Journal of Thermal Analysis, Vol. 52 (1998) 195-202

Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

DSC INVESTIGATION OF SOME TESTING AND CALIBRATION COMPOUNDS, PARTICULARLY DURING COOLING

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Abstract

Two compounds are described with interesting properties for use in DSC. The first compound is adamantane ($C_{10}H_{16}$), with a reversible solid-solid transition at 208.62 K [1], suitable for DSC calibration at this low temperature [2]. The second compound is 4,4'-azoxyanisole ($C_{14}H_{14}N_2O_3$), with a liquid crystal range between 390 and 407 K [3]. This compound shows two transitions on heating, with a large heat effect at 390 K and a small heat effect at 407 K. For this reason, this substance is well suitable for testing the sensitivity and the resolution of DSC instruments [4]. For both compounds not only the heating, but also the cooling behaviour is investigated.

Keywords: adamantane, 4,4'-azoxyanisole, DSC calibration during cooling, testing of DSC sensitivity, undercooling test

Introduction

For calibration of DSC instruments above 273 K normally pure metals are used (Ga, In, Pb, Zn), with well known temperatures and heats of melting [2, 5]. For reason of undercooling effects, calibration is mostly done in the heating mode. For calibration in the cooling mode only compounds without measurable undercooling effects can be used, but most compounds however, metals and non-metals, show more or less undercooling. Particularly gallium, but also water and organic substances can be easily undercooled below their thermodynamic melting temperature.

For calibration below 273 K however, less compounds exist. In Ref. [2] two suitable substances are mentioned, namely mercury, melting at 234.32 K (ΔH=11.62 J g^{-1}) and adamantane, with a well determined transition in the solid phase at 208.62 K, with ΔH=24.78 J g^{-1} [1]. It will be demonstrated, that both compounds are suitable for DSC calibration, also in the cooling mode [6].

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

For testing of DSC instruments another compound is proposed by Van Ekeren, Hol and Witteveen, namely 4,4'-azoxyanisole [4]. This compound shows two transitions on heating: a solid → liquid crystal transition at about 390 K, with a large heat effect ($\Delta H \approx 120$ J g^{-1}) and a liquid crystal → isotropic liquid transition at about 407 K, with a very small heat effect ($\Delta H \approx 2$ J g^{-1}). This last transition is fast and reversible, and can also be used in the cooling mode, but the crystallization shows a great undercooling effect. The Dutch Thermal Analysis Society (TAWN) made a round robin test with this compound for testing the resolution of a DSC – with a large amount of sample and a high heating rate (5 mg, 20 or 10 K min^{-1}) – and the sensitivity – with a small amount (0.25 mg) and low heating rate (0.1 or 1 K min^{-1}) [4].

This contribution discusses the application of this test for a specific DSC instrument, and also the behaviour of this substance at different heating and cooling rates.

Experiments and results

A DSC instrument from Rheometric Scientific (DSC-GOLD) was used, with a liquid nitrogen cooling device for programmed cooling. Calibration of temperature and DSC signal was made at a heating rate of 10 K min^{-1}, using adamantane, Hg and Ga for the low temperature range, and Ga, In and Sn for the high range. So we expect that figures, measured at +10 K min^{-1} will be best.

The samples were of the highest obtainable purity: the metals >99.999% and the other compounds >98%, and are used without further purification. The samples, except mercury, were contained in flat aluminium crimped pans, with a mass of about 30 mg. Only mercury was measured in a hermetically sealed aluminium pan (mass 48 mg). The sample amount was 5–7 mg for most samples, and for mercury 13.5 mg.

Firstly, the figures are given, used for calibration [1, 2, 5]

Adamantane:	transition at	208.62 K;	ΔH=24.78 J g^{-1}
Hg:	melting at	234.28 K;	ΔH=11.63 J g^{-1}
Ga:	melting at	302.92 K;	ΔH=79.87 J g^{-1}
In:	melting at	429.75 K;	ΔH=28.62 J g^{-1}
Sn:	melting at	505.08 K;	ΔH=60.40 J g^{-1}

After calibration, adamantane was measured at a heating rate of +10 K min^{-1}, and a cooling rate of –10 K min^{-1}. The extrapolated onset temperatures T_o are determined, together with the same figures for mercury and gallium. These figures are:

	T_o (+10 K min^{-1})/	T_o (–10 K min^{-1})/	Difference/
		K	
Adamantane	208.71	207.49	1.22
Hg	234.08	233.14	0.82
Ga	303.05	264.89	38.16

We see that adamantane, just like mercury, shows only little difference between heating and cooling. Gallium however shows a great undercooling effect, and can only be used in the heating mode.

In order to examine, if the difference between heating and cooling onset temperatures is caused by instrumental factors, or maybe by a slight undercooling effect, adamantane is measured at different heating and cooling rates: plus and minus 10, 5 and 1 K min^{-1}. The results are shown in Fig. 1 and in Table 1. In Fig. 1 the heating and cooling peaks are shown, as measured by DSC. We see that the extrapolated onset temperatures T_0 of the endothermic heating peaks and the exothermic cooling peaks are about the same, with an identical shape for heating and cooling curves. In Table 1, the measured values of T_0 are summarized. We see that at decreasing rate the onset temperatures of the heating curves decrease, and of the cooling curves increase. The difference between heating and cooling is lowered from 1.22 K at 10 K min^{-1} to 0.03 K at 1 K min^{-1}. The mean value of the onset temperatures for heating and cooling is about constant.

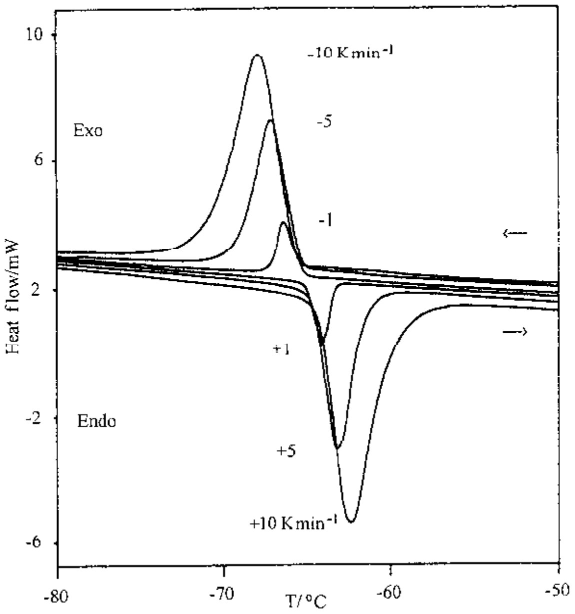

Fig. 1 DSC runs of 5.350 mg adamantane with successive heating and cooling rates. Purge gas N_2 at 1.0 l h^{-1}. Degrees centigrade (°C)=K–273.15

This can only be explained by the assumption that the temperature differences are caused by the heat transport inside the applied heat-flux DSC, because a thermal lag must exist between sample and sensor. The mean temperature $\bar{T}$ however, remains constant at different heating and cooling rates, because of a symmetrical heat transport during heating and cooling.

Table 1 Heating and cooling of 5.350 mg adamantane with different rates (10, 5 and 1 K min^{-1}). The extrapolated onset temperatures T_0 (K), the temperature difference ΔT and the mean value $\bar{T}$ between heating and cooling with the same rate are given. Further, the measured heat effect ΔH (J g^{-1}) is given

Rate/ K min^{-1}	Heating		Cooling		ΔT/K	$\bar{T}$/K
	T_0/K	ΔH/J g^{-1}	T_0/K	ΔH/J g^{-1}		
10	208.71	24.66	207.49	–24.96	1.22	208.10
5	208.30	23.48	207.80	23.67	0.50	208.05
1	208.05	22.59	208.02	–22.33	0.03	208.03

When undercooling should appear, no constant value of $\bar{T}$ is expected. Further the crystallization peak should show a very steep increase at the beginning of the exothermic peak P, resulting into a different shape for heating and cooling curves. For these reasons we may assume that no perceptible undercooling exists. So adamantane can be used for calibration, as well during heating as during cooling runs.

Some remarks can be made:

– Since the preliminary calibration was made with a heating rate of +10 K min^{-1}, the figures, measured at this heating rate, show the best agreement with the literature values.

– The measured heat values decrease with decreasing rate. This is probably caused by a more difficult determination of the base line, when the heating and cooling rates decrease, and also the peak heights.

The second investigated compound (4,4'-azoxyanisole) has interesting properties for testing DSC instruments. The reason is, as already mentioned, that this compound has a liquid crystal range between 390 and 407 K. The first transition at 390 K corresponds with a high amount of heat (ΔH=120 J g^{-1}), while the second transition at 407 K shows a small heat effect (ΔH=2 J g^{-1}).

So the DSC curve shows two peaks on heating: a large peak, immediately followed by a small peak. Application of a large amount of sample and a high heating rate (5 mg, 20 K min^{-1}) makes it possible to test the resolution (Fig. 2).

Use of a small sample amount (0.25 mg) and a slow heating rate (0.1 or 1 K min^{-1}) gives a measure for the sensitivity (Fig. 3).

The exact procedure is described by Van Ekeren, Hol and Witteveen [4]. In this contribution DSC runs are made in heating and cooling mode. Such a heating and cooling run is shown in Fig. 4. In that figure we see that the low temperature peak (solid → liquid crystal) shows severe undercooling. The second peak, however, is completely reversible on heating and cooling (liquid crystal → isotropic liquid). So the sensitivity can also be tested in the cooling mode, since only the reversible peak and the baseline are needed, but the resolution can only be measured during heating, because both peaks are necessary.

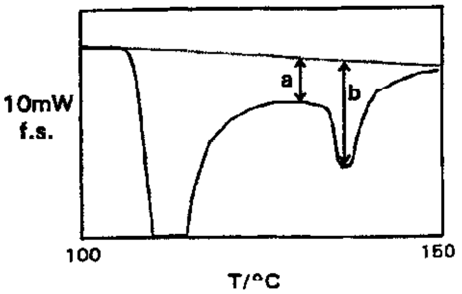

Fig. 2 The TAWN resolution test with 5 mg sample at +20 K min^{-1}. Purge gas N_2 at 1.0 l h^{-1}. Degrees centigrade (°C)=K–273.15. The resolution is given by the quotient *a/b*. [4]

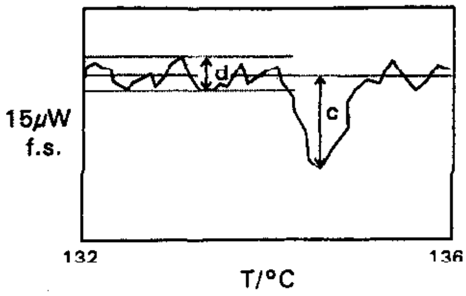

Fig. 3 The TAWN sensitivity test with 0.25 mg sample at +0.1 K min^{-1}. No purge gas. Degrees centigrade (°C)=K–273.15. *c* is the height of the peak (at 410 K) and *d* is the peak to peak noise between 405 and 407 K. The sensitivity is given by the quotient *c/d*. [4]

The results of the resolution tests are compiled in Table 2. See also Fig. 2. In this Table the resolution quotient *a/b* is given. A decrease of this qoutient corresponds with an increase of the resolution. A fast instrument, with a small time constant, will have a high resolution and so a low value of *a/b*.

However, it is not possible that *a/b* becomes zero as indication for complete resolution. The reason is that the liquid crystal phase has a higher specific heat than the surrounding phases. This will mean that always a remaining endothermic heat flow is visible in the liquid crystal range, even when the peaks are totally separated. Comparison of the heating rate effect shows that the resolution quotient decreases with decreasing heating rate, but never becomes zero: 20 K min^{-1}, *a/b*=0.40; 10 K min^{-1}, *a/b*=0.15 and 5 K min^{-1}, *a/b*=0.10.

In Table 2, also a resolution measurement is included for the DSC-SP, being a newly developed DSC cell from Rheometric Scientific. At 20 K min^{-1} the resolution quotient is 0.26, so the SP – cell has a better resolution than the DSC-GOLD (*a/b*=0.40).

Results of the sensitivity test are given in Table 3. See also Fig. 3. In this Table measurements at +1 K min^{-1} and –1 K min^{-1} are included. Further, for the DSC-SP also results at a heating rate of +0.1 K min^{-1} are given. The peak to peak noise d is for the DSC-GOLD cell about 10 μW, and the peak height c about 30μW (at 1.0 K min^{-1}), resulting in a sensitivity quotient c/d being about 3.0 for a heating and cooling rate of 1.0 K min^{-1}. The figures for the DSC-SP cell are better: at

Table 2 Resolution test with 5 mg 4,4'-azoxyanisole at different heating rates. a is the minimum distance between baseline and DSC curve (mW) and b is the height of the high temperature peak (mW). The resolution is given by the quotient a/b. Further the extrapolated onset temperatures of both peaks T_0 (1) and T_0 (2) are given. Two different instruments are tested

Instrument	Heating rate/ K min^{-1}	a/mW	b/mW	a/b	T_0 (1)/K	T_0 (2)/K
DSC-GOLD	+20	0.807	1.860	0.43	390.61	407.95
DSC-GOLD	+20	0.684	1.782	0.38	–	–
DSC-GOLD	+10	0.215	1.413	0.15		
DSC-GOLD	+ 5	0.097	0.960	0.10	390.30	407.55
DSC-SP	+20	0.621	2.366	0.263	390.67	407.59

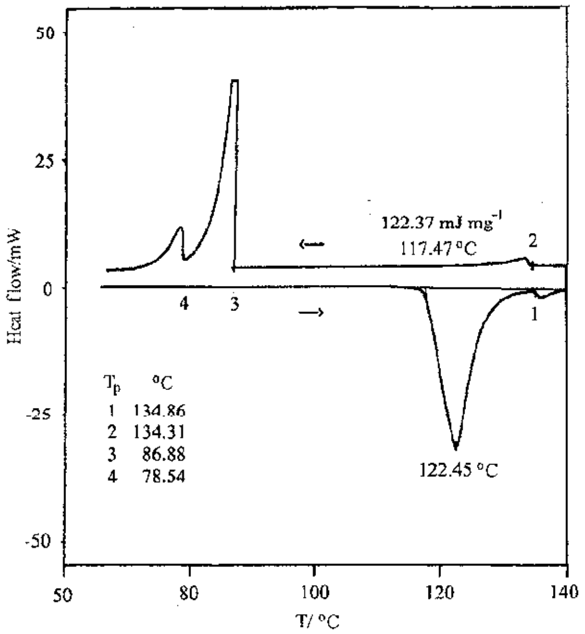

Fig. 4 DSC runs of 4.653 mg of 4,4'-azoxyanisole at successively +20 and –20 K min^{-1}. Purge gas N_2 at 1.0 l h^{-1}. Degrees centigrade (°C)=K–273.15. The low temperature peak shows strong undercooling but the small high temperature peak remains at about the same temperature (extrapolated onset 408.01 and 407.46 K, respectively). Exothermal is up and endothermal is down

Table 3 Sensitivity test with about 0.25 mg of 4,4'-azoxyanisole. Heating and cooling rate 1.0 and 0.1 K min^{-1}. *d* is the peak to peak noise between 405–407 K (μW) and *c* is the height of the high temperature peak (μW). The sensitivity is given by the quotient *c/d*

Instrument	Heating/Cooling rate/ K min^{-1}	*c*/μW	*d*/μW	*c/d*
DSC-GOLD	+1.0	24.6	8.1	3.03
	+1.0	30.0	8.5	3.53
	–1.0	29.4	10.6	2.77
DSC-SP	+1.0	17.0	1.75	9.70
	+0.1	2.30	2.20	1.00
	–1.0	18.5	1.45	12.7

1.0 K min^{-1} is the peak noise *d* about 1.6 μW, while the peak height *c* is about 18 μW at + or –1 K min^{-1}, so the sensitivity quotient *c/d* is about 11 (at 1 K min^{-1}). This is much better than for the DSC-SP being *c/d*=3. It was also possible to do the experiment at +0.1 K min^{-1}, but only for the DSC-SP. Now the peak is still clearly visible, giving a sensitivity quotient *c/d*=1.

Conclusions

– Adamantane, having a solid → solid transition at 208.62 K, can be used for DSC calibration, both for DSC signal and temperature.

– Since this transition is fast and reversible, the compound can be used in the heating mode and also during cooling.

– Maybe there is no undercooling because of the compact molecular shape of adamantane.

– Mercury, melting at 234.28 K is also suitable for DSC calibration during heating and cooling.

– Gallium however, melting at 302.92 K, shows severe undercooling and can only be used in the heating mode.

– Another compound with interesting transitions is 4,4'-azoxyanisole.

– This compound shows two transitions: solid → liquid crystal at about 390 K, with a great heat effect, and liquid crystal → isotropic liquid at about 407 K, with a small heat effect.

– The transition at 407 K is fast and reversible, and can be applied in the heating and in the cooling mode.

– The transition at 390 K shows undercooling. So application is only well possible during heating reactions.

– The resolution of a DSC instrument can be tested with a large amount of sample and high heating rate (5 mg; 20 K min^{-1}).

– The sensitivity can be tested with a small amount of sample and a small heating or cooling rate (0.25 mg; 0.1 or 1.0 K min^{-1}).

– By application of these tests, different DSC instruments can be compared.

– Of course, not only these tests are important. Also factors like robustness, price, gas handling, etc. are important.

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