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APPLICATIONS OF DIFFERENTIAL SCANNING CALORIMETRY TO THE STUDY OF THERMAL ENERGY STORAGE*

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ABSTRACT

DSC is a versatile tool for investigating the behavior of materials that store energy by melting or by undergoing solid-state transitions. Heating scans measure the enthalpy that can be stored and cooling scans yield the enthalpy that may be recovered from the material. Exotherms also provide information about supercooling. The automatic and rapid thermal cycling features of the instrument system can be used to greatly accelerate thermal decomposition that may arise from the daily duty cycle of the storage medium. These chemical reactions, as well as those between the medium and its containment or with substances added to improve performance, can be detected from changes in the thermal spectra. In this study, DSC methods were applied to sodium sulfate decahydrate, paraffin wax, urea, and phthalimide. For $Na_2SO_4 \cdot 10H_2O$, DSC measurements showed a decrease in heat of fusion with thermal cycling and, also, considerable supercooling; with added $Na_2B_4O_7 \cdot 10H_2O$ (borax), supercooling was greatly lessened but not entirely eliminated. Paraffin wax did not supercool nor were there any indications that thermal cycling or contact with aluminum degraded its thermal performance. Urea, when thermally cycled, decreased in melting point and in heat of fusion; this compound also supercooled about 50° in DSC experiments. Phthalimide, $C_6H_4(CO)_2NH$, did not decompose when thermally cycled through its melting point, but it did exhibit marked supercooling. However, lesser supercooling of urea and phthalimide in test tube-scale experiments suggests that supercooling derived from DSC should be applied with caution. For phthalimide, the enthalpy of fusion, determined in this study, equalled 48.1 cal/g.

INTRODUCTION

In the development of reliable means for storing energy by melting or by other phase changes, three important physico-chemical factors can be readily identified. First, the energy of transition of the medium should be high and the transition should

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occur at a temperature relevant to the storage application. Second, the energy which, for the most part, is charged isothermally should be discharged or extracted reversibly; kinetic impediments such as supercooling or low diffusion rates should be negligible or at least tolerable. Third, the thermal-storage medium should not undergo thermal decomposition nor should it react with its containment or with materials added to catalyze precipitation (nucleating agents) or to increase thermal conductance (metallic fillers); such chemical reactions are likely to degrade the energy-storing potential of the medium and to shift the temperature at which the energy is stored.

It is the purpose of this paper to show that DSC is an efficient tool for examining all three of these factors. The capabilities of DSC instrumentation for measuring transition temperatures and enthalpies are obvious and require no further elaboration in this paper. It is also obvious that the transition energy that can be stored in a medium is directly related to the area under the endothermic peak; of course, the inverse process, the energy that may be extracted or discharged from the medium is measured by the area under the exothermic peak. However, storage and discharge may not be symmetrical processes; the observed heat of crystallization is frequently less than the heat of melting, and the temperature at which freezing first occurs is usually less than the melting point. By DSC, one can easily measure the extent of these discrepancies; for examining the extent of supercooling, DSC provides a rapid means of measurement, and it is of interest to check the results against more conventional measurements with samples at least a thousand-fold larger. For judging if a sample has decomposed as a result of thermal cycling, DSC, with its rapid and automatic means for cycling milligram-sized samples, permits greatly shortened lifetime tests for thermal decomposition. Determining if chemical reactions occur between the medium and containment or additives (for nucleation and conductivity improvement) can be accomplished rapidly by obtaining thermal spectra with and without the additives.

The DSC procedures will be described in terms of four phase-change media. Other substances have been examined by these techniques as part of an ongoing program at Oak Ridge National Laboratory for the selection and evaluation of media for thermal storage up to temperatures of 250°C. Two other studies[1, 2] have utilized DSC in evaluating phase-change media for thermal storage. Lane et al.[1] obtained the heat of fusion of twenty materials melting between 8 and 84°C; however, to evaluate supercooling and degradation by thermal cycling, conventional cooling curve methods and DTA were used. Murrill and Breed[2] used DSC for determining solid-phase transition enthalpy for thermal control applications in space vehicles.

EXPERIMENTAL

All DSC data were obtained with a Perkin-Elmer Model DSC-2. Samples were encapsulated in aluminum pans (so-called "volatile sample" pans) with allowance for vapor space. This type of container, rather than the standard pan, was preferred because it could better accommodate the volume changes that accompany phase transition. Indium standards, used for calibration purposes, were likewise contained in volatile sample pans. Heating and cooling scan rates, as well as other instrument settings are noted below for each of the four materials studied.

Areas under DSC curve peaks were measured with high precision (uncertainties of 0.3% for areas of about 100 cm^2) by a method which is, in essence, electronic planimetry. The recorded diagram is placed on a flat bed of sensors called an Elograph, manufactured by Elographics Co., Oak Ridge, Tenn. The area to be evaluated is selected by pressing a stylus at successive points along the curve, each press causing the sensors to produce a pair of digital coordinates. The digital information is transmitted to a PDP-8/i computer which processes the coordinates by successive application of the trapezoidal rule. Calculation of the area enclosed by successive pressings is signalled by pressing the stylus against the part of the Elograph set aside for terminating the calculation. The calculated area is printed by a teletype unit.

For determining supercooling in samples weighing several grams, the materials were contained in test tubes, each fitted with a metal-sheathed chromel–alumel thermocouple passing through a glass stopper fashioned from capillary tubing and polyglass tape. The thermocouple was connected to a digital temperature indicator, Doric Model DS-350. Samples were melted by placing the test tube in a water, oil, or air bath set about 10 degrees above the melting point. After melting, a sample was cooled at about 1°/min by reducing power to the bath, or at 10°/min by removing the test tube from the bath. The onset of crystallization was observed both directly and by noting temperatures on the digital indicator. After runs were completed with urea and phthalimide, small amounts of sample were removed for subsequent DSC measurement of supercooling. For these, cooling scan rates were selected to match those used in the test tube experiments.

RESULTS AND DISCUSSION

Sodium sulfate decahydrate, $Na_2SO_4 \cdot 10H_2O$

This salt hydrate was first proposed as a phase-change thermal storage medium about thirty years ago[3]. One drawback to its wide-scale application is that its high heat of transition is not retained through very many thermal cycles[4]. The aqueous solution produced on heating also supercools, but small additions of borax, $Na_2B_4O_7 \cdot 10H_2O$, appear to effectively catalyze recrystallization[5]. In the present study, $Na_2SO_4 \cdot 10H_2O$, was examined to test DSC methods for obtaining data on supercooling and on degradation of thermal performance.

Measurements were carried out on five samples of high-purity material (Fisher Certified, Fisher Scientific Co., Fair Lawn, N.J.); three samples also contained from 3 to 6 wt.% reagent-grade borax (B & A Specialty Chemicals Division, Allied Chemical Co., Morristown, N.J.). All samples were alternately heated and cooled up to ten times with the heat of transition derived from each recorded endotherm and exotherm.

In the initial heating scan of each sample (taken at 1.25, 2.5, or 5°/min), 53–57 cal/g were absorbed at about 32°C; this value is less than the 58.6 cal/g determined

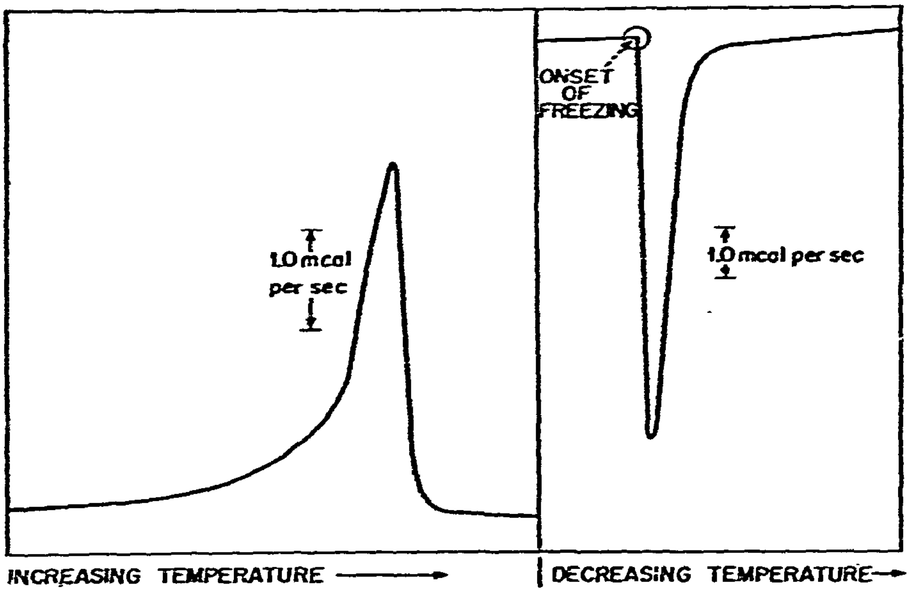

Fig. 1. Endotherm and exotherm of $Na_2SO_4 \cdot 10H_2O$ with 4% $Na_2B_4O_7 \cdot 10H_2O$ taken consecutively at the same scan rate (5°/min) and chart speed. The calorimetric sensitivity of the exotherm is one-half that of the endotherm.

from adiabatic calorimetry[6]. The discrepancy is mostly the result of inevitable evaporation losses that occur during weighing and crimping. Subsequent endotherms showed absorption of 22–55 cal/g at 32°C, the highest values occurring when the solidified sample was maintained overnight at 25°C. All exotherms showed that the heat released varied between 25 and 34 cal/g, crystallization occurring at 22–25°C for the samples with borax and between −10° and −13°C for samples without borax. Neither the energy released nor the extent of supercooling seemed to depend on cooling rate which varied between 0.31 and 10°/min.

Supercooling can generally be seen in a DSC experiment in two ways: (a) by the narrower shape of the exothermic peak, and (b) by the temperature at which crystallization first begins, usually considerably less than the melting temperature obtained from the preceding endotherm (see Fig. 1). Our DSC results showed that borax markedly reduces, but does not eliminate, supercooling of $Na_2SO_4 \cdot 10H_2O$. Supercooling in these mixtures obtained by DSC methods is somewhat greater than supercooling observed by Telkes[5] for much larger samples sealed in glass tubes. She reports that crystallization always occurred on cooling when the temperature reached 30.0–30.5°C, corresponding to supercooling of less than 2°.

The degradation observed for the enthalpy of transition is almost certainly due to the very slow rates of recombination. When $Na_2SO_4 \cdot 10H_2O$ is heated at or above 32.4°C, the "phase transition" that occurs is actually the formation of a saturated solution of anhydrous $NaSO_4$; this process proceeds rapidly. The reverse of this process, i.e. the recombination of the anhydrous salt with the aqueous solution, proceeds far less readily. In large containers, one can appreciate the difficulty of totally recombining the dense anhydrous salt at the bottom of the vessel with most of the solution which may be several centimeters distant. In the DSC experiments, the height of liquid never exceeded 0.8 mm, i.e. the diffusion distances through the solution were negligible. Thus, some other factor inhibited the recombination reaction. The recent suggestion by Biswas[7] that recombination will be limited by the diffusion rate of water through the solid $Na_2SO_4 \cdot 10H_2O$ that forms around the anhydrous sulfate is a plausible explanation for the diminished heat of transition observed by DSC methods.

Urea, $CO(NH_2)_2$

There is a body of evidence, including some DSC data[8], indicating that urea gradually decomposes at its melting temperature, 132.7°C. However, because of its low price and relatively high heat of fusion[9], urea might still be considered an attractive heat storage medium provided that its thermal decomposition is self-limiting; this would be the case, in a closed system, if the only decomposition products were biuret and ammonia, viz.

$$2\,CO(NH_2)_2 \rightleftarrows NH_2CONHCONH_2 + NH_3(g)$$

The starting material for all measurements was reagent-grade urea supplied by Fisher Scientific Co., Fairlawn, N.J. Initial DSC runs indicated supercooling of approximately 50° and a gradual lengthening of the leading edge of the melting peak with each successive endotherm.

The longest run consisted of 29 cycles in which each heating scan was carried out at 5°/min; each exothermic scan was taken to temperatures necessary to assure crystallization, scanning rates varying from 1.25° to 10°/min. The results of this run confirmed trends noted from the initial runs. The extent of supercooling remained about 50°; it was slightly less, 45–48°, at cooling rates of 1.25 and 2.5°/min. For endotherms, the temperature of the leading edge and of the peak decreased gradually; after six cycles, curvature in the leading edge made evaluation of melting point more uncertain. The first endotherm yielded a heat of fusion of 55.2 cal/g, somewhat less than the literature[9] value of 57.8 cal/g, the latter derived from solubility measurements; our lesser value may be due to partial decomposition in the first heating through the melting point. Subsequent endotherms revealed decreases in the heat of fusion and these are plotted in Fig. 2; although the decrease in heat of fusion was linear by the 6th endotherm, the apparent heat of fusion had not leveled out at the termination of the run. Also plotted in Fig. 2 are the temperatures of the endothermic peaks; these also tend to decrease with thermal cycle and similarly reflect the gradual decomposition of urea at its melting temperature.

This DSC evaluation of urea as a thermal storage medium is pessimistic, but it does not rule out this compound entirely. As will be noted below, the supercooling is not as serious for larger samples. Moreover, the possibility exists that urea, as the predominant component of a eutectic, might be more stable at a lower (eutectic) temperature. However, for any thermal storage application, urea would have to be kept dry so as to prevent its hydrolysis.

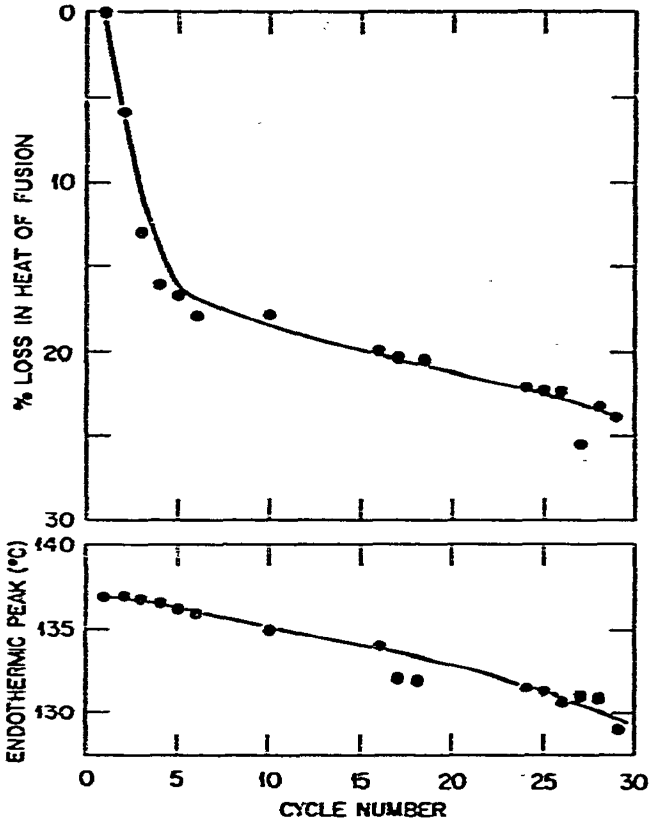

Fig. 2. Decreases in heat of fusion and melting peak temperature versus cycle number for a sample of urea. Heat of fusion based on 55.2 cal/g obtained from the first endotherm. All endotherms at 5°/min.

Paraffin wax

This material was first proposed as a phase-change thermal-storage medium in the early 1970's (see ref. 4). It is predominantly a mixture of normal alkanes, and, in the absence of air or other oxidants, appears to be chemically stable. Like the normal alkanes (C_{18} to C_{36}) of which it is composed, paraffin waxes usually exhibit one or more first-order solid transitions approximately 10° below the melting range. Paraffin waxes melt over a range of temperature and upon cooling, crystallize in the same temperature range, i.e. they do not supercool. It is therefore interesting to use this material to check, among other things, how closely the exothermic spectrum would match the endothermic spectrum.

The paraffin wax reported here was refined from "Pennsylvania-Grade" crude oil and is designated "112/118 White Scale Wax". Its thermal behavior (heat of fusion and solid transition, melting range, low thermal conductivity) is similar to that of other refined paraffin waxes examined in our laboratory. This specific wax was selected for study because it has two solid transitions in addition to the melting transition. These transitions not only add to the thermal storage potential, but also

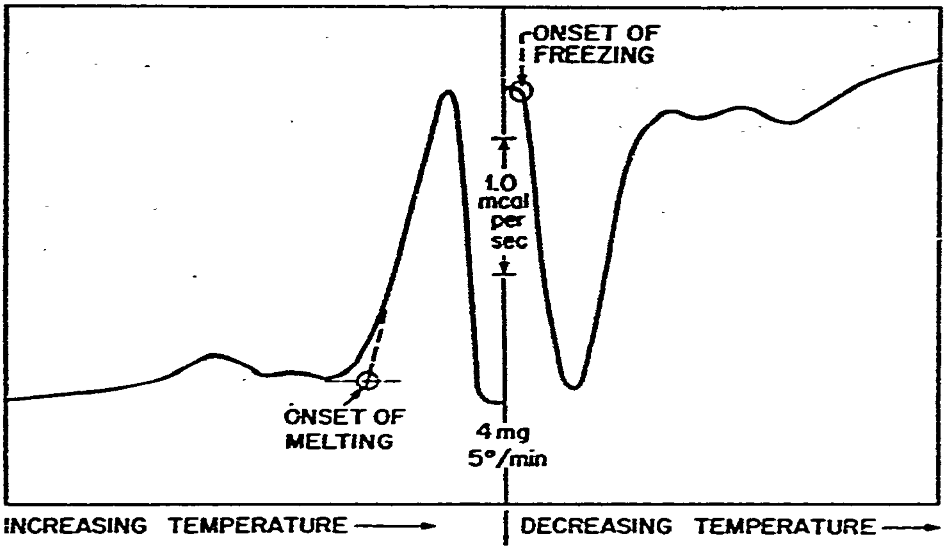

Fig. 3. Thermal spectra of a paraffin wax (112/118 White Scale Wax). Endotherm and exotherm taken at the same scan rate and chart speed.

serve as additional thermoanalytic "fingerprints" by which chemical changes in the wax can be detected.

A typical DSC spectrum for the 112/118 White Scale Wax is presented in Fig. 3 in which endotherm and exotherm were both obtained at 5°/min. In the endothermic branch, the temperature difference between the leading edge of the melting peak and the melting peak itself is about the same as the melting range (42–48 °C) for this wax observed in other devices — hot-stage apparatus and visual observation of test-tube samples immersed in a water bath. Perhaps the most interesting feature of the spectrum is that endotherm and exotherm have nearly symmetrical profiles as might be expected of a material that does not supercool. An especially noteworthy feature is that the slope of the leading edge of the crystallization peak is almost parallel to the slope of the trailing edge of the melting peak (see Fig. 3). For a substance that supercools (e.g. $Na_2SO_4 \cdot 10H_2O$, see Fig. 1) the leading edge of the crystallization peak is more nearly perpendicular to the base line than is the trailing edge of the melting peak.

Another purpose of the DSC investigation of paraffin wax was to confirm its thermal stability. Two types of experiments were used. In the first, several samples were repeatedly cycled between 10 and 70° (by setting the instrument mode switch on "automatic") at heating and cooling rates of 20°/min; one sample was cycled 1743 times. Thermal spectra, exotherms as well as endotherms, were recorded intermittently to monitor chemical changes in the wax. No changes were observed in transition temperatures or in the profile of the transitions.

The second experiment to test thermal stability also considered the problem of the poor heat-transfer properties of the wax; a simple way of improving heat transfer is to immerse in the wax a good thermal conductor such as aluminum. However, the aluminum oxide film on the metal may catalyze isomerization reactions, which would probably lower the melting point and heat of fusion of the wax. To test these ideas, two glass cylinders of wax were maintained as liquid at 49 °C in a water bath for some 1202 h. In one cylinder, a piece of corrugated aluminum was immersed in the wax; the other cylinder contained only the wax control sample. Thermal spectra taken at the end of the test period showed identical thermal behavior between the two heated samples and these were also identical with the spectrum obtained with the starting material.

The two types of experiments just described indicate the excellent thermal stability of paraffin wax.

Phthalimide, $C_6H_4(CO)_2NH$

Commercially available material (Baker Grade, melting point 235–237 °C, J. T. Baker Co., Phillipsburg, N.J.) was used as received. By DSC measurement, the melting point was found to be 234 °C. Solid-phase transitions in the range −63 to 234 °C were searched for, but none was observed. A sample that was alternately heated and cooled twenty six times between 200 and 240 °C showed only minor, random variations in melting point and in heat of fusion; the favorable thermal stability is most likely associated with the fused-ring structure of the compound. During cooling scans, phthalimide was observed to supercool approximately 28°. Test tube study indicated much less supercooling, but samples removed for DSC from the test tube experiments showed roughly the same extent of supercooling as fresh material (see Table 1).

From areas under endothermic curve peaks, the heat of fusion was found to be 48.1 ± 0.5 cal/g. This value is the average of twelve endotherms where the area exceeded 90 cm^2; the uncertainty (0.5 cal/g) is equal to one standard deviation. The molar heat of fusion is 7.08 kcal; this corresponds to $\Delta S_f/R = 7.0_2$. The relatively high (dimensionless) entropy of fusion suggests a rather weak hydrogen bond in the liquid state; compare H_2O for which $\Delta S_f/R = 2.65$. As might be expected from similarities in structure, the entropy of fusion of phthalimide is close to that of phthalic anhydride, $C_6H_4(CO)_2O$, for which $\Delta S_f/R$ is 6.9 (ref. 10).

TABLE 1

EXTENT OF SUPERCOOLING[a] OF UREA AND PHTHALIMIDE

Cooling rate (deg min^{-1})	*Urea (°C)*		*Phthalimide (°C)*	
	DSC[b]	*Test tube*[c]	*DSC*[b]	*Test tube*[c]
10	48–52	13–20	28–30	2–5
1.25	49–52	30–34	26–28	0–2

[a] Extent of supercooling is defined as melting temperature [$CO(NH_2)_2$ = 133 °C, $C_6H_4(CO)_2NH$ = 234 °C] minus the temperature at which freezing is first observed.

[b] Samples were taken from test tube experiments.

[c] Sample size 10–15 g.

Supercooling data obtained with urea and with phthalimide (see Table 1) show that DSC measurement of this phenomenon should be used with caution. Clearly, for the same cooling rates as in test tube experiments, DSC measurements seemed to magnify supercooling tendencies; also, cooling rates seemed to be far less important in the DSC samples than in the test tube experiments. The supercooling results for these two compounds when combined with the results for paraffin wax and $Na_2SO_4 \cdot 10H_2O$ suggest the following: (a) in cases where DSC exotherms exhibit little or no liquid supercooling, then supercooling will probably be minimal with a far larger mass of material; (b) where DSC reveals strong supercooling tendencies, it would be prudent to confirm these tendencies by other means with much larger samples.

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