

EFFECTS OF HEATING RATE AND PARTICLE SIZE ON TEMPERATURES AND SPECIFIC ENTHALPIES IN QUANTITATIVE DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Heating rate and particle size distribution may affect peak parameters in quantitative DSC. We studied these effects with a factorial design using as test substances adipic acid (melt without noticeable decomposition), naphazoline nitrate (melt with decomposition), potassium nitrate (solid–solid transition) and sodium citrate dihydrate (dehydration). A commercial heat-flux DSC equipment was used.

We found that heating rate and particle size distribution have a large, and hitherto unexpected, effect on the temperature values, temperature intervals and specific enthalpy, even for the pure melt of adipic acid. Therefore it was concluded that heating rate and particle size distribution should be standardized if accurate quantitative data are required, such as in the determination of transition temperatures and enthalpies, kinetic parameters and molar impurity.

INTRODUCTION

In a series of papers [1–4], we presented the results of investigations about the extent to which experimental variables influence the results of differential scanning calorimetry (DSC). The variables investigated were the apparatus adjustment, sample and reference properties, and the atmosphere and we concluded that the effects of these factors, although often not of great importance in qualitative work, are nevertheless significant and should be taken into account if accurate quantitative data is wanted.

One of the most striking conclusions of these experiments was the fact that the heating rates and particle size distributions of the samples could significantly affect

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peak characteristics [3,4]. This could have a bearing on the determination of, for example, specific enthalpy, purity analysis and kinetic parameters. We therefore conducted another series of experiments in a factorial design to study the effects of heating rate and particle size distribution on temperatures and specific enthalpies. This paper reports our findings.

EXPERIMENTAL

Materials

As models for substances with interesting thermodynamic behaviour we used the following compounds.

Adipic acid, HOOC(CH₂)₄COOH

This melts without noticeable decomposition at 151°C and is described in ref. 5.

The mean diameter by weight of the material was 67 μm. We also used fractions < 32 μm and ≥ 160 μm and a sample which was triturated in a mortar with pestle and which had diameters < 32 μm.

Naphazoline nitrate

Naphazoline nitrate, the nitrate of 4,5-dihydro-2-(1-naphthalenylmethyl)-1H-imidazole, melts at 167–170°C with decomposition. It is described in ref. 6.

The mean diameter by weight was 91 μm. We also used sieve fractions < 32 μm and ≥ 400 μm and a triturated sample which was < 32 μm.

Potassium nitrate, KNO₃

This undergoes a solid–solid transformation at 128°C. It is described in ref. 7.

The mean diameter by weight of the granular batch was 255 μm. We also collected sieve fractions < 160 μm and ≥ 354 μm and a triturated sample which was < 160 μm.

Sodium citrate dihydrate, C₆H₅Na₃O₇ · 2 H₂O

This becomes anhydrous at 150–160°C. It is described in ref. 6.

The mean diameter by weight was 320 μm and we used sieved samples with sizes between 106 and 212 μm, ≥ 500 μm and a triturated sample which had a sieve diameter between 106 and 212 μm.

Apparatus

The equipment was a Mettler TA 2000 A heat-flux DSC system which has been described elsewhere [1].

Weighings were done on an electronic Mettler ME30 micro-balance and were reproducible within 0.040 mg. Holders with samples were weighed before and after the analysis.

Sample and reference cups were always positioned accurately in the furnace. An Ott planimeter (type 30139) was used to determine the areas under the curves.

Calibration

For calorimetric and temperature calibration, we used ultrapure indium (purity > 99.999%).

Characterization of the DSC curves

The evaluation of the DSC curves was done on the following basis. The *onset temperature*, T_i , (B in Fig. 1) is the point on the temperature scale where the curve first departs from the baseline. The *peak temperature*, T_p , (C in Fig. 1) is the point on the temperature scale of maximum distance from the baseline. The *extrapolated onset temperature*, T_c , (G in Fig. 1) is determined according to ICTA guide lines [8].

In heat-flux DSC, T_p indicates the end of a melting transition. Then, $T_p - T_i$ is the total temperature interval for the transition to take place, and $[(T_p - T_i)/\beta]$ ($t_p - t_i$) is the total transition time (sec) if β is the heating rate in K sec^{-1} .

The difference between extrapolated onset temperature and onset temperature, $T_c - T_i$, indicates the onset interval or the speed of starting of the transition and the smaller the difference between peak temperature and extrapolated onset temperature, $T_p - T_c$, the steeper the descending line of the peak. These differences can also be described in units of time by dividing them by the heating rate used.

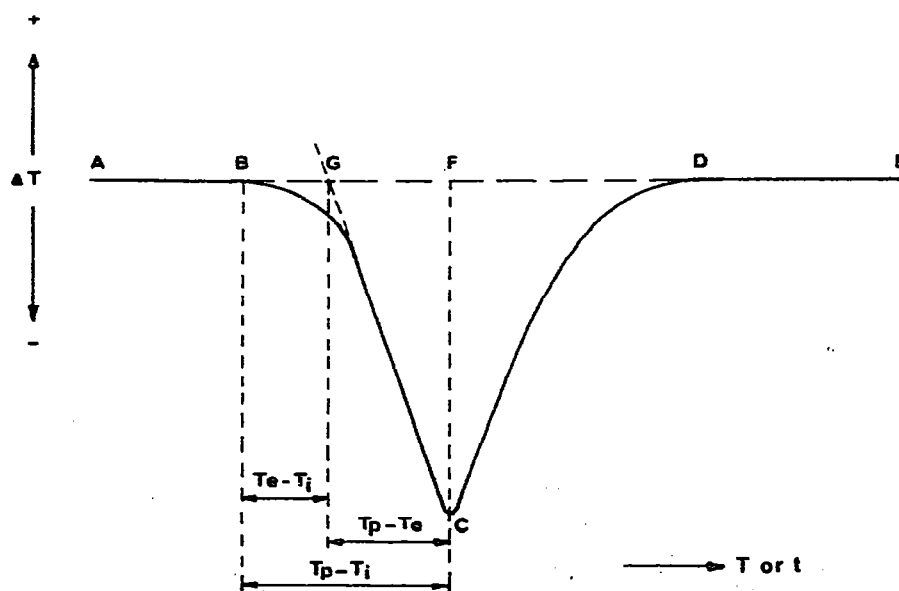


Fig. 1. Formalized DSC peak.

From the peak area (BCD in Fig. 1), the *specific enthalpy change*, ΔH_s (in J g^{-1}), is determined.

Study design

With each compound, the following conditions were used: sample mass 1.960–2.040 mg weighed accurately; sample holders with pierced lids; no dilution; no reference compound; atmosphere, stream of air at $24\text{--}36 \text{ ml min}^{-1}$. The variables were: heating rate (β), $\beta_1 = 0.01 \text{ K sec}^{-1}$, $\beta_2 = 0.08 \text{ K sec}^{-1}$, $\beta_3 = 0.32 \text{ K sec}^{-1}$; particle size distribution (Z). $Z_1 =$ small particles (sieved out), $Z_2 =$ complete particle size spectrum, $Z_3 =$ large particles (sieved out), $Z_4 =$ triturated particles (sieved out).

Each run of 12 curves was carried out by the same person on the same day (with the same calibration constant). The curves were recorded in random order for each run. Three independent runs were carried out per compound. Therefore, the number of degrees of freedom for the error determination was $\nu = 22$.

The effects of factors and their interactions on the curve parameters were tested for statistical significance by analysis of variance. Means per factor level were obtained to facilitate the interpretation of the effects. In addition, the standard deviations were estimated for each parameter.

RESULTS AND DISCUSSION

Mean values

Table 1 gives the mean values of the temperature determinations. Generally, the determination of the onset temperature, T_i , has a greater coefficient of variation than the determinations of the extrapolated onset temperature, T_c , and peak temperature, T_p . Especially for adipic acid, the coefficients of variation for T_c and T_p are extremely small ($< 0.1\%$). Thus, the reproducibility is concluded to be very good.

Table 2 gives the mean values for specific enthalpies. For the pure melt and the solid–solid transition, the coefficients of variation are small ($< 2\%$), but for the melting of naphazoline nitrate it is greater. This is explained by the influence of the surrounding atmosphere (leading to oxidation).

If thermal decomposition is the only reason for the thermal effect, as for the dehydration of sodium citrate dihydrate, the coefficient of variation is twice as much.

Generally, these results are in accordance with the values we reported earlier [4].

Table 3 gives the mean values of temperature and time differences. The temperature interval $T_p - T_i$ of the solid–solid transition (KNO_3) is small, which correlates with a small onset interval $T_c - T_i$. It must be concluded that the phase II crystals of potassium nitrate almost simultaneously transform into phase I. For the melting transitions, the onset interval is much greater. It should be remembered that the

TABLE 1
Mean values of temperature determinations

| Substance | T_i | | | T_c | | | T_p | | |
|-----------------------------|--------------|-------------|-------------|--------------|-------------|-------------|--------------|-------------|-------------|
| | Mean (°C) | s (°C) | C.V. (%) | Mean (°C) | s (°C) | C.V. (%) | Mean (°C) | s (°C) | C.V. (%) |
| Adipic acid | 146.16 | 1.12 | 0.77 | 151.05 | 0.12 | 0.08 | 151.33 | 0.09 | 0.06 |
| Naphazoline nitrate | 162.67 | 0.58 | 0.35 | 167.62 | 0.42 | 0.25 | 168.81 | 0.27 | 0.16 |
| Potassium nitrate | 128.46 | 0.26 | 0.20 | 129.74 | 0.20 | 0.15 | 131.23 | 0.27 | 0.20 |
| Sodium citrate dihydrate | 153.87 | 0.66 | 0.43 | 157.00 | 0.39 | 0.25 | 159.34 | 0.49 | 0.30 |

TABLE 2
Mean values of specific enthalpies

| Substance | Specific enthalpy ΔH_s | | |
|-----------------------------|--------------------------------|---------------------------|----------|
| | Mean (J g^{-1}) | s (J g^{-1}) | C.V. (%) |
| Adipic acid | 255.43 | 3.18 | 1.24 |
| Naphazoline nitrate | 93.51 | 2.17 | 2.32 |
| Potassium nitrate | 50.20 | 0.88 | 1.75 |
| Sodium citrate dihydrate | 372.71 | 15.51 | 4.16 |

TABLE 3
Mean values of temperature and time differences

| Parameter | Adipic acid | | Naphazoline nitrate | | Potassium nitrate | | Sodium citrate dihydrate | |
|-------------------|-------------|------|------------------------|------|----------------------|------|-----------------------------|------|
| | Mean | s | Mean | s | Mean | s | Mean | s |
| $T_p - T_c$ (K) | 0.27 | 0.12 | 1.19 | 0.42 | 1.48 | 0.18 | 2.34 | 0.56 |
| $T_p - T_i$ (K) | 5.17 | 1.14 | 6.14 | 0.64 | 2.77 | 0.24 | 5.48 | 0.74 |
| $T_c - T_i$ (K) | 4.90 | 1.14 | 4.95 | 0.57 | 1.28 | 0.23 | 3.13 | 0.64 |
| $t_p - t_c$ (sec) | 7 | | 32 | | 28 | | 91 | |
| $t_p - t_i$ (sec) | 138 | | 153 | | 63 | | 199 | |
| $t_c - t_i$ (sec) | 131 | | 121 | | 35 | | 108 | |

insensitivity of the instrument to detect early melting (deviation from baseline) is one of the most severe problems in quantitative purity analysis with DSC.

The interval during which the bulk of the sample melts, $T_p - T_c$, is smaller for adipic acid than for naphazoline nitrate, which indicates that adipic acid gives a purer melt than naphazoline nitrate.

Adipic acid, pure melt

Effect of heating rate

The heating rate has a significant effect on all parameters (Table 4). An increase in heating rate decreases the onset temperatures. The following considerations may help to explain this behaviour.

(a) At low heating rates, the thermal conditions both in the furnace and in the sample are near equilibrium; at high rates they are not.

(b) High heating rates may lead to a more non-uniform temperature distribution within the sample.

(c) Once a certain rate is exceeded, the system cannot respond rapidly enough to record the process accurately.

(d) Superheating may occur at high heating rates.

(e) In heat-flux DSC, the actual sample temperature is calculated from the measured furnace temperature, from which a term $\tau\beta$ is subtracted, where τ is the lag time. This is regarded as constant (30 sec), but at the higher rates, slight errors in τ may produce values of the sample temperature which are too low.

If a powder bed is considered to be an isotropic solid with linear heat flow and with a steady temperature difference, this heat flow can be described, in thermal

TABLE 4

Effects of heating rate and particle size on temperatures and specific enthalpies of adipic acid

| Factor | T_i (°C) $s=1.12$ K | T_c (°C) $s=0.12$ K | T_p (°C) $s=0.09$ K | ΔH_s (J g ⁻¹) $s=3.18$ J g ⁻¹ |
|---|-------------------------------|--------------------------|-------------------------------|---|
| Heating rate | | | | |
| $\beta_1=0.01$ K sec ⁻¹ | 148.22 ^a | 151.30 ^a | 151.46 ^a | 253.69 ^a |
| $\beta_2=0.08$ K sec ⁻¹ | 145.91 ^a | 151.19 ^a | 151.39 ^a | 259.33 ^a |
| $\beta_3=0.32$ K sec ⁻¹ | 144.34 ^a | 150.68 ^a | 151.13 ^a | 253.26 ^a |
| Particle size | | | | |
| Z_1 = small particles (<32 μ m) | 146.58 ^a | 151.07 | 151.39 ^a | 251.89 ^a |
| Z_2 = complete spectrum | 146.98 ^a | 151.07 | 151.26 ^a | 258.19 ^a |
| Z_3 = large particles (≥ 160 μ m) | 143.85 ^a | 151.10 | 151.43 ^a | 252.60 ^a |
| Z_4 = triturated particles (<32 μ m) | 147.21 ^a | 150.97 | 151.22 ^a | 259.03 ^a |
| Significant interactions | $Z \times \beta$ ^a | | $Z \times \beta$ ^a | |

^a Significant differences between levels at $P=0.01$.

analogy with Ohm's law, by

$$\frac{dQ}{dt} = \beta C_s = \frac{\Delta T}{R} = \frac{T_1 - T_2}{R} \quad (1)$$

where dQ/dt is the heat flow (rate of gain of thermal energy) (W), β the heating rate (K sec^{-1}), C_s the heat capacity of the bed (J K^{-1}), T_1 the temperature at the "hot" side and T_2 the temperature at the "cool" side of the bed, and R the total heat resistance in the powder bed (K W^{-1}). If we assume that, over small temperature intervals, R and C_s are not temperature-dependent, an increase in heating rate also increases ΔT . Thus T_1 becomes higher. This means a particle at the "hot" side of the bed may melt earlier, which leads to an early deviation from baseline and a decrease in T_i . The total amount of sample will then also be molten earlier, so that T_c and T_p will also become lower. This effect is stronger if R is higher. Therefore, if we want to measure the "theoretical" values for the melting of a pure substance, the heating rate should be as small as possible. This observation is in accordance with the well-known fact that, for the determination of purity by DSC, heating rates as low as possible (preferably $< 0.02 \text{ K sec}^{-1}$) should be used.

Interestingly, there is also a significant effect of heating rate on specific enthalpy: at the intermediate rate of 0.08 K sec^{-1} , it is 2% higher ($P = 0.01$) than at the lower and higher rates. At the lowest rate, appreciable sublimation, leading to a smaller sample and to a lower peak area, may account for this. At the highest rate, the baseline displacement was significantly increased. The peak area was always determined by drawing a straight interpolated baseline. At high baseline displacements, this procedure may give too low values. We did not see any increase in peak area with increasing heating rate, as was found by Barrall and Rogers [9] in a conventional apparatus.

The temperature differences (Table 5) decrease with decreasing heating rates. This was to be expected: low heating rates should lead to sharper melting peaks.

The time intervals decrease if the heating rates are increased. This, again, could be expected. Obviously, the values found make it impossible to calculate an overall standard deviation.

Effect of particle size distribution

Particle size distribution may also affect the adipic acid curves significantly (Tables 4 and 5). For large particles, the onset temperature is decreased and the onset interval and total interval are significantly greater, especially at the highest heating rate. Moreover, the enthalpy of fusion of large particles is significantly lower than that of the sample with complete size spectrum.

These effects may be accounted for by a greater thermal resistance in the large-particle sample than in the sample with finer particles. This is in accordance with the well-known fact that the use of diluting agents with high thermal resistance decreases heat transfer and diminishes the thermal effect and the peak area. Therefore, in eqn. (1), ΔT is higher for large particles, so that particles at the "hot" side of the bed may melt before releasing energy to other particles. This gives a lower

TABLES
Effects of heating rate and particle size on temperature and time differences of adipic acid

| Factor | $T_p - T_c$ (K) $s = 1.14$ K | $T_p - T_c$ (K) $s = 0.12$ K | $T_c - T_1$ (K) $s = 1.14$ K | $t_p - t_c$ (sec) | $t_p - t_c$ (sec) | $t_c - t_1$ (sec) |
|---|---------------------------------|---------------------------------|---------------------------------|----------------------|----------------------|----------------------|
| Heating rate | | | | | | |
| $\beta_1 = 0.01$ K sec ⁻¹ | 3.24 ^a | 0.16 ^a | 3.07 ^a | 324 ^a | 16 ^a | 307 ^a |
| $\beta_2 = 0.08$ K sec ⁻¹ | 5.48 ^a | 0.21 ^a | 5.27 ^a | 69 ^a | 3 ^a | 66 ^a |
| $\beta_3 = 0.32$ K sec ⁻¹ | 6.80 ^a | 0.46 ^a | 6.34 ^a | 21 ^a | 1 ^a | 20 ^a |
| Particle size | | | | | | |
| $Z_1 =$ small particles (<32 μ m) | 4.81 ^a | 0.32 | 4.50 ^a | 166 | 8 ^a | 157 |
| $Z_2 =$ complete spectrum | 4.28 ^a | 0.19 | 4.09 ^a | 100 | 4 ^a | 96 |
| $Z_3 =$ large particles (≥ 160 μ m) | 7.58 ^a | 0.33 | 7.25 ^a | 161 | 6 ^a | 155 |
| $Z_4 =$ unfurated particles (<32 μ m) | 4.01 ^a | 0.25 | 3.76 ^a | 125 | 9 ^a | 116 |
| Significant interactions | $Z \times \beta^a$ | $Z \times \beta^a$ | $Z \times \beta^a$ | | $Z \times \beta^a$ | |

^a Significant differences between levels at $P = 0.01$.

onset temperature and increases the onset interval and total transition interval.

For the complete size spectrum, the onset temperature and peak area are higher, but the peak temperature is lower than for the small particles. We can expect that the porosity of the sample with complete size spectrum is lower than that of the small particles, which apparently leads to a better heat transfer. However, we would expect the value for the milled-particles sample to be even lower than for the small particles. It is known that grinding yields fine fractions with structural disorders. Such a reduction in the degree of crystallinity is then superimposed on a reduction in particle size and induces a lowering of the transition temperature and peak area since less energy is required to destroy structures of lower crystal perfection. We can see in Table 4 that the triturated particles do indeed have a low peak temperature, but the onset temperature and specific enthalpy are even higher than for the complete size spectrum. This could be explained by the application of the Kelvin equation [10], which indicates that smaller particles show a higher transition enthalpy than larger ones. However, this equation should only hold for particles in the submicron size. A better explanation may be the breaking of electrostatic forces between aggregates (which requires energy that is added to the melting endotherm).

Another significant effect of particle size is the increase in $t_p - t_c$ for small particles. Apparently, it takes a longer time for small particles to melt the bulk of the sample. This effect is greater at low heating rates, that is if the energy input per unit time is smaller. It is explained by the fact that all particles separately contribute to the melting endotherm; the more particles that are present, the longer it takes to melt the bulk of the sample.

Naphazoline nitrate, melt with decomposition

Effect of heating rate

Naphazoline nitrate melts with decomposition. In principle, we observed the same influence of non-equilibrium on the temperature values as for adipic acid (Table 6), but (particularly at low heating rates) there is an additional effect of oxidation by the surrounding air. The oxidation products, as impurities, decrease the peak temperature.

Another effect of the oxidation is the evolution of some energy at longer transition times, which reduces the (endothermic) peak area at the lowest heating rate.

The same increase in temperature differences with increasing heating rate as with adipic acid was seen.

Effect of particle size

The effects of particle size on the peak parameters of naphazoline nitrate cannot be completely explained in the same way as with adipic acid, since with naphazoline nitrate the sample with the small particles gives the lowest temperatures and peak area. This could mean that the thermal conductivity of naphazoline nitrate is much greater than that of adipic acid. On the other hand, the decrease in specific enthalpy

TABLE 6

Effects of heating rate and particle size on temperatures and specific enthalpies of naphazoline nitrate

| Factor | T_i (°C) $s=0.58$ K | T_c (°C) $s=0.42$ K | T_p (°C) $s=0.27$ K | ΔH_s (J g ⁻¹) $s=2.17$ J g ⁻¹ |
|---|-------------------------------|-------------------------------|-------------------------------|---|
| Heating rate | | | | |
| $\beta_1=0.01$ K sec ⁻¹ | 164.78 ^b | 167.50 ^a | 168.27 ^b | 89.83 ^b |
| $\beta_2=0.08$ K sec ⁻¹ | 162.36 ^b | 167.93 ^a | 168.90 ^b | 95.71 ^b |
| $\beta_3=0.32$ K sec ⁻¹ | 160.88 ^b | 167.43 ^a | 169.27 ^b | 94.99 ^b |
| Particle size | | | | |
| Z_1 = small particles (<32 μ m) | 156.40 ^b | 165.17 ^b | 167.33 ^b | 82.12 ^b |
| Z_2 = complete spectrum | 165.52 ^b | 168.33 ^b | 169.06 ^b | 97.26 ^b |
| Z_3 = large particles (≥ 400 μ m) | 165.95 ^b | 168.69 ^b | 170.12 ^b | 98.60 ^b |
| Z_4 = triturated particles (<32 μ m) | 162.82 ^b | 168.33 ^b | 168.74 ^b | 96.04 ^b |
| Significant interactions | $Z \times \beta$ ^b | $Z \times \beta$ ^b | $Z \times \beta$ ^b | $Z \times \beta$ ^b |

^a Significant differences between levels at $P=0.05$.^b Significant differences between levels at $P=0.01$.

for small particles is much larger than with adipic acid. This can only be explained by the effect of oxidation, which is greatest for the small particles. This oxidation starts in the solid phase: it was shown earlier [2] that the baseline drift is increased if small particles are taken. The oxidation products are impurities and decrease the onset temperature, extrapolated onset temperature and peak temperature. The peak then becomes wider and so the temperature and time intervals are greater for smaller particles. The samples with triturated particles show the same effects as those with the sieved small particles but to a smaller extent. We assume that, as for adipic acid, the existence of aggregates and electrostatic forces which have to be broken is the prime reason for this behaviour.

Potassium nitrate, solid–solid transformation

Effect of heating rate

As regards the polymorphic transition of potassium nitrate, we saw an increase in temperature responses T_p and T_c at higher heating rates (Table 7). This is in accordance with the theories of Kissinger [11] and Ozawa [12]. The application of these theories has been described in the literature for the determination of the activation energy of polymorphic transitions [13], but from our results we conclude that many determinations at different heating rates must be carried out to obtain meaningful results.

For this transition, a higher heating rate also leads to larger temperature differences. This is in accordance with the findings of Moore and Rose [14] who

TABLE 7

Effects of heating rate and particle size on temperatures and specific enthalpies of potassium nitrate

| Factor | T_i (°C) $s=0.26$ K | T_c (°C) $s=0.20$ K | T_p (°C) $s=0.27$ K | ΔH_s (J g ⁻¹) $s=0.88$ J g ⁻¹ |
|---|--------------------------|--------------------------|--------------------------|---|
| Heating rate | | | | |
| $\beta_1=0.01$ K sec ⁻¹ | 128.43 | 129.26 ^b | 129.86 ^b | 49.93 ^a |
| $\beta_2=0.08$ K sec ⁻¹ | 128.54 | 129.88 ^b | 131.13 ^b | 49.78 ^a |
| $\beta_3=0.32$ K sec ⁻¹ | 128.41 | 130.09 ^b | 132.69 ^b | 50.88 ^a |
| Particle size | | | | |
| Z_1 = small particles (< 160 μ m) | 128.59 | 130.03 ^b | 131.20 ^b | 50.44 |
| Z_2 = complete spectrum | 128.54 | 130.11 ^b | 131.45 ^b | 49.94 |
| Z_3 = large particles (≥ 354 μ m) | 128.26 | 129.52 ^b | 131.30 ^b | 50.49 |
| Z_4 = triturated particles (< 160 μ m) | 128.45 | 129.31 ^b | 130.95 ^b | 49.92 |
| Significant interactions | | | | $Z \times \beta$ ^a |

^a Significant differences between levels at $P=0.05$.^b Significant differences between levels at $P=0.01$.

showed that peak widening of quartz transition due to grinding could be prevented by using very low heating rates.

Effect of particle size distribution

To interpret the effects of the particle size of potassium nitrate on the DSC peak parameters (Table 8), one should distinguish between at least 2 different factors.

(a) Grinding leads to a reduction in the crystal size or to an induction of lattice strain. The effect is a decrease in peak height, a shift of the transition peak to lower temperatures and a decrease in peak area.

As we can see in Table 7, only the shifts of T_c and T_p to lower values are statistically significant.

(b) In large particles, the thermal lags are greater and they may transform at slightly different temperatures. Therefore, the peak becomes wider, T_p is increased and T_c is reduced. This may even lead to irregular peak shapes, as was shown earlier [3].

Table 8 shows that the total temperature intervals $T_p - T_i$ are decreased with small particles, which is caused by the smaller thermal lags. However, in the case of the triturated particles, this decrease is caused by a decrease in onset interval, whereas for the sieved sample it is due to a smaller $T_p - T_c$. We assume that extremely small particles (in the submicron size) formed during grinding, transform first upon heating, but their contribution to the thermal effect is so slight that the instrument is not capable of detecting deviation from the baseline. The small particles of the sample which is only sieved out also transform earlier than the bulk of the sample, but their contribution to the thermal effect is larger and leads to a detectable deviation from the baseline.

TABLE 8
Effects of heating rate and particle size on temperature and time differences of potassium nitrate

| Factor | $T_p - T_i$ (K) $s=0.24$ K | $T_p - T_c$ (K) $s=0.18$ K | $T_c - T_i$ (K) $s=0.23$ K | $t_p - t_i$ (sec) | $t_p - t_c$ (sec) | $t_c - t_i$ (sec) |
|---|-------------------------------|-------------------------------|-------------------------------|----------------------|----------------------|----------------------|
| Heating rate | | | | | | |
| $\beta_1 = 0.01$ K sec ⁻¹ | 1.43 ^b | 0.60 ^b | 0.83 ^b | 143 ^b | 60 ^b | 83 ^b |
| $\beta_2 = 0.08$ K sec ⁻¹ | 2.60 ^b | 1.25 ^b | 1.34 ^b | 32 ^b | 16 ^b | 17 ^b |
| $\beta_3 = 0.32$ K sec ⁻¹ | 4.28 ^b | 2.59 ^b | 1.68 ^b | 13 ^b | 8 ^b | 5 ^b |
| Particle size | | | | | | |
| $Z_1 =$ small particles (<160 μ m) | 2.61 ^b | 1.17 ^b | 1.45 ^b | 60 | 23 ^b | 37 ^b |
| $Z_2 =$ complete spectrum | 2.91 ^b | 1.34 ^b | 1.57 ^b | 66 | 22 ^b | 46 ^b |
| $Z_3 =$ large particles (≥ 354 μ m) | 3.04 ^b | 1.78 ^b | 1.26 ^b | 68 | 35 ^b | 34 ^b |
| $Z_4 =$ triturated particles (<160 μ m) | 2.50 ^b | 1.64 ^b | 0.87 ^b | 57 | 34 ^b | 23 ^b |
| Significant interactions | | $Z \times \beta^a$ | | | $Z \times \beta^b$ | $Z \times \beta^a$ |

^a Significant differences between levels at $P=0.05$.

^b Significant differences between levels at $P=0.01$.

Sodium citrate dihydrate, dehydration

Effect of heating rate

As for the polymorphic transition of potassium nitrate, the temperature responses of the dehydration increase with higher heating rates (Table 9). We did not find any increase of temperature difference with higher rates, as we did with the other three substances. Only the onset interval, $T_c - T_i$, at the lowest rate was significantly smaller ($P = 0.05$) than at the higher rates.

The dehydration is governed by the formation and growth of nuclei which are formed primarily on the surface. These nuclei most frequently appear in lines of strain on the crystal and the S-shaped conversion curve is characterized by an induction period, acceleration period and a decay period. If the transition time becomes shorter, the S-form becomes steeper. This effect is contrary to the general widening of peaks at higher heating rates and the result is that $T_p - T_c$ does not change with heating rate.

We found the same effect of reduction of transition time by heating rate increase as with the other three substances.

Effect of particle size distribution

For small particles (milled or only sieved out) the induction period is longer than for larger particles, as the thermal effect for the release of hydrate water is much less and because the probability of branching of nuclei is smaller. This causes the onset

TABLE 9

Effects of heating rate and particle size on temperatures and specific enthalpies of sodium citrate dihydrate

| Factor | T_i (°C) $s=0.66$ K | T_c (°C) $s=0.39$ K | T_p (°C) $s=0.49$ K | ΔH_s (J g ⁻¹) $s=15.51$ J g ⁻¹ |
|--|--------------------------|--------------------------|--------------------------|--|
| Heating rate | | | | |
| $\beta_1 = 0.01$ K sec ⁻¹ | 147.88 ^b | 150.59 ^b | 152.97 ^b | 369.62 |
| $\beta_2 = 0.08$ K sec ⁻¹ | 154.10 ^b | 157.47 ^b | 159.69 ^b | 378.34 |
| $\beta_3 = 0.32$ K sec ⁻¹ | 159.62 ^b | 162.94 ^b | 165.36 ^b | 370.17 |
| Particle size | | | | |
| $Z_1 =$ small particles $106 < d \leq 212$ μ m | 153.74 | 157.28 ^b | 159.44 | 376.40 |
| $Z_2 =$ complete spectrum | 153.76 | 156.66 ^b | 159.23 | 368.04 |
| $Z_3 =$ large particles (≥ 500 μ m) | 154.17 | 156.74 ^b | 159.60 | 372.80 |
| $Z_4 =$ triturated particles $106 < d \leq 212$ μ m | 153.79 | 157.32 ^b | 159.09 | 373.60 |
| Significant interactions | $Z \times \beta^a$ | $Z \times \beta^b$ | $Z \times \beta^b$ | |

^a Significant differences between levels at $P=0.05$.

^b Significant differences between levels at $P=0.01$

interval $T_c - T_i$ to be larger for small particles and as T_i does not change with particle size (Table 9), T_c must be higher for small particles. As the peak temperature does not change either, $T_p - T_c$ is smaller for small particles.

The significant interactions on temperatures can be explained by the fact that the above-mentioned discrepancies between small and large particles become smaller if the heating rate is increased (and the transition time is shorter).

The effect of the induction of strains by grinding is so small that there is no detectable difference in response between the small sieved particles and the triturated samples.

SUMMARY AND CONCLUSIONS

With a factorial design, we studied the effects of heating rate and particle size distribution on peak parameters in quantitative DSC. We used a commercial heat-flux DSC equipment and studied the following compounds: adipic acid (melts without noticeable decomposition), naphazoline nitrate (melts with decomposition), potassium nitrate (solid-solid transformation) and sodium citrate dihydrate (dehydration).

Significant main effects and interactions were detected by analysis of variance. The DSC peaks were evaluated in terms of onset temperature, extrapolated onset temperature, peak temperature, differences between these temperatures, transition times and specific enthalpy changes.

The small coefficients of variation for the temperature determinations and for the specific enthalpy values (1.2–4.2%) showed that the reproducibility of the determinations was very good.

For adipic acid, we found that a higher heating rate gave lower temperatures, which was explained in terms of thermal equilibrium and superheating. We also saw a significant increase in the values for temperature differences with high heating rates. The specific enthalpy at the intermediate rate was 2% higher than at the lower and higher rates. Particle size also affected the responses of the adipic acid curves: for large particles, onset temperature and specific enthalpy were lower and peak temperature, onset interval and total temperature interval were higher. These effects were explained in terms of heat transfer through the powder bed.

The effects of heating rate and particle size distribution on naphazoline nitrate were attributed to oxidation during melting. The oxidation products are impurities; they lower the temperature values and widen the peak. As energy is supplied by the oxidation, the endothermic peak area is reduced. The influence of oxidation is greater at low heating rates and with small particles.

For the polymorphic transition and the dehydration, we saw an increase in temperature responses with higher heating rates. For potassium nitrate, increase in heating rate also led to an increase in temperature differences. Decrease in crystal perfection by grinding led to a shift of transition peak to lower temperatures and a reduction of peak area. Due to thermal lag, large particles gave a wider peak.

For the dehydration reaction, the effects of size distribution were explained by the longer induction period in the conversion curve for smaller particles.

For all substances, the transition times were short at high heating rates.

In conclusion, it can be stated that heating rate and particle size distribution have a large, and hitherto unexpected, effect on DSC peak parameters. Even for the pure melt of adipic acid, the temperature values, intervals and specific enthalpy were affected by both heating rate and particle size. Therefore, care should be taken to standardize heating rate and particle size distribution if accurate quantitative data, such as transition temperatures, enthalpies, kinetic parameters and molar impurity must be obtained.

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