Journal of Thermal Analysis, Vol. 33 (1988) 297–304

ON THE COMPLEX INFLUENCE OF THE EXPERIMENTAL PARAMETERS AND THE PROPERTIES OF THE SUBSTANCES ON THE REPRESENTATION OF SOLID-LIQUID TRANSITIONS STUDIED WITH A DIFFERENTIAL SCANNING CALORIMETER

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Due to the increasing importance of quantified results of dynamic calorimetric measurements, the influence of single experimental parameters has been studied by some authors. We found that these results can be represented correctly only in a complex form. According to this experience, the experimental parameters were changed on the basis of statistically planned experiments. The numerous measurements were carried out with samples of indium, 1,3-dinitrobenze and polyethylene prepared in different ways. The results were evaluated in a complex form. The evaluation of the experimental data revealed a significant influence of the substance properties and the experimental parameters.

Due to their efficient performance and adaptability, the methods of dynamic calorimetry (power DSC, heatflux DSC, quantitative DTA) have proved a success. One of the numerous applications is the investigation of solid-liquid phase transitions. The results of these measurements are influenced by the experimental parameters and the properties of the investigated substances.

Some authors [1–9] have studied the influence of only one or two experimental parameters on the results of dynamic measurements. In our opinion, such measurements do not adequately consider the multiple effect of the thermal resistances within the sample and in the contact between the sample and the sensor. Therefore, we have attempted to record the influence of the experimental parameters sample mass (m), sensitivity (E) and heating rate (β) on the solid-liquid transition in a complex manner.

Both the temperatures and shapes of the recorded peaks were investigated. Measurements were made with a Perkin-Elmer DSC–2 differential scanning calorimeter, connected to a recorder.

The following substances, prepared in different ways, were investigated;

- indium: chips;
- 1,3-dinitrobenzene: powder, tablet and solid molten mass;
- polyethylene (M_w = 238,000 g/mol): powder, tablet and foil.

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Special interest was devoted to 1,3-dinitrobenzene as a typical agent of common samples. Its thermal conductivity is given in [10]:

1,3-dinitrobenezene: – powder: $\lambda = 0.06$ W/m deg
– tablet: $\lambda = 0.10$ W/m deg
– solid molten mass: $\lambda = 0.15$ W/m deg

The recorded peaks were characterized according to [11], as shown in Fig. 1.

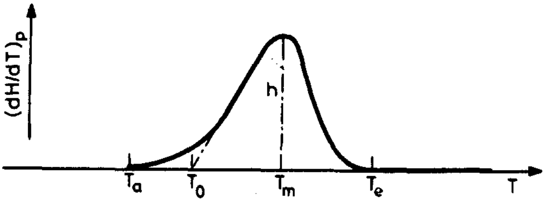

Fig. 1 Typical DSC peak of a phase transition

To find the relationships $T_{a,o,m,e,} = f(m,E,\beta)$, we varied the experimental parameters according to statistically planned experiments. This was done separately for each substance and preparation.

The enthalpy changes of the solid-liquid transitions were determined from the peak areas by means of a planimeter. Such determinations are optimum only if the peak areas have the shape of an equilateral triangle. This may be achieved through an appropriate selection of the experimental parameters.

T_o characterize the shape of the peak, we defined a shape factor y:

$$y = 0.5 * \sqrt{3} * (T_e - T_o)/h \qquad (1)$$

where $(T_e - T_o)$ represents a length. Shape factor y has the following meanings:

$y = 1$: the shape of the peak is an equilateral triangle;
$y > 1$: the shape of the peak is an obtuse-angled triangle;
$y < 1$: the shape of the peak is an acute-angled triangle.

To interpret the results, we have defined limiting values for the height of the peak and the shape factor itself:

$$0.2 \leqslant y \leqslant 5.0$$
$$50 \text{ mm} \leqslant h \leqslant 200 \text{ mm}$$

From the multitude of results, we present only some typical examples in this paper. Detailed results will be given in [12].

We found correlations between the peak temperatures and the experimental parameters, e.g. for 1,3-dinitrobenzene, solid molten mass:

$$T_m = 361.7 - 0.0319*E + 0.3685*m + 0.420*\beta + 0.011*E*m + 0.0193*m*\beta - 0.02254*m^2 - 0.0099*\beta^2 \quad (2)$$

where T_m is given in Kelvin, m in mg, E in mcal s^{-1}, and β in deg min^{-1}. The residual standard deviation was $s_R = 0.18$ deg.

Other functions not mentioned are analogous in form. Correlation (2) confirms our assumption that the influence of the experimental parameters on the peak temperatures may be exactly described only by complex considerations. The evaluation of single dependences leads necessarily to incomplete findings.

Figures 2 and 3 show the peak temperatures as functions of the sample mass and the heating rate for 1,3-dinitrobenzene.

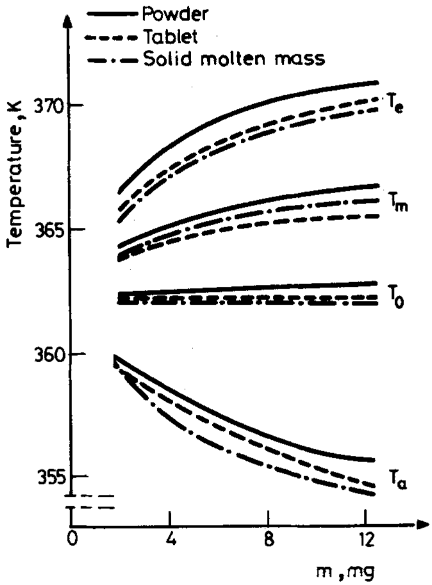

Fig. 2 Peak temperatures as a function of sample mass (1,3-dinitrobenzene). $E = 5$ mcal/s; $\beta = 5$ deg/min; PV = 40 mm/min.

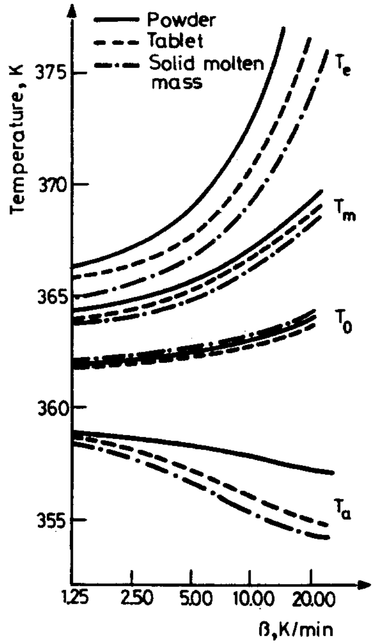

Fig. 3 Peak temperatures as a function of heating rate (1,3-dinitrobenzene). $E = 5$ mcal/s; $m = 5$ mg; PV = 40 mm/min.

In conclusion, it can be stated that:

– Of the caharacteristic temperatures T_a, T_o, T_m and T_e of a DSC peak, the extrapolated onset temperature T_o is the least influenced. This supports the recommendation [1, 13] that the onset-temperature should feature as well-defined measuring quantity.

– The small increase in T_o with increasing heating rate indicates the problems of heat transport. This effect is observed most clearly for the powder sample.

– Obviously, the dependence of T_a and T_e is attributable to the better visual perceptibility owing to the higher sample mass (Fig. 2) or the higher heating rate (Fig. 3). In addition to this effect, problems of heat transport become apparent with increasing heating rate. The result is that the T_e curves are shifted strongly to higher values. The sample with the lowest thermal conductivity (powder) exhibits this behaviour more distinctly than the other samples.

– The influence of the sample condition on the shape of the peaks is shown in Fig. 4. These curves confirm the calculations on the basis of the investigated functional relationships.

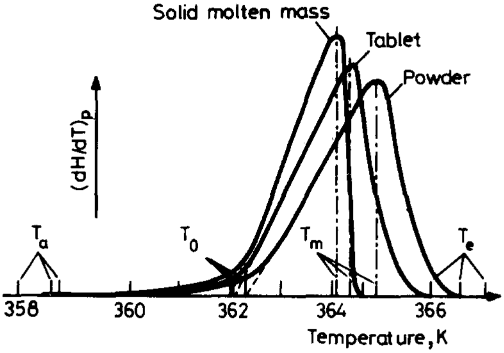

Fig. 4 Influence of sample state on the peak shape (1,3-dinitrobenzene). $E = 5$ mcal/s; $m = 5$ mg; $\beta = 2.5$ deg/min; PV = 40 mm/min.

– Figure 5 shows the characteristic temperatures found under constant conditions. Even at the low heating rate of 2.5 deg min^{-1}, the thermal conductivity of the sample exerts a strong influence on the measured temperatures, with the exception of the extrapolated onset-temperature.

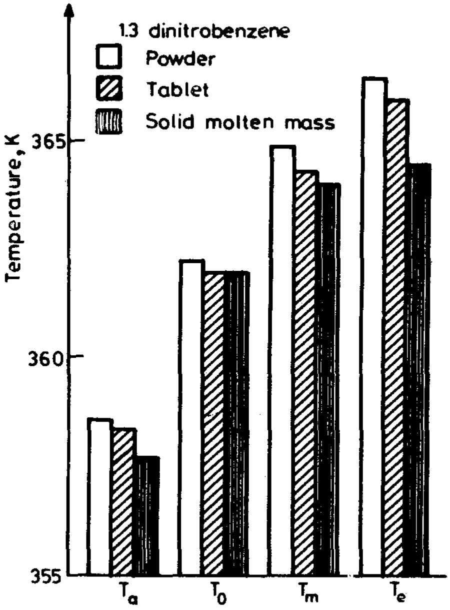

Fig.5 Influence of the sample state on the peak temperatures (1,3-dinitrobenzene). $E = 5$ mcal/s; $m = 5$ mg; $\beta = 2.5$ deg/min; PV = 40 mm/min.

– On account of the very good thermal conductivity of indium, $\lambda = 86.0$ W m^{-1} deg^{-1} [14], the characteristic temperatures are found in a small temperature range (Fig. 6). The dependence of these temperatures on the heating rate will be registered only at higher heating rates.

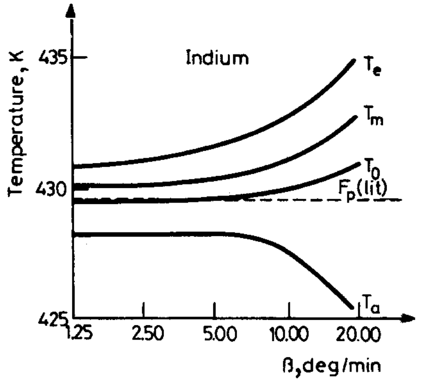

Fig. 6 Peak temperatures as a function of heating rate (indium). $E = 5$ mcal/s;. $m = 5$ mg; PV = 40 mm/min.

– The differences within the melting range of the investigated substances are shown in Fig. 7. The large melting range of the polyethylene sample can be clearly seen.

– The discussed differences with respect to the thermal conductivity, caused by the different natures of the substances and by the modes of preparation of the samples, also influence the shape factor y, as can be seen in Fig. 8. When the sample mass, chart speed, sensitivity and heating rate are kept constant, flatter peaks are obtained for the 1,3-dinitrobenzene powder than for tablet of the same substance.

– As can be expected with of power-compensation DSC, the enthalpimetric result is independent of the experimental parameters if the shape of the peak is favourable for determination of the area ($0.5 < y < 2.0$). We found the following values for the enthalpy of fusion:

– indium:	$\Delta H^{SL} = 28.6$ J/g
– 1,3-dinitrobenzene:	$\Delta H^{SL} = 100.4$ J/g
– polyethylene:	$\Delta H^{SL} = 212.0$ J/g

The relative error was ± 1.2%.

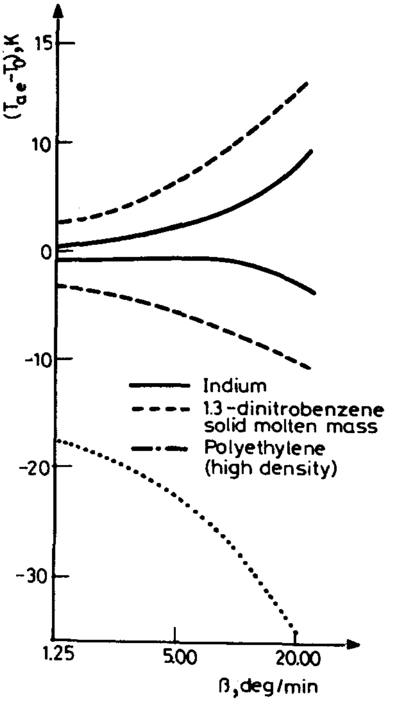

Fig. 7 Comparison of the peak interval for all investigated samples as a function of heating rate. E = 5 mcal/s; m = 5 mg; PV = 40 mm/min.

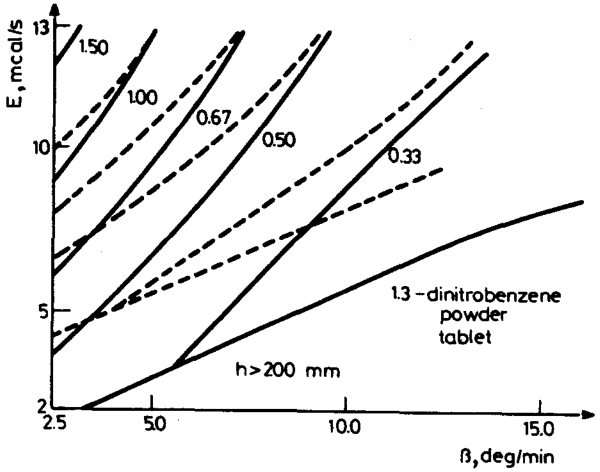

Fig. 8 Shape factor y as a function of sensitivity and heating rate (1,3-dinitrobenzene as powder or tablet). m = 5 mg; PV = 80 mm/min.

The results of our investigations provide an insight into the complex character of the considered dependences and their effects on the shapes of the measured signals. They permit a critical evaluation of values obtained in a similar way.

Further, it is possible to formulate instructions for the substance-specific preparation of the sample and to select the best experimental parameters. Thus, our investigations contribute towards the attainment of reliable and comparable values.

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Zusammenfassung — Die zunehmende Bedeutung quantifizierbarer Ergebnisse von dynamischen kalorimetrischen Messungen veranlasste die Autoren [1–9] zur Untersuchung des Einflusses einzelner experimenteller Parameter. Nach unseren Erfahrungen können diese Ergebnisse nur in komplexer Form dargestellt werden. Entsprechend wurden die Versuchsbedingungen nach einem statistischen Plan variiert. Zahlreiche Messungen wurden mit unterschiedlich präparierten Indium-, 1,3-Dinitrobenzen- und Polyethylen-Proben durchgeführt und die Ergebnisse in komplexer Form ausgewertet. Dabei zeigte sich ein signifikanter Einfluss der Probeneigenschaften und der Versuchsbedingungen.

РЕЗЮМЕ — Исходя из значимости количественных результатов динамических калориметрических измерений, рядом авторов было изучено влияние параметров одного эксперимента. В настоящем сообщении показано, что эти результаты могут быть представлены корректно только в комплексной форме. В связи с этим, экспериментальные параметры были изменены на основании статических диаграмм экспериментов. Проведены многочисленные эксперименты с образцами индия, 1,3-динитробензола и полиэтилена, полученных различными способами. Оценка результатов, проведенная в комплексной форме, показала значительное влияние свойств вещества и экспериментальных параметров.