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Note

The effect of inert solids on the differential scanning calorimetric behavior of benzoic acid*

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In evaluating sample purity by differential scanning calorimetry (DSC) it is often recommended that the sample be melted and crystallized at least once prior to carrying out an analytical scan at high resolution[1,2]. It is evident that a necessary (but not sufficient) condition for the validity of a purity measurement by DSC is that sequential scans of a given sample be identical. Premelting can serve several functions: first any irregularities in the thermogram due to melting of a large crystal will be eliminated[3]; second an initial high scan rate run will aid in identifying the presence of polymorphic solids and the occurrence of chemical reactions[2,4]; and third the sample may be brought into more uniform thermal contact with the pan. The work reported in this note concerns the irregularities found in a series of high resolution scans of high purity benzoic acid and the effect of the addition of various "inert" solids upon this phenomenon.

Experimental

Samples of benzoic acid (National Bureau of Standards: certified purity 99.98%), cinnamic acid (Gallard–Schlesinger; purity >99.9%), naphthalene (Baker Analyzed Reagent), and neburon (1-butyl-3-(3,4-dichlorophenyl)-1-methyl urea, which was generously supplied by Mr. Al Thurston of the Southeast Water Laboratory, Athens, Georgia, and shown by mass spectrometry to be 99% pure) were examined in a Perkin–Elmer DSC-2 scanning calorimeter. Samples, ranging in size from 1 to 2 mg, were weighed on a Cahn electrobalance (model G-1612) and sealed in a volatile sample pan by the conventional technique[5]. The sample containers were prewashed with methylene chloride to remove cutting oil and dried in an oven at 150°C. All materials, in their original containers, and the deoiled aluminum sample pans were stored in a dessicator. The DSC's baseline was adjusted and the calorimetric and temperature axes calibrated according to the manufacturer's instructions. An indium

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standard was used for calorimetric calibration. The temperature axis was calibrated using indium, zinc, and lead standards as supplied by the manufacturer. In accord with Plato and Glasgow[3], the instrument was maintained at 400 K in flowing dry nitrogen when not in use. The sample chamber was purged with nitrogen during a run, and in order to match heat capacities, all samples were run versus a gold reference pan. Care was taken to carefully reproduce the position of the platinum sample cell covers. The sample purities were calculated according to the procedures outlined by Driscoll, Duling and Magnotta[6].

Results and discussion

The thermograms of benzoic acid shown in Fig. 1 (curves a–d) were obtained after three pre-melts (heating rate, 5 K/min; cooling rate, 2.5 K/min). The material spontaneously crystallizes at 350 K. After the third crystallization the sample was heated to 6 K below the endothermic maximum, maintained at a constant temperature for 5 min, and then scanned at 0.31 K/min. The four subsequent scans (i.e. melts 4–7) are shown in this figure. Under conditions of high resolution, i.e. 0.31 K/min and fast chart rate, two distinct peaks (separated by 0.15 K) are evident in the fusion of benzoic acid. At higher scan rates these peaks show up as a single, broad, skewed endotherm. The occurrence of this phenomenon makes the measurement of purity impossible under these experimental conditions. Although others[2,4] have measured the heat of fusion of benzoic acid by DSC, there does not appear to be any report concerning the measurement of its purity.

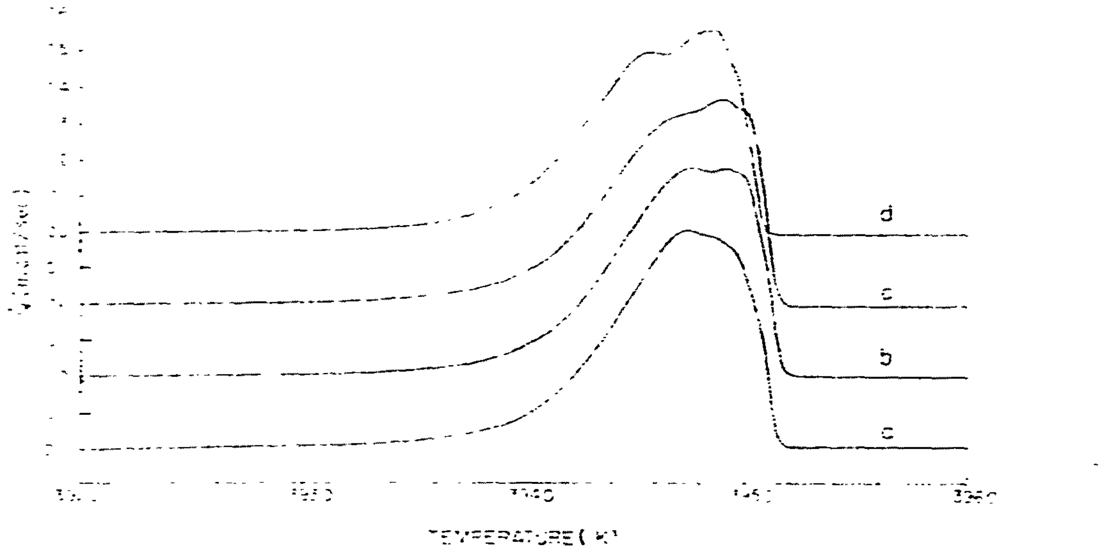

Fig. 1. Fusion endotherm of 1.3 mg of benzoic acid after three premelts. Scan rate 0.31 K/min. a, run 1 (fourth melt); b, run 2 (fifth melt); c, run 3 (sixth melt); d, run 4 (seventh melt).

The problem was decreased considerably, but not entirely eliminated, by encapsulating tight fitting aluminum discs in the sample cell as has been recommended in a number of other reports on DSC purity[1,2]. We have found that the problem is virtually eliminated by adding a layer of crushed glass (5–8 mg, average particle size 65 microns) to the top of the sample. This quantity of glass is just sufficient to fill the sample pan to the brim. The seventhand eighth consecutives cans of a sample of benzoic acid are shown in Fig. 2, curves a and b. There is very little evidence of a split peak under these conditions. It should be noted that the crushed glass was washed with copious amounts of concentrated perchloric acid, distilled water, methanol and finally distilled water. It was then dried at 150 °C. Other additives such

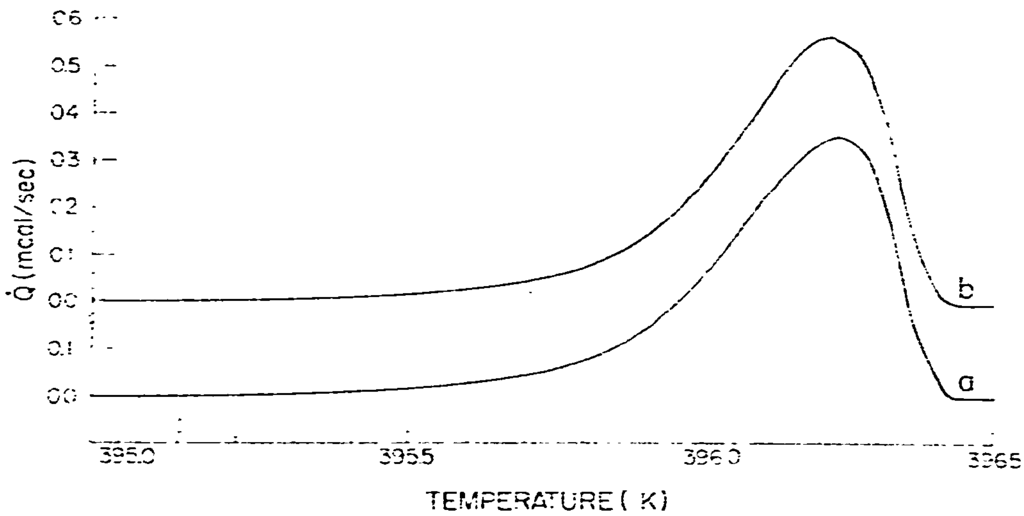

Fig. 2. Fusion endotherm of 1.2 mg of benzoic acid containing 8.0 mg of glass. Scan rate 0.31 K/min. Premelted six times under the same conditions as Fig. 1. a, run 1 (seventh melt); b, run 2 (eighth melt).

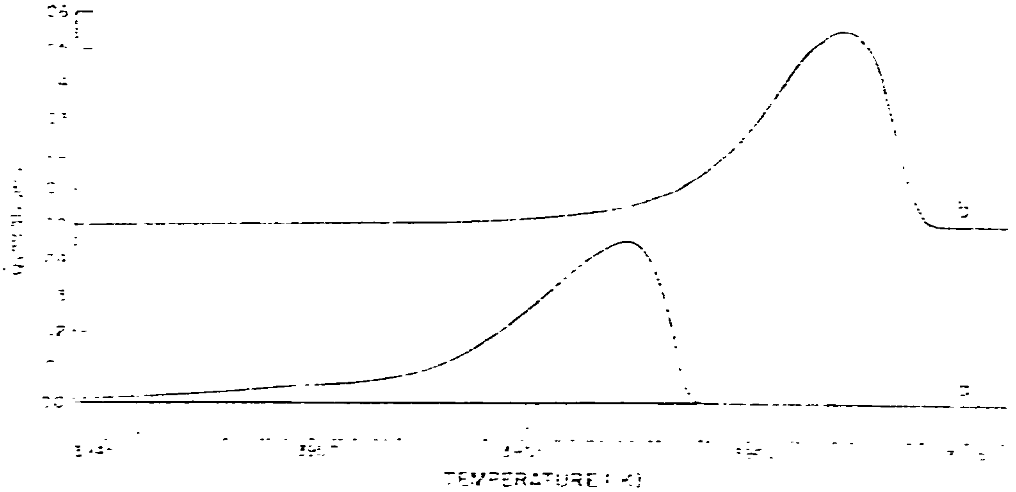

Fig. 3. Comparison of the effect of glass placed on top of (curve b) and below (curve a) the sample. The fifth melt of each sample is shown. Scan rate 0.31 K/min.

as alumina and commercial sylilized glass broadened the peak and shifted it to a lower temperature. We believe that this was due to the presence of impurities in the added solids and also to the reactivity of alumina toward benzoic acid.

Several experiments were run with the sample placed on top of the crushed glass. A typical result is shown in Fig. 3 (curve a). The thermogram has a plateau prior to the main peak whose maximum occurs at 396.3 K. This curve cannot be analyzed for purity, but it does illustrate the extreme distortions which can take place when the sample is physically distributed over regions of the pan which are not in good thermal contact with the controller. It is important to note that the curve presented was obtained after three premelts.

Although double peaks such as those indicated in Fig. 1 are sometimes due to polymorphism in the solid, we believe that in this case it is related to sublimation of benzoic acid. Morawetz's data on the heat of vaporization of benzoic acid[7] indicate a vapor pressure of 4.6 torr at the melting point. Repeated melts show enhancement of the effect whereas repeated melting in the case of polymorphism usually converts the solid to one form[4]. When samples of benzoic acid were run in the non-volatile containers, it was possible to drive virtually all of the material out of the sample cell in three or four runs. This was indicated by a decrease in the area of the fusion endotherm, the presence of crystallized benzoic acid above and around the pan, and a decrease in the weight of the sample. We believe that the peak at higher temperature (see Fig. 1, curve d) results from the melting of benzoic acid which has been deposited on the roof of the sample container. The peak at the lower temperature represents fusion of that part of the sample which is in good thermal contact with the cell holder. Even at the very low scan rate employed in this work, a small temperature gradient exists across the cell. The powdered glass confines the sample to a very small volume on the bottom of the cell and thereby maintains the entire sample in good thermal contact with the cell holder.

Powdered glass has several additional effects on the thermogram of benzoic acid. First the melting point as obtained by extrapolation of the thermal resistance line drawn through the endothermal maxima to the baseline[1] shifts upon addition of glass to 395.7 K and is in good agreement with the literature melting point (395.525 K, see Table 1). In the absence of glass the extrapolated melting point is considerably lower (Table 1). Second, addition of glass invariably decreased the magnitude of the change in the baseline preceding and following fusion. Last, the crystallization point shifts to a higher temperature. These effects are due in part to the closer thermal contact between the sample and the cell as a result of the confinement of the sample to the bottom of the pan. A secondary result of the glass is to provide a larger surface area for the formation of nuclei and thereby enhance the rate of crystallization of the melt.

A number of other materials have been studied in the presence and absence of powdered glass. Our results for some of these compounds are given in Table 1. There is no indication that the additive had any effect at all on the measured purity. There are certainly instances where glass could interfere with purity assay, e.g. if its large surface area catalyzed the chemical decomposition of the sample or if a sample which

TABLE 1

EFFECT OF GLASS ON THE THERMAL PROPERTIES MEASURED BY DSC

Material		*T*[a] *mp, K*	*T*-[b], *K*	Δ*H*-, *cal mole*$^{-1}$	*Purity*[c], %
Benzoic acid	W.G.[d]	395.7	367	4084 ± 70	99.98 ± 0.01
	N.G.[e]	394.0	350	—	—
	Ref.[f]	395.5[7]	—	4148[8]	99.98
Cinnamic acid	W.G.	406.5	401	4031 ± 55	99.96 ± 0.01
	N.G.	406.7	395	4149 ± 135	99.95 ± 0.02
	Ref.[f]	406.1[11]	—	4854[8]	>99.9
Naphthalene	W.G.	352.4	337	4402 ± 50	99.96 ± 0.02
	N.G.	352.6	338	4373 ± 50	99.96 ± 0.02
	Ref.[f]	353.4[9]	—	4494[8]	—
Neburon	W.G.	373.4	348	5988	99.88 ± 0.02
	N.G.	373.4	348	6161	99.89 ± 0.02
	Ref.[f]	374.6[3]	—	7100[3]	>99

[a] Melting point as described in the text. [b] Crystallization point as obtained from the freezing exotherm. [c] Calculated according to the method of ref. 6. [d] W.G. indicates sample run with glass. [e] N.G. indicates sample run with no glass. [f] As obtained from the literature or manufacturers' specifications.

is reactive toward the Si-OH groups of the glass were examined. All of the materials thus far studied were reasonably low melting (<450 K): it is probable that the glass would be more reactive at higher temperatures. Where discrepancies exist between a measurement obtained in this work and those cited elsewhere, e.g. the heat of fusion of cinnamic acid, the results for samples run in the presence of glass were not statistically more discordant than those without glass. There appears to be a major discrepancy between our value for the heat of fusion of neburon and that obtained by Plato and Glasgow. This may be due to the presence of a non-eutectic impurity in either one or both of the materials: however, the sample employed in this work was also assayed by mass spectrometry and shown to be >99% pure.

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