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APPLICATION OF THE Q-DERIVATOGRAPH FOR EVALUATION OF THE MELTING ENTHALPIES OF LOW-MELTING COMPOUNDS

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A Q-derivatograph was used for quantitative studies on low-melting compounds. The apparatus was calibrated with four selected compounds. Their melting temperatures were between 30 and 90°, while their melting enthalpies were known from the literature and were verified by DSC. The calibration curve turned out to be a straight line, and a mean calibration coefficient was determined between 30 and 90°. The Q-derivatograph was then applied for quantitative studies of oligoethyleneadipate (OEA-2000), with a melting temperature between 46 and 55°, depending on its crystal form. The values of ΔH_m depended on its morphological form, which was associated with the magnitude of the internal stresses.

DTA is regarded by some investigators as a qualitative method, and DSC is recommended for quantitative studies of the thermal effects of phase transitions [1]. However, a DTA apparatus in which the sample and the reference material are isolated (i.e. when there is no heat flow between the sample and the reference material) can be used for quantitative studies after calibration [2]. The average accuracy in the determination of the enthalpies of phase transitions by DTA is now ±5% [3].

There is a lack of information in the literature about the application of DTA curves obtained with a Q-derivatograph for the evaluation of melting enthalpies (ΔH_m) of low-melting compounds, e.g. initial oligomers for the synthesis of polymers. There is also a lack of verified standards with determined values of ΔH_m, and at the same time with melting temperatures (T_m) between 30 and 90°, which can be used for the calibration of DTA apparatus. The only known standard in this range of temperature is *o*-terphenyl, but this is used only for the calibration of the temperature scale [4].

For the evaluation of ΔH_m with the use of a Q-derivatograph, we propose the equation below, similar to that used in DSC [5]:

$$H_m = K\frac{F}{M \cdot V} \tag{1}$$

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where: H_m = melting enthalpy, J/g,
K = calibration coefficient (for a given apparatus), J/m · s,
F = peak area, m^2,
M = sample weight, g,
V = recorder paper speed, m/s.

The value of K depends on many parameters of the apparatus work, and particularly on temperature. The relation between the value of K and the temperature of work is usually presented as a calibration curve [6].

In this paper the value of K for a Q-derivatograph was evaluated with the use of selected, pure, crystalline, organic compounds. Their T_m are between 30 and 90°, and the only phase transition they undergo in this range of temperature is melting. Despite the fact that their ΔH_m values are known from the literature [7, 9], they were examined by DSC.

The average K value was then used to determine the ΔH_m values of oligoestradiols (OED), which depend on their crystal forms. The results obtained with the Q-derivatograph were verified through DSC.

Experimental

Conditions of studies with a Perkin–Elmer DSC–2 microcalorimeter:

— heating rate: 2.08×10^{-2} degree/s (1.25 deg/min),
— recorder paper speed: 8.33×10^{-5} m/s (5 mm/min),
— range of apparatus scale: 4.1868×10^{-2} J/s (10 mcal/s),
— sample weight: 0.01–0.06 g,
— start temperature: 270 K.

Three samples of each chosen compounds were prepared in three ways:

(1) The melted compounds were poured into aluminium crucibles and left to crystallize freely at room temperature.
(2) The crystalline compounds were put into aluminium crucibles and covered with aluminium lids.
(3) The crystalline compounds were put into aluminium crucibles, which were closed hermetically. Since the scattering of the results was lowest for this group of samples, the results obtained in this way were taken into further consideration.

The ΔH_m values were calculated with the equation below [5]:

$$\Delta H_m = K_0 \frac{R \cdot A}{W \cdot S \cdot B} \qquad (2)$$

where: ΔH_m = melting enthalpy, J/g,
K_0 = calibration coefficient; here $K_0 = 1$,
R = range of apparatus scale, J/s,
A = peak area, m^2,
W = sample weight, g,
S = recorder paper speed, m/s,
B = constant; here $B = 0.237$ m

Conditions of DTA studies with the Q-derivatograph (MOM, Budapest):

— DTA sensitivity: 1/1,
— heating rate: 2.08×10^{-2} degree/s (1.25 deg/min),
— recorder paper speed: 3.33×10^{-5} m/s(2 mm/min),
— range of temperature scale: 398 K,
— thermocouples in two variants: 1. Pt/Pt–Rh in a porcelain tube for the reference and in a quartz tube for the sample (thermocouple from dilatometric unit); 2. both termocouples in porcelain tubes (thermocouples for DTA only),
— testing on blocked balance,
— dilatometric bar in constant extreme top position,
— testing in atmospheric air with the use of a quartz cover,
— cylindrical crucibles made of Pt; depth 5×10^{-3} m, diameter 9.5×10^{-3} m (reference crucible empty),
— sample weight: 0.1–0.2 g.

The samples were prepared in two ways:

(1) Melted compounds were poured into the crucible and left to crystallize freely at room temperature. One portion of each compound was tested (melted) and crystallized several times.
(2) A portion of crystalline compound was put into the crucible and covered with a platinum lid. One portion was tested once only. Since the scattering of the results was lowest for this group of samples, the results obtained in this way were taken into further consideration.

The K values were calculated with the transformed Eq (1):

$$K = \frac{\Delta H_m \cdot M \cdot V}{F} \tag{3}$$

Melting temperatures and peak areas were determined as exemplified in Fig. 1. Peak areas were determined by cutting out the peaks, weighing them with an accuracy of 10^{-4} g and taking into account the density of the recorder paper.

Results and discussion

Compounds for calibration of Q-derivatograph.

For evaluation of K with the Q-derivatograph, four pure compounds were used: 2-methylnaphthalene (MN), benzophenone (BF), 4-nitrotoluene (NT) and 1,3-dinitrobenzene (DNB). These compounds were chosen because of their relatively high ΔH_m values, with their T_m in the same range as for the OED studied in our paper.

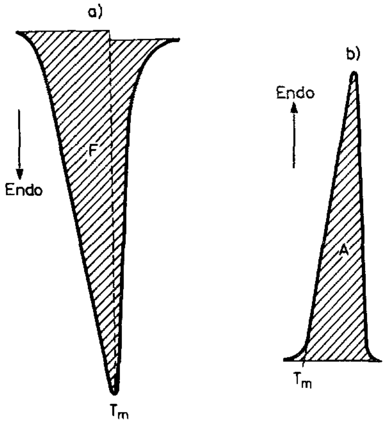

Fig. 1 A DTA (a) and a DSC (b) curves for the determination of ΔH_m and T_m

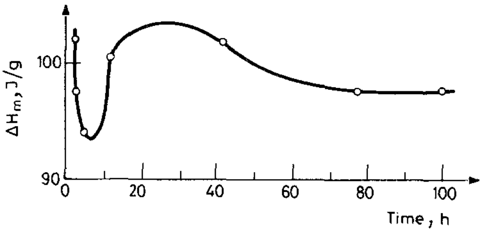

Fig. 2 ΔH_m versus time for DNB

It is characteristic that each of these compounds exists in various, stable or unstable crystal forms [8]. This was confirmed during our studies of one portion of a given compound, when it was melted during tests and crystallized at room temperature several times. The presence of such unstable crystal forms is illustrated in Fig. 2, where the results for DNB are showsn. The intraconversion from the unstable to the stable crystal form of DNB proceeds slowly. Such transformation is extremely slow for MN. However, samples which had been melted, crystallized and seasoned in crucibles for a long time had the same ΔH_m as samples of commercially available material, within an accuracy of ±2%. For this reason, in further studies we used samples of commercial material, which were put into the crucible immediately before testing and were tested only once.

The ΔH_m values of the chosen compounds, as determined from the DSC curves, are given in Table 1. These values were used for the evaluation of K with a Q-derivatograph. Table 1 also contains ΔH_m values from the literature. The T_m values for the compounds are given in Table 2.

Table 1 The values of ΔH_m determined with the use of DSC curves and the values found in literature for the compounds used to the calibration of Q-Derivatograph

Reference	ΔH_m, J/g			
	MN	BF	NT	DNB
DSC	76.4 ± 2.1%	90.8 ± 1%	106.7 ± 1%	98.0 ± 1.4%
(7)	85.4	91.8	126.7	121.4
(8)	84.2, 84.5	90.9	112.6	103.4

Table 2 The values of T_m determined from DSC and DTA curves and the values found in literature for the compounds used to the calibration of Q-Derivatograph.

Reference	T_m, °C			
	MN	BF	NT	DNB
DSC	32	50	54	91
DTA	34	49	53	89
(7)	34.6	48	51.6	90.8
(8)	32–34	46–48.5	51.25–52.9	89.8

The ΔH_m values determined from the DSC curves turned out to be smaller than the literature values (except for BF), which may have been a result of testing compounds that were not analytically pure. The differences between the T_m values were negligible and may have been due to the different method of their determination.

Calibration of the Q-derivatograph

The relation found between K and T_m with the Q-derivatograph for the chosen compounds is shown in Fig. 3. K was independent of either the type of thermocouple or the presence of the dilatometric bar. Its value was 0.4114 ± 2% J/m · s and was constant in the temperature range between 30 and 90.

The accuracy of the determination of peak areas, when the DTD thermocouple is used for the sample, depends on the mutual positions of the two thermocouples, i.e. the one for the sample and the other for the reference. These positions are different from what is proper when the DTA thermocouple is used for the sample. Only then is proper and reproducible determination of the base line in the region of the peak possible. The mutual positions of the thermocouples, and examples of DTA for NT and DNB which were obtained during our studies, are shown in Fig. 4. The positions of the thermocouples are quite opposite to what is recommended in the

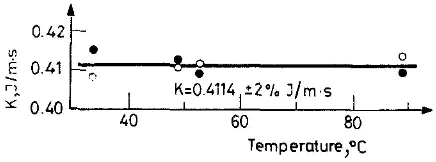

Fig. 3 The calibration curve of Q-Derivatograph in the range of temperature between 30°C and 90°C.
● thermocouple DTD
○ thermocouple DTA

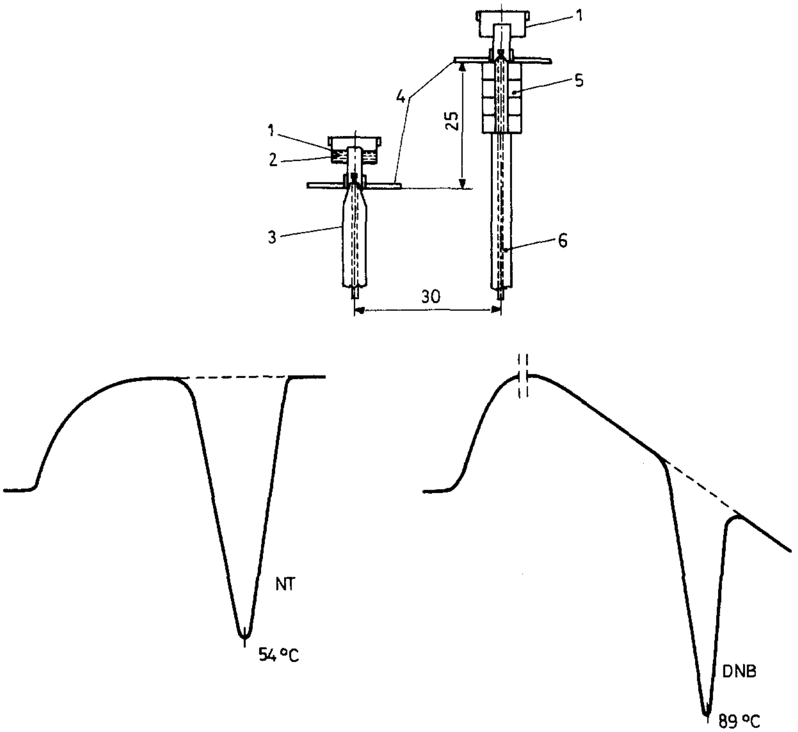

Fig. 4 The scheme of the mutual position of the thermocouple of sample and the thermocouple of reference and DTA curves for NT and DNB corresponding with it:
1 — platinum crucible with platinum lid,
2 — sample,
3 — the thermocouple of sample in quartz tube (DTD),
4 — flat platinum crucible (as a holder),
5 — porcelain beads,
6 — the thermocouple of reference in porcelain tube

Table 3 The results of the studies of OEA–2000.

No.	Crystal form and morphology form [10]	The conditions of preparing of samples, T, °C; τ, s	ΔH_m, J/g	
			DTA	DSC
1.	β form, radial spherulites	melting: $T=100$; $\tau=1.2\times10^3$ crystallization: $T=14$, $\tau=3.6\times10^3$	53.8	54.0
2.	α form, needle like spherulites	melting: $T=100$; $\tau=1.2\times10^3$ crystallization: $T=38$; $\tau=5.4\times10^5$	54.0	54.5
3.	β and α form, frenged spherulites	melting: $T=100$; $\tau=1.2\times10^3$ crystallization: $T=28$; $\tau=0.2\times10^3$	44.4	46.0

literature, i.e. both crucibles ought to be fixed at the same level [9]. The results of our studies show that the mutual positions of the DTD thermocouples should be selected for studies of a given substance if ΔH_m is to be evaluated with an accuracy of at least ±2%.

It should be noted that the density of the recorder paper is not constant throughout its length. This considerably influences the accuracy of calculation, and we recommend determination of the density of the paper for each curve from a piece of the paper near the curve. This holds both for the paper for the Q-derivatograph and for the paper of the microcalorimeter produced by Perkin–Elmer.

Studies of OED

After the calibration coefficient for the Q-derivatograph had been determined, we could use this apparatus for studies of oligoethyleneadipate with a molecular weight of 2047 (OEA–2000) and T_m = 46–55°. The results of the studies were verified by means of DSC.

OEA–2000 was melted, then put into crucibles and crystallized. The conditions of melting and crystallization are given in Table 3, together with the results of the studies.

Table 3 shows that the DTA and DSC results are practically identical within the error limits. ΔH_m for the samples of spherulites was considerably smaller than for the samples of radial and needle-like spherulites. The difference was about ten times higher than the limit of error of the methods, so it was a result of the differences between the internal states of the samples.

The differences in ΔH_m may have been caused by the high intensity of internal stresses in the samples of spherulites. We know that spherulites, in contrast to radial and needle-like spherulites, display a sharp maximum in the density of intra-spherulite cracks [10]. This fact is presumed to be a result of the internal stresses higher than the breaking stress, which arise as a result of crystallization. This hypothesis was confirmed by the above results of our studies.

Conclusions

The Q-derivatograph can be applied for quantitative studies of the ΔH_m of low-melting compounds when the calibration curve or the mean value of calibration coefficient in a given range of temperature is determined.

For the Q-derivatograph, $K = 0.4114$ J/m·s in the temperature range 30–90°, independently of the kind of thermocouples.

Only selected compounds can be used as standards for calibration. Their T_m must be in a given range of temperature and must be known, their ΔH_m must be high and known, and the only phase transition they can undergo in this temperature range is melting. They should exist in a stable form immediately before melting.

Quantitative DTA studies on low-melting compounds with the Q-derivatograph can reveal differences in ΔH_m associated with the various internal states of the samples.

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Zusammenfassung — Ein Q-derivatograph wurde zur quantitativen Untersuchung von tiefschmelzenden Verbindungen benutzt. Die Apparatur wurde mit vier ausgewählten Verbindungen kalibriert, deren Schmelzpunkte zwischen 30 und 90° liegen und deren Schmelzenthalpien aus der Literatur bekannt sind und mittels DSC verifiziert wurden. Die Kalibrationskurve ist eine Gerade und für den Bereich von 30–90° wurde ein mittlerer Kalibrierungskoeffizient ermittelt. Der Q-Derivatograph wurde dann zu quantitativen Untersuchungen von Oligoäthylenadiapat (OEA–2000) mit von der Kristallform abhängigen Schmelztemperaturen zwischen 46 und 55° eingesetzt. Die Werte von ΔH_m hängen von der morphologischen Form ab, die mit der Größe der inneren Spannung in Zusammenhang gebracht wird.

Резюме — Q-дериватограф был использован для количественного исследования низкоплавящихся соединений. Для калибровки аппаратуры были взяты четыре соединения, температура плавления которых находилась в интервале температур 30–90°, а энтальпия их плавления была взята из литературных источников и проверена методом ДСК. Градуировочная кривая представляла собой прямую линию и был определен средний коэффициент градуировки в области температур 30–90°. Затем Q-дериватограф был использован для количественного определения олигоэтиленадипината, плавящегося, в зависимости от кристаллической формы, между 46 и 55°. Значения ΔH_m зависят от морфологической формы, связанной с величинами внутренних напряжений.