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DSC CALIBRATION DURING COOLING

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Abstract

A number of compounds are investigated for DSC calibration during cooling. Adamantane and Zn show fast reversible transitions and can be applied both for temperature and for heat calibration. A third compound, namely 4,4'-azoxyanisole, has a liquid crystal to isotropic liquid transition at 409 K. This compound can be used for temperature calibration. Heat calibration with this compound is more problematic because of the small heat effect and the construction of the baseline. Two other compounds, namely Hg and Pb, show a slight undercooling. Nevertheless they can be used for heat calibration, and possibly also for temperature calibration during cooling.

Keywords: adamantane ($C_{10}H_{16}$), avoidance of sample/pan reactions, 4,4'-azoxyanisole ($C_{14}H_{14}N_2O_3$), DSC calibration during cooling, Ga, Pb, Hg, reversible transitions, undercooling, Zn

Introduction

DSC instruments are normally calibrated using compounds showing first order transitions with well known temperature and heat effect. These calibrations are made in the heating mode. Because of the existence of a time lag, the extrapolated onset temperature T_o varies with the heating rate.

The greatest accuracy is reached with different heating rates and extrapolation to zero-heating rate [1, 2]. This is however a time-consuming method.

A faster method is to compare the investigated compound with some calibration compounds in the appropriate temperature region and with one constant heating rate (for instance 10 K min^{-1}). When the thermal mass of the applied samples does not differ too much, an identical time lag can be expected for all these samples, resulting into a fast practical calibration.

Calibration during cooling is more problematic, because most compounds show undercooling effects. Some compounds however, show no undercooling and behave symmetrically during heating and cooling with the same rate. Application of these compounds results into a fast calibration method, also during cooling. When the applied DSC instrument behaves symmetrically during heating and cooling, which is the case for most heat flux instruments, the mean value $\overline{T}$ of the extrapolated onset temperatures T_o of these compounds for heating and cooling with the same rate is constant and independent of the absolute value of the heating and cooling rate. This

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value $\overline{T}$ corresponds to the value of T_0, determined by extrapolation to heating rate zero, but can be determined in a much faster way!

Until now three different compounds are found to behave symmetrically: adamantane, 4,4'-azoxyanisole and Zn [3]. Other compounds, like Hg and Pb, show slight undercooling effects, while Ga and Sn have a very large undercooling.

In this article experiments under various heating and cooling rates are described for the 'reversible' compounds, and compared with the melting transitions of Hg (234.32 K, ΔH=11.62 J g^{-1}), Ga (302.91 K, ΔH=79.87 J g^{-1}) and Pb (600.61 K, ΔH=23.02 J g^{-1}).

– Adamantane has a reversible solid-solid transition at 208.62 K, with ΔH= 24.78 J g^{-1} [4, 5].

– Zinc melts at 692.677 K with ΔH=111.97 J g^{-1} [1, 6].

– 4,4'-Azoxyanisole shows two transitions on heating:

I, a melting reaction solid → liquid crystal at about 389 K (ΔH=112 J g^{-1}) and II, a liquid crystal → isotropic liquid transition at about 409 K (ΔH=2–4 J g^{-1}) [3, 7, 8].

The first transition in the 4,4'-azoxyanisole curve (I) has a very large undercooling effect, but transition II is completely reversible. Application of this compound has some disadvantages because no exact calibration figures exist in literature and the heat effect of the second peak is very small. The measured value of this heat effect depends on the construction of the base line.

So this compound is surely not an ideal substance for calibration purposes, but it was taken into account because no other appropriate compounds are known in this temperature range.

Experiments and results

A DSC instrument from Rheometric Scientific (DSC-GOLD) was used with a liquid nitrogen cooling device for programmed cooling [3]. Temperature and DSC signal were calibrated at a heating rate of 10 K min^{-1}, using adamantane, Hg and Ga for the low temperature range, and In, Sn, Pb and Zn for the high temperature range.

Samples of the test-substances were of the highest obtainable purity: the metals >99.999% and the other compounds >98% are used without further purification.

The samples, except Hg, were contained in flat aluminium crimped pans, with a mass of about 29 mg. Hg was measured in a hermetically sealed aluminium pan (mass 48 mg). In order to avoid chemical reactions between the aluminium pans and Ga, Pb and Zn, samples of these metals were embedded in 10–20 mg alumina (Al_2O_3) powder.

The sample amount was 2–14 mg, except for 4,4'-azoxyanisole. Because of the small heat effect a greater amount of this compound was taken, namely 25 mg.

An experiment existed in subsequent heating and cooling of a sample with the same absolute rate, giving an endothermic peak on heating and an exothermic peak on cooling. As discussed before, the compound 4,4'-azoxyanisole has a transition I

with a large heat effect at 389 K, followed by the reversible transition II with a small heat effect at 409 K. Particularly at high heating rates this could give problems, because peak II should disappear in the end phase of peak I [7]. This can however be avoided because peak I has a great undercooling effect [3]. So after the first heating run the sample can be cooled down to below 373 K without solidification. The following experiments only show peak II, provided that the sample is not cooled down below 373 K.

The results of the experiments are given in Table 1 and in the Figs 1–3.

Table 1 Results of heating and cooling runs for various samples at several rates

Sample mass/mg	Rate/ K min^{-1}	Heating		Cooling		ΔT/K	$\bar{T}$/K
		T_o/K	ΔH/J g^{-1}	T_o/K	ΔH/J g^{-1}		
$C_{10}H_{16}$ 5.350	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	208.04
Hg 13.65	10	234.20	11.42	231.11	−11.33	3.09	–
	5	233.98	11.52	231.21	−11.12	2.77	–
	2	233.75	11.60	231.31	−10.50	2.44	–
Ga 2.339	10	303.06	76.98	278.49	−77.76	24.57	–
Azoxy 25.10	20	409.49	4.31	407.81	−4.32	1.68	408.65
	10	409.11	4.43	408.25	−4.28	0.86	408.68
	5	408.92	4.36	408.52	−4.13	0.46	408.72
	2	408.84	3.92	408.69	–	0.15	408.76
Pb 11.875	10	601.23	23.40	598.01	22.71	3.22	–
Zn 2.487	10	691.89	111.94	690.54	−111.64	1.35	691.22
	10	691.69	114.28	690.54	−112.12	1.15	691.12
	10	691.88	111.61	690.47	−112.58	1.41	691.17
	10	691.74	112.33	690.57	−114.07	1.17	691.15
	5	691.38	111.74	690.70	−114.05	0.68	691.04
	1	691.19	111.18	690.93	−113.11	0.26	691.06

Azoxy=4,4'-azoxyanisole; $C_{10}H_{16}$=adamantane.

The measured heat effect ΔH (J g^{-1}), the extrapolated onset temperature T_o (K), the temperature difference ΔT and the mean value $\bar{T}$ between heating and cooling with the same rate, are given.

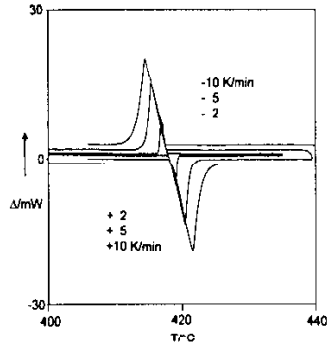

Fig. 1 DSC runs of 2.487 mg Zn, embedded in 10.7 mg alumina, with successive heating and cooling rates of 10, 5 and 1 K min^{-1}. Purge gas N_2 at 1 l h^{-1}. Degrees centigrade (°C)=K–273.15: up=exothermic: down=endothermic

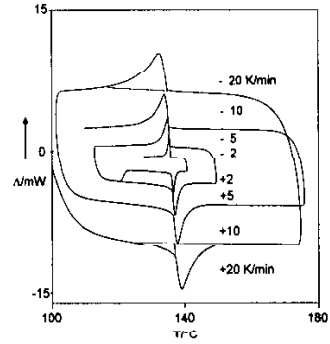

Fig. 2 DSC runs of 25.100 mg 4,4'-azoxyanisole with successive heating and cooling rates of 20, 10, 5 and 2 K min^{-1}. Only peak II (liquid crystal → isotropic liquid) is shown. Degrees centigrade (°C)=K–273.15

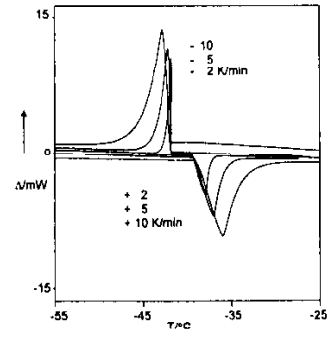

Fig. 3 DSC runs of 13.56 mg Hg in a hermetically sealed aluminium pan with successive heating and cooling rates of 10, 5 and 2 K min^{-1}. Degrees centigrade (°C)=K–273.15

Figure 1 shows that Zn behaves completely reversible during heating and cooling: the peaks are identical for heating and cooling at the same rate with equal shape, peak height and surface area. The difference ΔT of the onset temperatures is small and decreases with decreasing heating/cooling rate: about 1.3 K at 10 K min^{-1}, 0.68 K at 5 K min^{-1} and 0.26 K at 1 K min^{-1}.

The mean onset temperature $\overline{T}$ is nearly constant and varies between 691.06 and 691.22 K.

In order to test the reproducibility, several runs of Zn are given in Table 1, made at 10 K min^{-1} and on different days. We see that measured heat effects and (onset) temperatures are very stable: on heating T_0 varies between 691.89 and 691.74 K (lit. value 692.677 K) and the measured heat effect (ΔH) is between 111.61 and 114.28 J g^{-1} (lit. value 111.97 J g^{-1}).

It appears from these figures that the temperature calibration at the beginning of this series of experiments at a heating rate of +10 K min^{-1} could be improved.

The other compounds in Table 1, namely adamantane (T_0=208.71 K, lit. value 208.62 K), Hg (T_0=234.20 K, lit. value 234.32 K), Ga (T_0=303.06 K, lit. value 302.91 K) and Pb (T_0=601.23 K, lit. value 600.61 K) give better results.

Table 1 shows that adamantane, just like Zn, is completely reversible [3].

Results of 4,4'-azoxyanisole are given in Fig. 2 and in Table 1. The peak shape is not so sharp as is the case for Zn. This is caused by the fact that the value of the specific heat is greater in the liquid crystal range, than it is for the isotropic liquid [3]. This influences the peak shape at the lower temperature side, but the peak onset however is sharp and the extrapolated onset temperature T_0 can be determined very accurately.

The figures in Table 1 show that ΔT is small and varies from 1.68 K at 20 K min^{-1} unto 0.15 K at 2 K min^{-1}.

The mean temperature $\overline{T}$ is rather constant and varies between 408.65 and 408.76 K (mean value of four experiments: 408.70 K). So this compound also shows a reversible behaviour.

Figure 3 shows the DSC curves of Hg at various heating and cooling rates. Now a rather small undercooling effect is observed, but the shape of the cooling peaks differs strongly from the shape of the heating peaks. Also the peak height is much higher in the cooling mode.

It is remarkable that the height of the (under)cooling peaks varies only a little with different cooling rates. So Hg does not show a reversible behaviour and strictly speaking cannot be used for calibration during cooling. However, since the onset temperature is rather constant during cooling, varying from 231.11 K at −10 K min^{-1} to 231.31 K at −2 K min^{-1}, this could be a possibility to use such compounds, with only a small undercooling effect, for temperature calibration during cooling.

One should keep in mind that in the case of undercooling, the crystallization on cooling is not only determined by thermodynamics, but also by kinetics, such as the rate of nucleation.

The curves of Pb show similarities to those of Hg, also with a slight undercooling effect (3.22 K at −10 K min^{-1}). Other compounds, like Ga, show an undercooling ef-

fect that is considerably greater (about 38 K at −10 K min^{-1}), and can only be used in the heating mode [3].

In most cases, the measured heat effects correspond rather well with the literature values, both during heating and during (under)cooling. Only at low rates occasionally somewhat lower values are measured. Possibly it can be explained by the more difficult construction of the baseline at low rates.

Conclusions

– For DSC calibration during cooling, compounds are needed with fast reversible transitions.

– Two compounds are very well suitable, namely adamantane and Zn.

– Adamantane has a reversible solid ↔ solid transition at 208.62 K, with a heat effect of 24.78 J g^{-1}.

– Zinc has a reversible solid ↔ liquid transition (melting) at 692.677 K, with a heat effect of 111.97 J g^{-1}.

– A third suitable compound is 4,4'-azoxyanisole, showing a reversible transition at 409.11 K, as measured during this investigation with a heating rate of 10 K min^{-1}, being the rate of the preliminary calibration of the instrument. It concerns the liquid crystal ↔ isotropic liquid transition.

– Since the heat effect, belonging to the above-mentioned transition of 4,4' azoxyanisole, is very small (ΔH is measured to be 4.25 J g^{-1}), experiments are made with a high amount of sample (25 mg).

– Two other compounds, namely Hg and Pb, show a slight undercooling effect. So they are initially less suitable for DSC calibration during cooling.

– The onset temperature (T_o) of the (under)cooling peak, however, is found to be rather constant for Hg, namely 231.11 K at 10 K min^{-1} and 231.31 K at −2 K min^{-1}.

– It would be worthwhile investigating whether compounds with only a slight undercooling effect, could nevertheless be used for DSC calibration during cooling.

– In order to avoid reactions between aluminium sample pans and metal samples, it is advisable to embed Zn, Ga and Pb in alumina powder.

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