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DETERMINATION OF SOLIDUS AND LIQUIDUS TEMPERATURES BY MEANS OF A PERKIN–ELMER 1B DIFFERENTIAL SCANNING CALORIMETER

R. RADOMSKI and M. RADOMSKA

Institute of Organic and Physical Chemistry, Technical University, 50 370 Wrocław, Poland

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A Perkin—Elmer 1B DSC apparatus was used to test the O'Neill expression for the melting interval of pure compounds on samples of organic compounds 1—10 mg in weight. On the basis of O'Neill's model, an expression for the melting interval of solid solutions, ΔT, has been derived. The difference between ΔT and $T_l - T_s$ (T_l and $T_s =$ = liquidus and solidus temperatures) is discussed. A simple procedure for the determination of solidus and liquidus temperatures from DSC data is proposed.

List of symbols used

T	temperature of solidus-liquidus interface, K;
T_s, T_l	solidus and liquidus temperature, respectively, K;
T_i, T_f	initial and final transition temperature, respectively, in a DSC curve, K;
T_0	temperature of sample container bottom, K;
T_p	temperature of thermal energy source, K;
ΔT	temperature interval of non-isothermal or "complex" transition in a DSC curve, K;
ΔT_{iso}	temperature interval of isothermal transition in a DSC curve (temperature resolution of "sharp" transition), K;
$\dot{T}_p$	scanning rate, $K \cdot min^{-1}$;
ΔH	transition energy, J;
W	heat flow rate, $J\ min^{-1}$;
R_0	thermal resistance between sample and sample holder, $K \cdot min\ J^{-1}$;
r	sample thermal resistivity, $K \cdot cm \cdot min \cdot J^{-1}$;
η	specific transition energy, $J \cdot g^{-1}$;
ρ	sample density, $g \cdot cm^{-3}$;
m	sample weight, g;
A	area of contact between sample and sample pan, cm^2;
x	thickness of liquid layer, cm;
t	time, min;
Δt	time interval of transition (peak width), min.

Differential scanning calorimetry (DSC) has become a popular tool for investigating thermodynamic properties, and amongst others for the determination of phase diagrams. During studies of the phase diagrams of binary systems, three thermal events are most frequently observed: (i) isothermal ("sharp") transition, e.g. melting of pure compounds, melting of eutectic of peritectic alloys; (ii) non-isothermal ("diffusion") transition, e.g. melting of solid solutions; (iii) "complex" transition, e.g. melting of binary samples containing some eutectic or peritectic alloy. In this last case the melting can be regarded as a superimposition of sharp and diffusion transitions.

It is well known that in the DSC method both the onset and the end of any transition are a function of the scanning rate, and for this reason the determination of both solidus (T_s) and liquidus (T_l) temperatures in the same DSC experiment is a difficult practical problem. One can overcome this by carrying out two independent measurements, e.g. the determination of T_s by DSC and T_l by means of hot-stage microscopy [1]. The extraction of a true temperature sample by computer treatment of the DSC data [2] seems to be a promising but expensive approach. In this paper a simple and convenient procedure for the estimation of solidus and liquidus temperatures from the same DSC curve is proposed.

Experimental

Initial purification was carried out by crystallization as follows: naphthalene from benzene; anthracene from toluene; pentachlorophenol (PClOH) and hexachlorobenzene (HClB) from CCl_4. Diphenyl and pentachloronitrobenzene were initially purified by sublimation through activated carbon under vacuum. The details will be given elsewhere.

All the compounds were subsequently purified by vacuum sublimation and zone-refining; approximately 100 zone passes were made. An alloy between PClOH and HClB was prepared by weighing appropriate amounts of zone-refined components into glass ampoules. The ampoules were then sealed under vacuum. After sealing, the materials were melted, vigorously stirred, rapidly cooled to room temperature and then ground.

Samples masses for the DSC measurements were in the range 1.5 – 10 mg. All samples were sealed in standard aluminium pans. In order to avoid the decomposition of the material during melting, the encapsulation of PClOH and PClOH – – HClB alloys was made in a box filled with argon.

Measurements were performed using a Perkin – Elmer 1B DSC with an Ez 10 recorder (Czechoslovakia) with a chart speed corresponding to 1 cm per degree. The curves were recorded after the annealing of the sample holder assembly at 600 K for 15 minutes. Nitrogen was used as a purge gas. The measurements were carried out at four heating rates: 4, 2, 1 and 0.5 degree. $\min^{-1}$ and additionally at 0.25, 0.125, 0.062 and 0.031 degree . $\min^{-1}$ for two samples of naphthalene. In order to obtain the last four scanning rates, the control knob of the calorimeter was connected to an outer motor.

Results and discussion

Melting of pure compounds

The theory of sharp transitions in differential scanning calorimetry reported by O'Neill [3] has been developed by Gusenkov [4]. According to O'Neill, the temperature interval of sharp transition, ΔT_{iso}, is given by the relationship:

$$\Delta T_{\mathrm{iso}} = \left[\dot{T}_{\mathrm{p}} \Delta H \left(2R_0 + \frac{rm}{A^2 \rho}\right)\right]^{1/2} \tag{1}$$

The symbols used here are the same as in ref. [3] (except for ΔT and ΔT_{iso}).

We have tested O'Neill's formula with respect to three questions: (i) Does the melting interval of pure compounds ΔT_{iso}, increase linearly with the square root of the scanning rate, $\dot{T}_{\mathrm{p}}^{1/2}$? (ii) How do the initial, T_{i}, and final, T_{f} temperature of the melting peak depend on $\dot{T}_{\mathrm{p}}^{1/2}$? (iii) Do there exist operating conditions under which the melting of pure compounds can be considered as "the instrument-limited case" [3] where the thermal resistance of the sample, r, is negligible in comparison with the resistance between the sample and the sample hoder, R_0, and where the quantity $2R_0 + rm/A^2\rho$ can be regarded as a constant?

The melting interval was determined as shown in Fig. 1*a* ($\Delta T_{\mathrm{iso}} = T_{\mathrm{f}} - T_{\mathrm{i}}$). The results of ΔT_{iso} determination at four scanning rates for several pure organic compounds are shown in Fig. 2. As can be seen, the quantity ΔT_{iso} increases linearly with the square root of the scanning rate, in agreement with Eq. (1). It should be noted here that we did not observe the disappearance of ΔT_{iso} extrapolated to zero heating rate, if the sample was a solid solution or if the material was decomposing during the melting. Therefore, the plot ΔT_{iso} *vs* $\dot{T}_{\mathrm{p}}^{1/2}$ can be regarded as a test of the purity of the sample.

The dependence of the initial and final temperatures of the melting peak on $\dot{T}_{\mathrm{p}}^{1/2}$, as can be seen in Fig. 3, is also linear. The points of Fig. 3 give a good idea of the experimental scatter. The deviations from linearity are larger than those in Fig. 2 and the scatter of the T_{i} values is due, first of all, to the use of different samples. This last observations is not surprising, since it is well known that the accuracy of temperature determination by the DSC method is limited by the

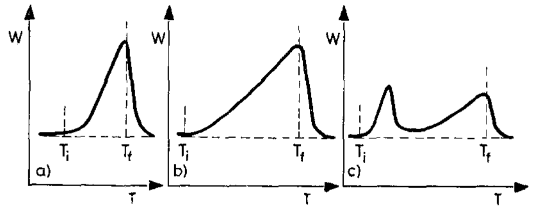

Fig. 1. Schematic representation of the DSC data treatment. a) curve of pure compound, $\Delta T_{\mathrm{iso}} = T_{\mathrm{f}} - T_{\mathrm{i}}$; b) curve of solid solution, $\Delta T = T_{\mathrm{f}} - T_{\mathrm{i}}$; c) curve of binary sample containing some eutectic alloy, $\Delta T = T_{\mathrm{f}} - T_{\mathrm{i}}$

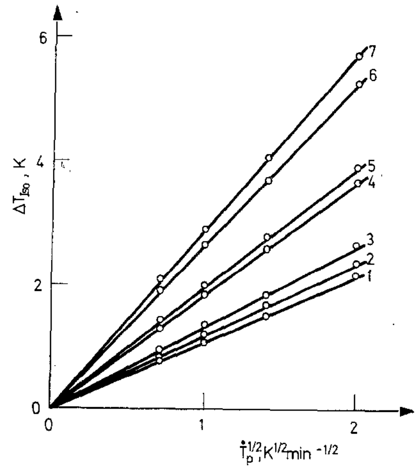

Fig. 2. Temperature interval of melting as a function of square root of scanning rate. 1 — hexachlorobenzene 2.372 mg, 2 — pentachlorophenol 4.053 mg, 3 — naphthalene 2.110 mg, 4 — pentachloronitrobenzene 9.382 mg, 5 — diphenyl 5.760 mg, 6 — naphtalene 9.083 mg, 7 — anthracene 9.730 mg

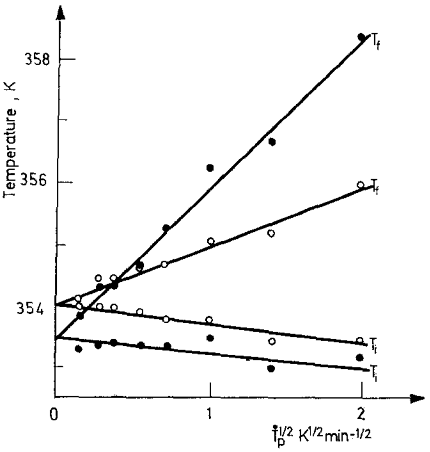

Fig. 3. Initial and final temperatures of melting peak in DSC curve against square root of scanning rate. —o— naphtalene 2.110 mg, —●—naphtalene 9.083 mg

reproducibility of thermal resistance between the sample and the sample holder, and it is not possible in standard operations to obtain an accuracy better than ±0.4 degree [5].

In our opinion, the linear dependence of T_i and T_f on the square root of the scanning rate can be used for the determination of a sharp transition temperature. By using this procedure, we have obtained a higher accuracy of the temperature

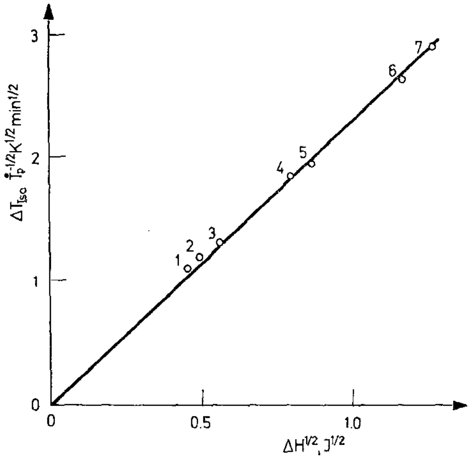

Fig. 4. Variation of $\Delta T_{\rm iso}(\dot{T}_p)^{-1/2}$ with square root of melting heat for the same samples as in Fig. 2. The slope $d(\Delta T_{\rm iso}\dot{T}_p^{-1/2})/d(\Delta H^{1/2}) = 2.3$ degree$^{1/2}$. min$^{1/2}$. J$^{-1/2}$. See text for details

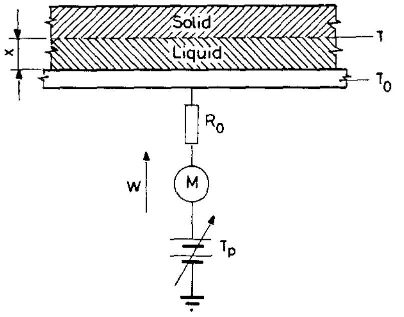

Fig. 5. Scheme of the sample geometry in the DSC apparatus according to ref. [3]. R_0 -- thermal resistance through which the thermal energy flows from temperature source (T_p) to the sample, M — thermal ammeter. See text for details

determination than by means of the measurements performed at one scanning rate (±0.3 and ±0.6 degree, respectively).

Re-plotting the results given in Fig. 2 in a new co-ordinate system, as shown in Fig. 4, allowed us to obtain an answer to the third question. Inspection of Fig. 4 shows that the quantity $\Delta T_{\rm iso}\dot{T}_p^{-1/2}$ increases linearly with the square root of the sample melting heat, $\Delta H^{1/2}$, the slope of this line being $d(\Delta T_{\rm iso}\ \dot{T}_p^{-1/2})/d(\Delta H^{1/2}) = 2.3$ degree$^{1/2}$ min$^{1/2}$ J$^{-1/2}$. The conclusion that can be drawn from this relationship is that the melting of the samples under consideration can be regarded as "the instrument-limited case".

This result indicates that under the conditions used in these experiments (organic compounds, samples in the form of melt 1.5 – 10 mg in weight, scanning rate 0.5

to 4 degree min^{-1}) the melting interval of pure compounds is governed basically by the scanning rate and the transition energy and does not depend on the kind of compound. Therefore, the diagram shown in Fig. 4 can be used for the estimation of the sharp transition interval of any sample if the transition heat is known.

Melting of solid solutions

On the basis of O'Neill's model [3], the melting interval of a solid solution could be derived. A schematic diagram according to [3] is shown in Fig. 5.

The heat flow rate, W, from the temperature source, T_p, through the holder to the sample, is given by Newton's law:

$$W = \frac{T_p - T_0}{R_0} \tag{2}$$

$$W = \frac{A(T_0 - T)}{rx} \tag{3}$$

The melting process can be described by the equation:

$$W = \eta A \rho \frac{dx}{dt} \tag{4}$$

which expresses the conservation of energy.

It will be assumed that the temperature of the solid-liquid interface, T, is given by:

$$T = T_s + \frac{T_l - T_s}{\Delta t} t \tag{5}$$

and that the temperature increases linearly with time:

$$T_p = T_s + \dot{T}_p t \tag{6}$$

After rearrangement and solving, yield the following relation:

$$\frac{\dot{T}_p}{2} t^2 - \frac{(T_l - T_s)}{2\Delta t} t^2 = R_0 A \rho \eta + \frac{r \rho \eta}{2} x^2 \tag{7}$$

For $t = \Delta t$, the quantity $\Delta H / A \rho \eta_0$ (thickness samples) may be substituted for x, and, since $\Delta T = \Delta t T_p$, Eq. (7) becomes:

$$\Delta T^2 - (T_l - T_s) \Delta T = \dot{T}_p \Delta H \left(2R_0 + \frac{rm}{A^2 \rho} \right) \tag{8}$$

Finally, the melting interval of the solid solution, ΔT, is obtained from Eq. (8):

$$\Delta T = \frac{T_l - T_s}{2} + \left[\frac{1}{4} (T_l - T_s)^2 + \dot{T}_p \Delta H \left(2R_0 + \frac{rm}{A^2 \rho} \right) \right]^{1/2} \tag{9}$$

It should be noted here that Eq. (9) for $T_l - T_s = 0$ gives Eq. (1) valid for pure compounds. Comparison of Eqs (9) and (1) provides the relation:

$$\Delta T = \frac{T_l - T_s}{2}\left[\frac{1}{4}(T_l - T_s)^2 + \Delta T_{\mathrm{iso}}^2\right]^{1/2} \tag{10}$$

Inspection of Eq. (10) reveals that the melting interval of the solid solution in the DSC method is related to two terms: the true melting interval of the solid solution, $T_l - T_s$, and the material-instrumental factor, ΔT_{iso}. In this context, the quantity ΔT_{iso} is the melting interval of the same sample, if its fusion was an isothermal transition. As mentioned above, this last factor can easily be estimated from the diagram in Fig. 4., if the fusion heat of the sample, ΔH, is known. Then, the true melting interval of the solid solution, $T_l - T_s$, can be calculated from the following equation:

$$T_l - T_s = \Delta T - \frac{\Delta T_{\mathrm{iso}}^2}{\Delta T} \tag{11}$$

In order to estimate the numerical values of the correction factor, $\Delta T_{\mathrm{iso}}^2/\Delta T$, we have measured the melting interval of six samples of PClOH–HClB mixture containing 0.502 mole fraction of HClB. The PClOH–HClB system was chosen since it is known to form solid solutions in the whole composition range [6]. Typical results for two samples are given in Table 1. The quantity ΔT_{iso} was estimated from the diagram in Fig. 4. Treatment of the DSC curves is demonstrated in Fig. 1b.

As can be deduced from Table 1 for the samples of miligram level, the correction factor has a trivial effect if we take into account that the accuracy of temperature determination in our DSC experiments amounted to ±0.3 degree.

Table 1

Melting interval (ΔT) of two samples of PClOH – HClB solid solution containing 0.502 mole fraction of HClB as a function of scanning rate ($\dot{T}_p$). Values of $T_l - T_s$ have been calculated according to Eq. (11)

m, mg	$\dot{T}_p$, K min^{-1}	ΔT, K	$T_l - T_s = \Delta T - \frac{\Delta T_{\mathrm{iso}}^2}{\Delta T}$
10.912	4	11.5	9.97 = 11.5 – 1.53
	2	10.8	9.97 = 10.8 – 0.83
	1	10.2	9.77 = 10.2 – 0.43
	0.5	9.8	9.57 = 9.8 – 0.23
1.510	4	10.0	9.72 = 10.0 – 0.22
	2	9.6	9.47 = 9.6 – 0.13
	1	9.4	9.34 = 9.4 – 0.04
	0.5	9.5	9.47 = 9.5 – 0.03

However, in the case of larger samples (about 10 mg in weight) the use of the correction factor was necessary.

Equation (11) implies that for solid solutions with small values of $T_1 - T_s$ the correction factor can be significant even under conditions of the high resolution of temperature (small samples, low scanning rates).

Conclusions

We propose the following procedure for determination of solidus and liquidus temperatures form the DSC curve.

The solidus temperature, T_s, may be determined in any way, for instance according to the procedure given by the manufacturer or by that proposed by us in the previous section, or by means of an isothermal temperature calibration method [7]. It is important to note that the T_s determination must be done in just the same way as was used during the correction of the indicated temperature scale of the instrument. Also, the samples should be 5–10 mg in weight. For samples smaller than 5 mg which are not pure compounds, a large fraction of the sample can be melted before the DSC trace rises detectably above the baseline [8]. In this case the uncertainty of the T_s determination may be significant. However, the melting of samples larger than 10 mg should be considered rather as "the sample-limited case", and for this the diagram given in Fig. 4 is not adequate.

The accurate value of the liquidus temperature, T_1, can be calculated as the sum of T_s and $T_1 - T_s$, the latter quantity being obtained as described below.

Firstly, the melting interval, ΔT, should be determined as is demonstrated in Fig. 1.

Solid solution

The $T_1 - T_s$ value may be derived from Eq. (11). In order to get the reading of ΔT_{iso} from the relationship given in Fig. 4, the sample fusion heat, ΔH, must be known. This should be determined experimentally, from the peak area in the curve. However, as a first approximation, the fusion heat of the solid solution can be estimated as the weighted sum of the fusion heats of the components. It was found [9] that, even for the weak charge-transfer complexes where the intermolecular interactions are stronger than those in solid solutions, the fusion heat of the complex is near the sum of the fusion heats of the components. In our experience, too large a difference in the experimental sample fusion heat and that calculated should be treated as an indication that some part of the melting heat was unrecorded due to the reasons mentioned by Davis *et al.*[8].

Sample containing some eutectic alloy

Two limiting cases may be distinguished, depending on the proportion of eutectic alloy to an excess component: "the sharp transition-limited case" and "the diffusion transition-limited case".

In the former case the true $T_l - T_s$ value is equal to $\Delta T - \Delta T_{iso}$, where ΔT_{iso} may be read from the diagram given in Fig. 4 for the ΔH value identified with the fusion heat of the eutectic portion of the sample. Of course, plotting of the melting interval, ΔT, against the square root of the scanning rate and then extrapolation to zero heating rate yields the same result.

Consequently, "the diffusion transition-limited case" can be treated as the melting of a solid solution. As can be deduced both from experimental results and from the comparison of Eqs (1) and (11), the difference between the transition interval as anticipated by thermodynamics and that measured from the DSC curve is much more in the sharp transitions than those involving diffusion. Therefore, if only the fusion of the eutectic portion is measurable, the melting of the whole sample can be considered as "the sharp transition-limited case".

The DSC data for the samples containing peritectic alloy may be treated in the same way as in the eutectic case.

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Zusammenfassung — Ein Perkin—Elmer DSC-Gerät 1B wurde zur Prüfung des O'Neill-schen Ausdruckes für den Schmelzbereich reiner Verbindungen an Proben organischer Verbindungen von 1—10 mg eingesetzt. Auf Grund des O'Neill-schen Modells wurde ein Ausdruck für den Schmelzbereich fester Lösungen, ΔT, abgeleitet. Der Unterschied zwischen ΔT und $T_l - T_s$ (T_l, T_s = Flüssig- und Fest-Temperaturen) wird erörtert. Eine einfache Methode zur Bestimmung von Fest- und Flüssigphasentemperaturen aus DSC-Daten wird vorgeschlagen.

Резюме — Дифференциальный сканирующий калориметр типа 1В фирмы Перкин—Эльмер был использован для проверки выражения О'Нейлля, установленного для интервала плавления чистых соединений на примере органических веществ взятых по весу 1—10 мг. На основании модели О'Нейлля было выведено ΔT для интервала плавления твердых растворов. Обсуждено различие между ΔT и $T_Л$—$T_С$, где $T_Л$ и $T_С$ — температуры ликвидуса и солидуса. Предложен простой метод определения температур ликвидуса и солидуса из данных ДСК.