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On temperature calibration of power compensation DSC in cooling mode

C. Schick[a] and G.W.H. Höhne[b]

[a]Hochschule Güstrow, Institut für Physik, O-2600 Güstrow, F.R.G.

[b]Universität Ulm, Sektion für Kalorimetrie, Postfach 4066, W-7900 Ulm, F.R.G.

Abstract

Differential scanning calorimeters (DSC) are used to determine transition temperatures on cooling. Often temperature scale corrections are linear extrapolated from temperature calibration on heating. For power compensated DSC this extrapolation is not possible in an easy manner due to the influence of the power compensation control circuits. Therefore it is necessary to calibrate the calorimeter on cooling. A smectic-nematic phase transition can be used for this calibration. For four different power compensated DSC a deviation between temperature scales up to 0.7 K in heating and cooling mode is observed.

1. INTRODUCTION

There are several papers dealing with temperature calibration of DSC on heating (see e.g. [1-5]). One of the central aims in this studies is to observe the influence of thermal lag in the DSC cell and in the sample itself on sample temperature. There is taken into account the influence of heating rate, sample weight, heat conductivity, position of sample and so on. There are some symmetry arguments that the proposed corrections can also be used for the cooling mode of DSC [1].

For heat flux DSC this symmetry is normally given. But for power compensated DSC the symmetry of the DSC-cell may be disturbed due to the complicated electronic control circuits. For this reason it is necessary to proof the symmetry at least for this type of calorimeters by calibrating the DSC in cooling mode.

From calibration on heating it is known that the heating rate dependence of the temperature shift is linear. If the symmetry is kept it should be possible to extrapolate this straight line to negative rates (cooling) without any discontinuity at zero heating rate. To proof the symmetry of the power compensated DSC this rate dependence of

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the temperature shift has to be determined at low heating and cooling rates.

Calibration on cooling is not so simple because the commonly used calibration materials (melting of pure compounds) tend to more or less supercooling of the first order transition [6]. Thus it was necessary to find substances which have a clearly defined transition on cooling with a rather small but nevertheless well known supercooling.

2. EXPERIMENTAL

At first we tested three different PERKIN-ELMER DSC (two DSC-2; one DSC-7) using a Indium (99.9999% purity) sample. The same sample and the same reference as well was measured in the range of scanning rates from 40 K/min to -40 K/min in 16 logarithmic steps. Additionally this sample was measured in a heat flux DSC (MCB; Thermanalyse France) using a heating and cooling rate of about 0.1 K/min to determine the supercooling in the quasi-isothermal case. All measurements were carried out within three weeks. In Fig.1 and Tab.1 the results are shown.

The supercooling of this Indium sample was determined as 2.2 K with the heat flux DSC. The values measured with the DSC were corrected with this supercooling (Fig.1 "corrected"). For all powercompensated DSC a positive deviation from the extrapolation of the calibration on heating occurs leading to a discontinuity at zero heating rate. That means, there seems to be an additional heat flux (compensation power) to the sample heater while cooling. From the results in Fig.1 the following is valid:

(i) There are different steps (0.05 up to 0.5K) of discontinuity at zero heating rate for different DSC

(ii) There are different slopes for the rate dependence of temperatur-correction depending on the apparatus in question

From (i) it follows that it is necessary to proof the symmetry (the error) for each power compensated DSC used to determine temperatures in cooling mode and from (ii) that the calibration must be carried out for different rates [1].

Because the supercooling of an Indium sample may depend on the history (number of melting-crystallization cycles) of the sample it can not be used as a reference for calibration in cooling mode. Therefore a phase transition without supercooling should be used as a test material for calibration in cooling mode.

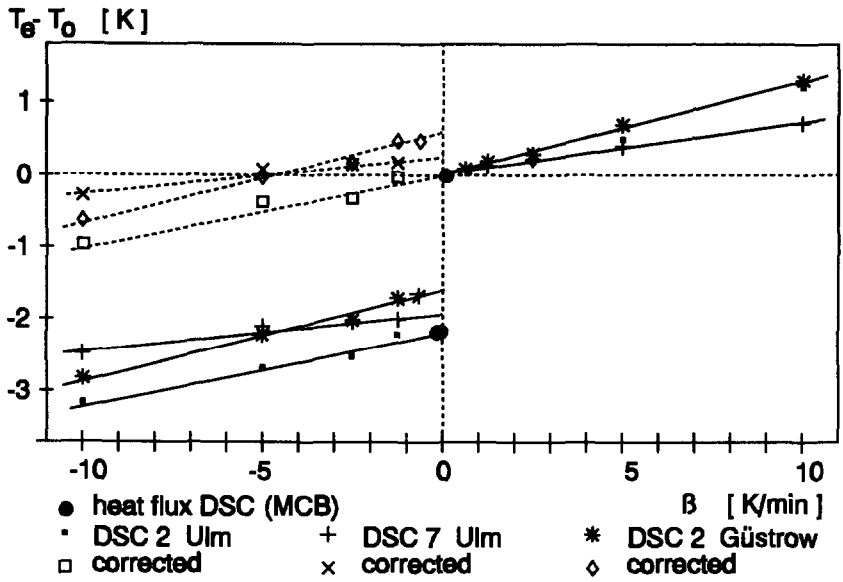

Figure 1. Rate dependence of the tansition temperature deviation of three power compensated DSC for Indium. T_e-extrapolated peak onset; T_o-transition temperature at heating rate zero; the corrected values are from $(T_e - T_o)_{meas.} + 2.2\ K_{supercool.}$

From a thermodynamic point of view a second order transition doesn't show any supercooling. So the lamda-transition of amonium chloride at 244 K was used for testing the calibration at heating and cooling. But, unfortunately, this transition doesn't show well defined transition temperatures in the DSC curves like the peak onset [1] in the melting curve of pure compounds.The peak maximum of a second order transition is well defined. But there is a sample weight dependence of the peak maximum temperature in DSC curves [1], so it has to be corrected to zero sample weight. In Fig.2 the results are shown.

As can be seen the corrected maximum temperature of the lamda-transition is not a linear function of the rate as should be the case for calibration. So it is not possible to use the NH_4Cl transition as a standard neither for heating nor for cooling mode.

An other class of transitions with the possibility of very low supercooling are transitions of liquid-crystalline (LC) phases [6,7]. After testing the phase transition behavior of some different liquid crystals the smectic-nematic transition of hydroquinone bis(4-n-nonyloxy-benzoate) was selected as best suited for a calibration test experiment in four different power compensated and the named heat flux DSC. In Fig.3 and Tab.1

the results are presented.

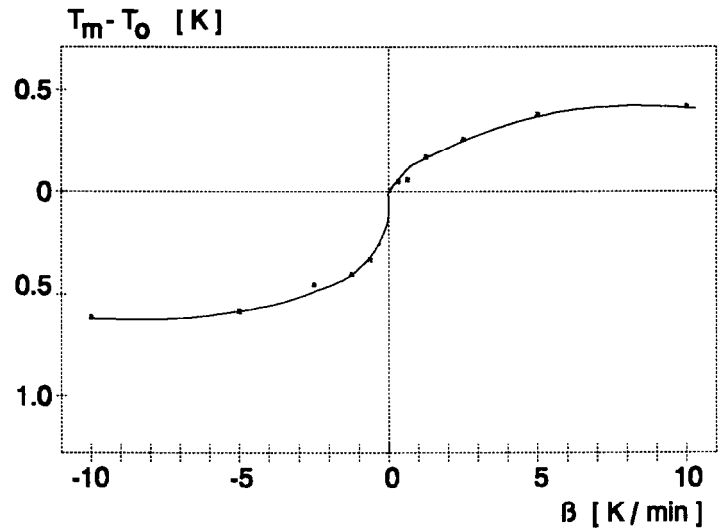

Figure 2. Rate dependence of the temperatur deviation for NH_4Cl (DSC-2; Güstrow). T_m–temperature of the peak maximum, heat flux corrected with the slope of the ascending flank of an Indium melting peak at same heating rate [1]

The measurements with the heat flux DSC result the supercooling to be less than 0.1 K. Taking into account this residual supercooling the difference between the temperature scales in cooling and heating mode results in a value of about +0.6 K (see Tab.1).

3. DISCUSSION

For power compensated DSC a symmetry in temperature correction between heating and cooling mode is not valid. The resulting shift of the temperature scales depends on the calorimeter and it's individual adjustment and on the measuring conditions as well. See for example DSC–2(Ulm) ΔT_{In} = 0.05 K and ΔT_{LC} = 0.76 K. The reason for this unsymmetry is not known yet. First experiments [8] show an influence of the heat flux itself and of the difference between the heat fluxes into the sample and the reference in case of unsymmetry. That means the operation of the

average temperature and the power compensation control circuits result in additional heat fluxes to the sample compared with a standard calibration with Indium and thus an additional temperatur shift occurs.

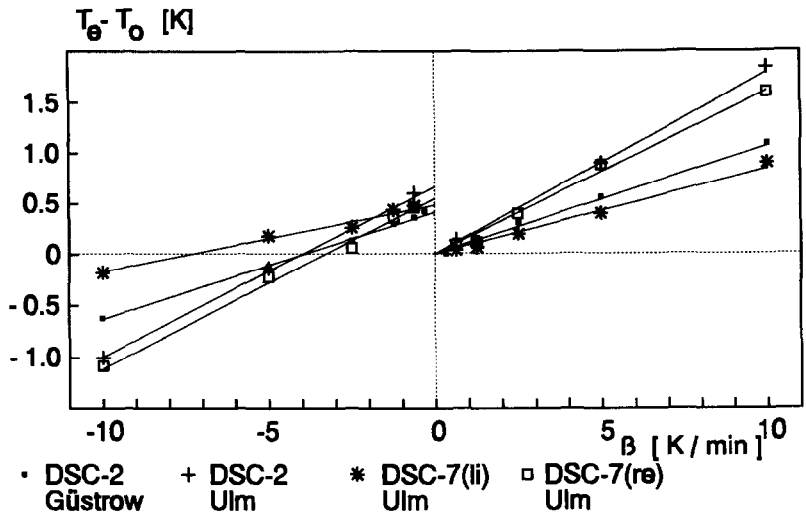

Figure 3. Rate dependence of the temperature deviation of four power compensated DSC for the smectic-nematic transition of hydroquinone bis(4-n-nonyloxy-benzoate)

Table 1
Step in the rate dependence of temperature deviation at zero heating rate for different samples and different DSC corrected with the residual supercooling from the MCB measurement (last column)

Sample	Calorimeter DSC-2 Güstrow	DSC-2 Ulm	DSC-7(li) Ulm	DSC-7(re) Ulm	MCB Ulm
Indium	0.52 K	0.05 K	0.35 K		2.2 K
LC	0.51 K	0.76 K	0.57 K	0.65 K	≈0.1 K

4. CONCLUSIONS

(i) Power compensated DSC show significant differences between the temperature scales in heating and cooling mode.
(ii) For temperature determination in cooling mode with an accuracy better than 1 K a separate determination of the discontinuity at zero heating rate is necessary for power-compensated DSC.
(iii) The conditions for calibration and measurement runs should be the same (the same heat capacity for calibration and measurement in sample and reference pan).
(iv) The used transition of the calibration material should tend to low supercooling (limiting the accuracy of the temperature determination on cooling) and should not show any kinetic behavior.

The results from hydroquinone bis(4-n-nonyloxy-benzoate) show that phase transitions of liquid crystals can be used as a test material for temperature calibration check on cooling. Further investigations are necessary to find phase transitions with lower supercooling and to understand all influences both from electronics and sample parameters on the temperature scales in power compensated DSC.

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