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THE SUPERCOOLING OF ACETAMIDE

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ABSTRACT

The supercooling of acetamide has been investigated by conventional cooling curves and differential scanning calorimetry (DSC), and the results from each technique appear to correlate well. The extent of supercooling was found to be linearly dependent on $1/\sqrt[3]{(\text{mass})}$ of acetamide. The addition of small quantities of amorphous carbon caused a significant reduction in the tendency to supercool, with optimal concentrations in the region of 0.5%. Thermal cycling studies over 200 cycles indicated no significant chemical degradation for acetamide in the absence or presence of carbon. A decrease in the enthalpy of fusion was attributed to the conversion of the stable rhombohedral to the metastable orthorhombic form of acetamide. The rate of this conversion was independent of the presence of carbon.

INTRODUCTION

Several reports have appeared in the literature on the potential of organic compounds to act as phase change materials (PCMs) in the storage of thermal energy through the endothermic solid–liquid phase transition, and then to retrieve this energy in the reverse exothermic liquid–solid phase change [1–3]. Most of these studies have been concerned with the measurement of the phase transition temperature, the magnitude of the enthalpy of fusion (which governs the energy density), and the chemical stability over many hundreds of heat–cool cycles [4,5].

Another important parameter in cycling behaviour is the reversibility of melting and solidification. Many organic materials show promise as latent heat stores, but display the undesirable characteristic of "super"- or "under"-cooling. This not only impedes the recovery of heat energy on the discharge stage of the cycle, but may lead to heat wastage on a crystallisation surge. One practical way to overcome this problem is via heterogeneous nucleation in which nucleating agents are used as seed materials to enhance or induce crystallisation. Although nucleating agents are often chosen on the basis of similarity in cell dimensions to the crystallising substance [6], it is also possible to use inert materials to provide surfaces on which crystallisation can occur.

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The most common elementary method for examining supercooling involves a containment vessel, temperature probe and a temperature time recorder, for the determination of a cooling curve. However, DSC is also a potentially useful technique for studying supercooling. The purpose of this work is essentially twofold. The first objective is to evaluate the applicability of the DSC technique to the study of supercooling, and to correlate the results obtained with those from the conventional cooling curve method. The second objective is to study the effect of the addition of amorphous carbon as a nucleating agent on the supercooling properties of acetamide. Acetamide is used as a model in this study, rather than for its intrinsic value as a candidate PCM.

EXPERIMENTAL

Chemicals

Acetamide (BDH laboratory grade) melting in the range 77–81°C was recrystallized twice from ethyl acetate.

Activated carbon (Ajax Chemical Co.) from ashed coconut shells was used without further treatment. Examination by optical microscopy showed that the particle size was fairly uniform and of the order of 10 μm.

Procedure

Samples were prepared by crushing to a fine powder and where carbon was required, by thorough mixing of the required amounts.

Thermal analysis

(1) DSC measurements, with a DuPont 990 thermal analyser and DSC cell (Model 900600-902) equipped with a laboratory designed and constructed cooling jacket [5], were made on samples sealed in aluminium pans. Samples were cycled between 30 and 110°C at 10°C min^{-1} under N_2. Apparatus for the sequential automatic cycling and processing of data has been previously described [5].

(2) Cooling curves were traced from the cooling of melts in contact with a copper constantan thermocouple in the body of the melt, all in a cylindrical glass boiling tube. The sample was heated to 110°C and allowed to cool to room temperature in an air jacket, under an atmosphere of nitrogen, and the thermocouple output fed to a recorder.

Adsorption areas

Measurements of nitrogen adsorption on a gas handling vacuum line using the volumetric technique for surface area studies and application of the

BET expression, provided information on the effective adsorptive area of the carbon for gaseous nitrogen.

More specifically, the adsorption of acetamide from aqueous solution was determined by the iodometric titration of acetamide in solution at adsorption equilibrium.

RESULTS AND DISCUSSION

Acetamide

The DSC trace for a typical heat–cool cycle of acetamide is presented in Fig. 1, and shows the melting endotherm and solidification exotherm. The two peaks are clearly offset from one another, and the difference between the extrapolated onset temperature of melting (T_m) and the extrapolated onset temperature of freezing (T), is taken as a measure of the supercooling effect, ΔT. The backward "skew" of the crystallisation peak is typical of

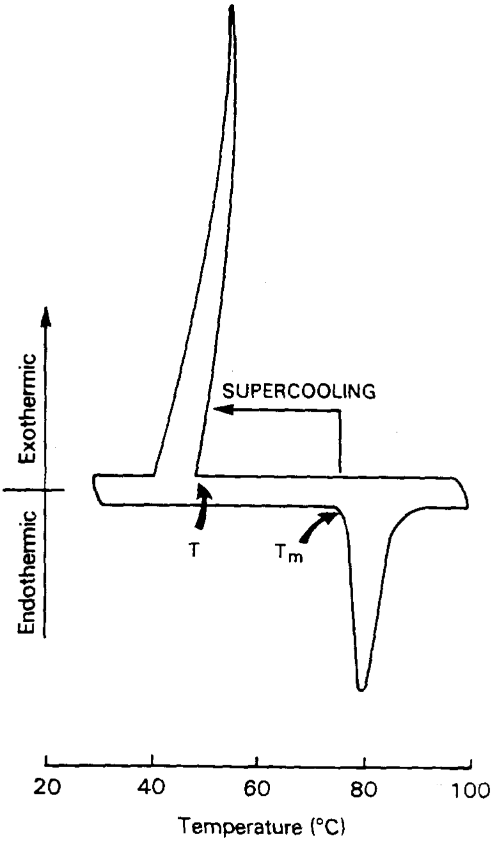

Fig. 1. DSC trace for acetamide for one melt–freeze cycle.

supercooled liquids, as the liquid/solid system is heated back towards the expected crystallization temperature by the release of energy on solidification. The very sharp onset of solidification, as demonstrated by the very rapid movement away from the baseline at *T*, is also typical, as once the barriers have been overcome crystal growth occurs at a rapid rate.

After a few cycles on the DSC apparatus, a second endotherm appears (see Fig. 2) at a temperature below that of the original. This can be attributed to the formation of the metastable orthorhombic form of acetamide from the melt [7], whereas the original peak is from the rhombohedral form which is obtained when acetamide is recrystallised from ethyl acetate [8]. Over the temperature range 67–77 °C, the enthalpy of melting of the orthorhombic polymorph was found to be 50 kJ kg^{-1} lower than that of the rhombohedral form, which is a significant loss in energy storage capacity.

The DSC results can be compared with those obtained by cooling curve methods (Fig. 3), where supercooling may be taken as the difference between the lowest temperature of the cooling liquid (*T*) and the plateau of arrest

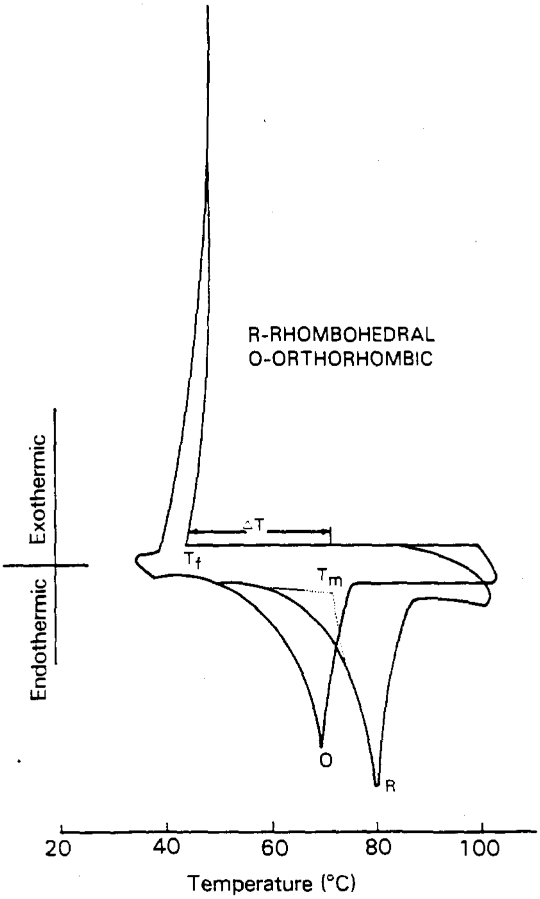

Fig. 2. DSC trace of an acetamide sample subjected to several melt–freeze cycles.

(T_f), i.e., $\Delta T = T_f - T$, at a cooling curve discontinuity. The dramatic effect of mass on supercooling is demonstrated by the results shown in Fig. 4 and Table 1. For very small sample sizes, small changes in sample mass caused significant changes in ΔT. For mass increments $\gtrsim 500$ mg, however, a constant small change in ΔT occurred. This clearly indicates the need for care in the interpretation of supercooling effects measured in DSC experiments, where sample sizes in the range 5–50 mg are used. Once this effect is realised, however, it is also evident that the DSC technique provides a very sensitive means of probing supercooling phenomena.

According to Lane (ref. 9, p. 119), the principles developed to describe the thermodynamic stability of supercooled solutions can by analogy be applied to the crystallisation of pure melts. Both processes involve the formation of nuclei which, if stable, promote crystal growth and produce particles.

Application of the well-known Gibbs–Thomson expression for the vapour pressure of liquid droplets and equivalency of solution and melting processes [9] leads to the Ostwald–Freundlich relation (eqn. 1) which predicts a lowering in melting point for smaller diameter particles.

$$\Delta T = \frac{T_f 2\sigma M}{\Delta H_f \rho} \frac{1}{r} \qquad (1)$$

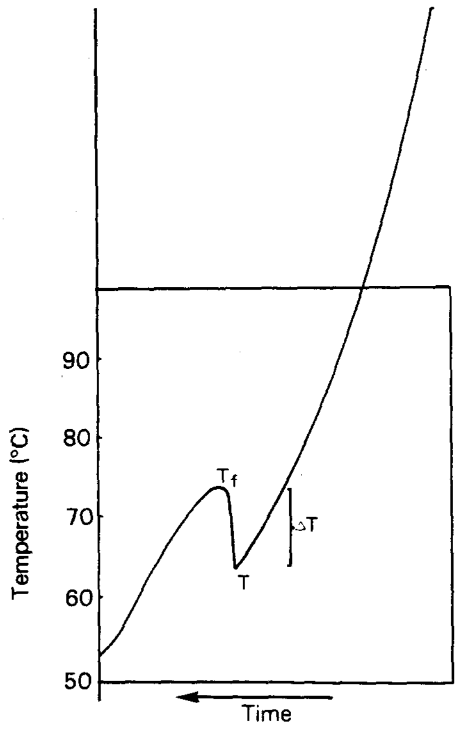

Fig. 3. Cooling curve for acetamide.

where T_f is the melting point of the material, M is the molecular weight, ΔH_f is the enthalpy of fusion, r is the particle radius, ΔT is the extent of supercooling, and σ is the interfacial surface energy. This equation implies that the greater the interfacial surface tension in the melt, the greater will be the resistance to the formation of particles, and the greater the degree of supercooling. High heats of fusion, however, cause ready nucleation, and supercooling effects are therefore smaller.

If the assumption is made that the particles are spheres, then

$$\bar{v} = 4/3\pi r^3 \text{ and } \bar{m} = \bar{v}\rho$$

TABLE 1

Mass effect on the degree of supercooling of acetamide

Supercooling, ΔT (°C)	Mass of acetamide (mg)	Supercooling, ΔT (°C)	Mass of acetamide (mg)
46.1	5.3	14.7	124.0
38.4	8.7	14.0	205.0
37.5	9.4	11.2	580.0
37.4	9.7	6.6	1830
36.6	10.9	3.2	13600
32.9	13.5	3.1	15000
30.0	16.5	2.7	16700
24.3	33.4	2.2	20000

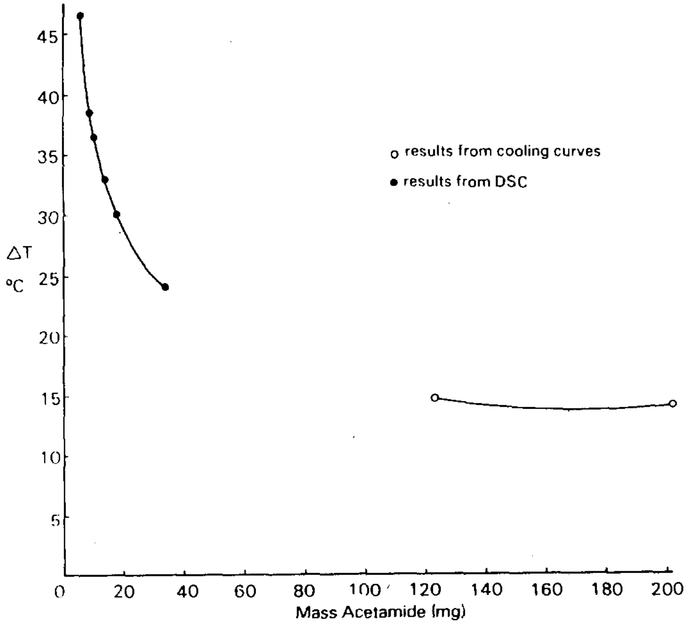

Fig. 4. Mass effect on the degree of supercooling of acetamide.

where $\bar{v}$ is the volume, $\bar{m}$ the mass and ρ the density of each particle. Therefore

$$r = \sqrt[3]{\left(\frac{3\bar{m}}{4\pi\rho}\right)}$$

For a narrow distribution of particle radius, which implies particles of near uniform size and therefore mass, the total sample mass (m) is $n_t\bar{m}$ where n_t is the number of particles formed. From this, an equation relating the total sample mass to the extent of supercooling (ΔT) can be derived.

$$\Delta T = \frac{T_f 2\sigma M}{\Delta H_f \rho} \frac{1}{\sqrt[3]{\left(\frac{3}{4\pi\rho}\right)}} \frac{1}{\sqrt[3]{m}} = \frac{k}{\sqrt[3]{m}} \qquad (2)$$

where k incorporates constants characteristic of the substance. Equation (2) states that ΔT will decrease as the mass of the melt increases, and this is related to the greater nucleation frequency per sample as the mass increases.

When the ΔT values from this work, for cooling curves as well as DSC experiments, are plotted against $1/\sqrt[3]{m}$, a linear dependency is observed (Fig. 5). The correlation coefficient for the plot is 0.999. These results may simply reflect the smoothing effect of a cube-root plot, but we suggest that they tend to support the argument given.

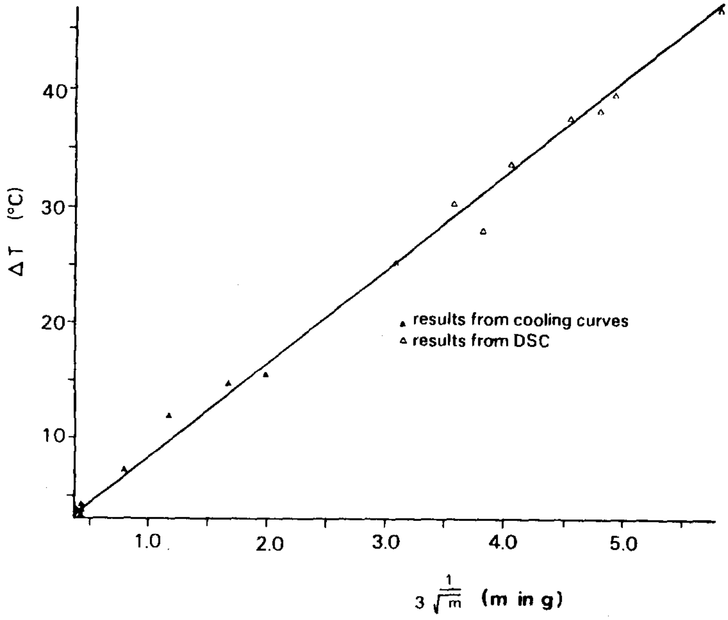

Fig. 5. The relationship between degree of supercooling and mass of acetamide based on the Jones and Partington expression.

Acetamide with carbon

A guide to the selection of a nucleating agent suggests that it should be isomorphous with the crystallizing material or at least with lattice spacings no more than, say, 15% different [6]. It should of course be essentially insoluble, thermally stable, unreactive and remain well dispersed in the melt. (Interfacial free energy of nucleating agent/melt compared with crystallizing solid/melt is also a factor.) Several materials were tested but for reasons of effectiveness and cost an amorphous material, activated carbon, was selected.

The effective adsorption area of the carbon for nitrogen was determined to be 780 m^2 g^{-1} which is in the range expected for many carbons. More particularly, carbon adsorbs acetamide from aqueous solution (Fig. 6), and our results are in broad agreement with those of Rosene et al. [10]. We conclude that there is convincing evidence for the adsorption of acetamide onto activated carbon which enhances the argument for heterogeneous nucleation.

Reduction of supercooling, or increase in the crystallization rate on the addition of carbon, is clearly seen in Fig. 7. Just as the net free energy change, ΔG, in a chemical reaction may be distinguished from the free energy of activation, ΔG^*, so may the free energy of nucleation and crystal growth be distinguished from a free energy of activation for these processes.

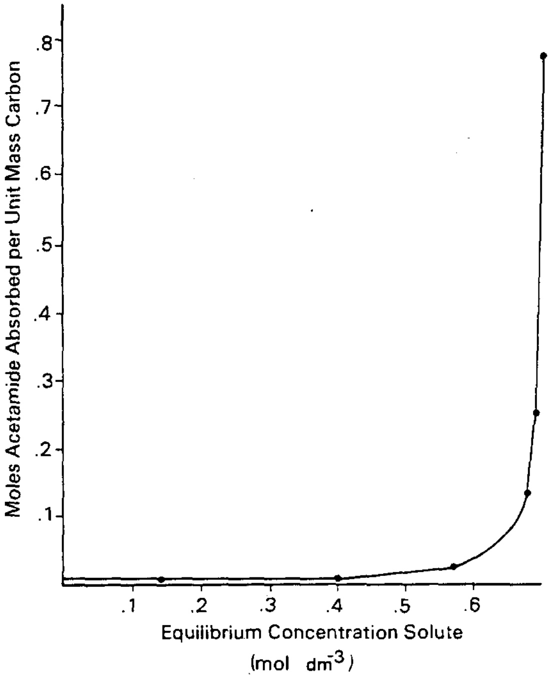

Fig. 6. Langmiur Freundlich isotherm for acetamide adsorption onto activated carbon.

A valid speculation may be that carbon acts by lowering the activation free energy barrier, i.e., it provides a path with a lower free energy of activation by the adsorption on, and crystallization of, acetamide molecules. When this initial monolayer, or a few have been formed, crystallization may then continue as if on an acetamide solid seed. Activated carbon may be described as a "physical" catalyst for the nucleation process. Whatever the fundamental reason, the practical outcome is that a relatively small amount of carbon produces a substantial reduction in supercooling.

Chemical stability over several heating–cooling cycles has been previously described as a factor in the selection of a material as a latent heat store, or PCM [4,5]. Results for about 200 DSC cycles on acetamide, both in the absence and presence of carbon, are shown in Fig. 8a and b. We suggest that the decline in the enthalpy of the phase change from 225 kJ kg^{-1} (13.28 kJ mol^{-1}) to 175 kJ kg^{-1} (10.33 kJ mol^{-1}) is due to a transition between the two crystalline forms, and that there is little chemical degradation of acetamide, at least over this number of cycles. More significantly, activated carbon appears not to act as a catalyst for chemical decomposition under these conditions and the carbon also appears to retain activity as a nucleating agent over many cycles. The absence of chemical breakdown can only be established by chemical analysis but the results are persuasive.

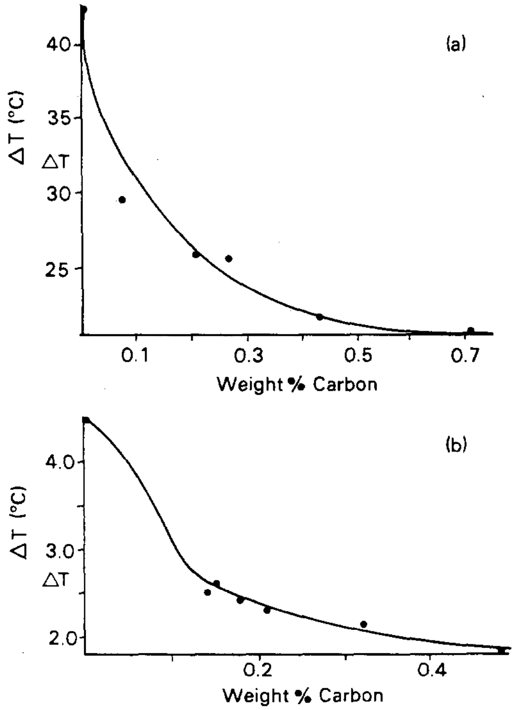

Fig. 7. The effect of activated carbon on the degree of supercooling in acetamide. (a) Each sample mass 13 mg acetamide; (b) each sample mass 13000 mg acetamide.

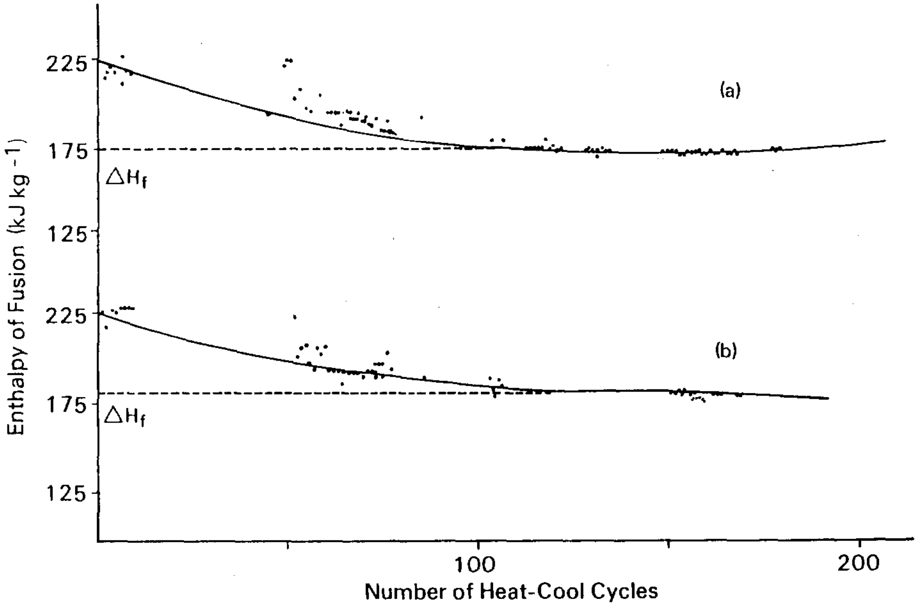

Fig. 8. DSC cycling studies on the thermal stability of (a) acetamide, (b) acetamide containing 0.75% activated carbon.

CONCLUSION

The DSC technique proved suitable as a tool for investigating supercooling phenomena, and proved to be superior to conventional cooling curve methods in the quantity of information provided.

Activated carbon proved to be an effective nucleating agent in the reduction of supercooling during the melt–freeze cycle of acetamide. Over 200 melt–freeze cycles, no significant chemical degradation of acetamide was apparent, and little loss in the effectiveness of the carbon was observed. However, acetamide converted entirely to the unstable orthorhombic polymorph after approximately 100 cycles, with a consequent loss in enthalpy of melting of 50 kJ kg^{-1}, and, hence, loss of energy storage efficiency.

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