcooling (K)
1	12.296	79	48	31
2		69 [a]	50	30
3		69 [a]	51	29
4		69 [a]	49	31
5		81	50	31
6		80	50	30
7		82	51	31
8		80	51	29
9		80	52	28
10		81	51	30
		[a] 69.0 ± 0°C 80.4 ± 0.9°C	50.3 ± 0.8°C	30 ± 0.7 K

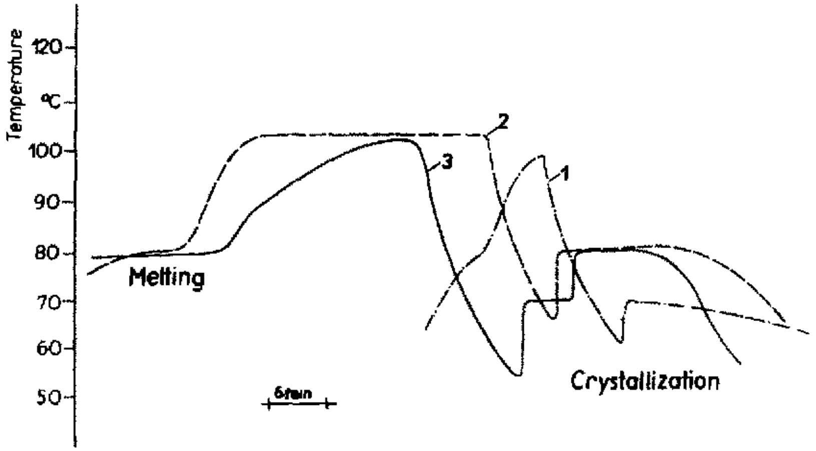

Fig. 3. Solidification curves of acetamide during Newton cooling, 1–3 sample number. 1, unstable form; 2, stable form; 3, stable and unstable forms.

form "keeps indefinitely" and can only be transformed to the stable form by seeding. According to this the transformation from the unstable to the stable form is not possible without addition of nuclei. This indicates that in the given test conditions nuclei of both modifications are present in the subcooled melt. This assumption is confirmed by a simple Newton cooling of larger samples (about 5 g) of molten acetamide in Ti–Pd ampoules with internal iron–constantan jacket thermocouples. In spite of the larger sample and a higher probability of nucleation a high subcooling up to 30 K is found similar to the DTA cycles. Crystallizations can be observed at 69°C and at 79°C. It is specially interesting that 2 solidification ranges coexist in some cycles (Fig. 3), an effect which is also observed with an extreme subcooling (quenching in liquid nitrogen). The presence of two endothermic peaks after some cycles, also observed by Dunn [6] using DSC measurements, confirms the effects found. It is therefore probable that after a large number of heating cycles the change to the unstable form is complete.

Melting enthalpy and storage density

In each case Fig. 4 shows the first melting process of three acetamide samples. The peak form is not very reproducible because of the thermal conductivity.

The melting point has a mean value of 80.3 ± 0.3°C (T_{ON}). The mean melting enthalpy was calculated as 264 ± 2 kJ kg^{-1} (Table 3). This value is in good agreement with the melting enthalpies given elsewhere [1,9,16,17] for the stable form (Table 1). The melting enthalpy of the unstable form which crystallizes in the second spectrum and all further thermal spectra is approximately 50 kJ kg^{-1} lower at 212–218 kJ kg^{-1}. This value is between the values for melting enthalpy of the unstable form given by Müller [9] and

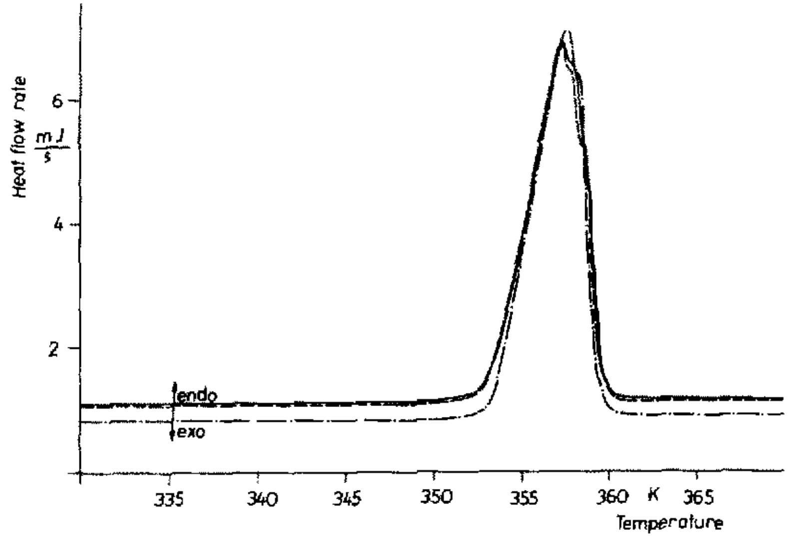

Fig. 4. DSC melting peaks of acetamide during the first melting, 1–3 sample number: —— sample 1, — — — sample 2, ·—·—· sample 3.

Dunn [6]. An exact measurement of the melting enthalpy is not obtained from our measurements as the unstable form could not be obtained in a pure form.

With the density of the melt being 998 kg m^{-3} [2] a storage density of 264 MJ m^{-3} for the high-melting form and a value of 211–217 MJ m^{-3} for the low-melting form is obtained. Consequently, a significant loss in storage capacity of about 20% occurs with crystallization of the unstable form of the acetamide from the subcooled melt.

Thermal capacities

The C_p-functions of acetamide above and below the melting point were not available from the literature and therefore were experimentally de-

TABLE 3

Melting enthalpy of acetamide (stable form)

Sample no.	Weight (mg)	T_F (T_{ON}) (K)	$\Delta_F H_{SP}$ (kJ kg^{-1})
1	8.47	353.4	263.7
2	7.74	353.4	263.7
3	7.24	353.6	265.1
		353.5 ± 0.3 K (±80.3°C)	264.2 ± 2 kJ kg^{-1}

TABLE 4

Thermal capacities of acetamide (stable form) between 300 and 400 K

T (K)	C_p (measured) (kJ kg^{-1} K^{-1})			$\overline{C_p}$ (kJ kg^{-1} K^{-1})	C_p (calculated) (kJ kg^{-1} K^{-1})
	Sample 1	Sample 2	Sample 3		
298	–	–	–	–	1.467 (extrapolated)
300	1.483	1.492	1.485	1.487	1.481
310	1.536	1.568	1.561	1.555	1.550
320	1.603	1.630	1.625	1.619	1.619
330	1.689	1.721	1.708	1.706	1.688
340	1.776	1.819	1.804	1.799	
350	2.204	2.236	2.079	2.173	
360	undef.	6.155	4.606	–	
370	2.776	2.841	2.872	2.829	2.814
380	2.814	2.889	2.887	2.863	2.867
390	2.871	2.966	2.936	2.924	2.920
400	2.913	3.021	2.985	2.973	2.973

termined. The results of three measurement series in the temperature range 300–400 K are summarized in Table 4. The differences between the individual measurements are not significant at the confidence level 0.95 and thus averaging of $\overline{C_p}$ is possible. The fitted values for the temperature intervals

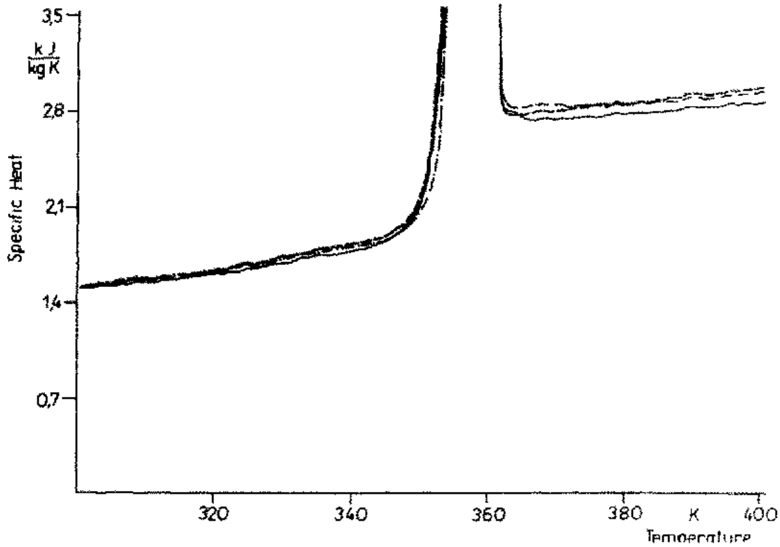

Fig. 5. Experimentally determined C_p function, 1–3 sample number: —— sample 1, — — — sample 2, · — · — · sample 3.

TABLE 5

Linear regression of the C_p-functions $C_p = A + B(T - T_0)$ for the temperature ranges 300–330 K and 370–400 K

Sample no.	Temperature range (K)	T_0 (K)	A (kJ kg^{-1} K^{-1})	B (kJ kg^{-1} K^{-2})	Corr. coeff.
1	300–330	300	1.469 ± 0.002	$0.0067 \pm 1.4 \times 10^{-4}$	0.9917
	370–400	370	2.766 ± 0.002	$0.0050 \pm 1.1 \times 10^{-4}$	0.9899
2	300–330	300	1.487 ± 0.003	$0.0072 \pm 1.6 \times 10^{-4}$	0.9905
	370 ± 400	370	2.830 ± 0.002	$0.0063 \pm 1.3 \times 10^{-4}$	0.9918
3	300–330	300	1.487 ± 0.002	$0.0068 \pm 1.5 \times 10^{-4}$	0.9903
	370–400	370	2.846 ± 0.002	$0.0045 \pm 1.5 \times 10^{-4}$	0.9790

below the melting point (300–330 K) and above the melting point (370–400 K) are summarized in Table 4. The linear regression of the general form

$$C_p = A + B(T - T_0) \tag{1}$$

(C_p = specific thermal capacity; A, B = regression coefficients; T_0 = initial temperature) within these intervals is effective in each case (Fig. 5). The following fitted functions are obtained from the measured data (Table 5):

$$C_p = 1.481 + 0.0069(T - 300);\ 300\text{–}330\ \text{K} \tag{2}$$

$$C_p = 2.814 + 0.0053(T - 370);\ 370\text{–}400\ \text{K} \tag{3}$$

In each case these functions are valid up to $T_F = 353.5$ K in a good approximation.

Theoretical storage density

As can be seen from Table 4, the specific heats of acetamide near the melting point are in the range 1.5–3 kJ kg^{-1} K^{-1} which is expected to be low for organic compounds. Consequently, the portion of the so-called "sensible heat" absorbed and released by the melt and the solid will be considerably smaller compared with the melting heat ("latent heat"). As in the case of latent heat storage a portion of the sensible heat is always utilized, and a value for the theoretically storable heat is obtained from the sum of melting enthalpy and the portions of the sensible heat above and below the melting point.

Form the measured value of the melting enthalpy of 264 kJ kg^{-1} a theoretical storage capacity of 310 kJ kg^{-1} is obtained for the temperature range 343.5–363.5 K. The portion of the sensible heat is 46 kJ kg^{-1} corresponding to 14.8%. In most applications of latent heat storage properties a temperature range as narrow as possible is preferred, thus further lowering the portion of the sensible heat of the total capacity of the storage unit.

CONCLUSIONS

Our investigations show that the storage capacity of acetamide, 264 kJ kg^{-1} is more favourable than other organic compounds and consequently, the substance is a promising storage material. However, in the static operation of an acetamide latent-heat storage unit considerable difficulties are to be expected for two reasons.

Firstly with large samples the system is highly subcooled so that the heat of crystallization is released at a lower temperature compared with the melting point, resulting in high energy losses. Moreover, a high subcooling has an unfavourable effect on the velocity of heat transfer between the heat transfer medium and the environment.

Secondly the unstable low-melting form of acetamide also crystallizes from the subcooled melt, the storage density of which is significantly lower. No doubt heterogeneous nucleation agents (in the simplest case activated carbon) can be added to reduce subcooling; however, according to Dunn [6] this has no effect of the velocity of the transformation of the stable to the unstable form. Consequently, the application of heterogeneous nucleation agents does not appear very promising.

From previous experience the intrinsic nucleation is much better under dynamic conditions and possibly a modification change does not occur. However, in this case the high vapour pressure, with an enthalpy of sublimation of 57.19 kJ mol^{-1} [18] in the temperature range 20–33°C has a disturbing effect.

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