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DSC CALIBRATION BELOW 0°C

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Abstract

This contribution deals with the calibration of a DSC apparatus between −100 and 0°C using compounds with well-known temperature and heat of transition. Only a few suitable substances are mentioned in literature. For that reason another compound, adamantane, is proposed with a solid–solid transition at −64.56°C and a heat of reaction being 24.78 J/g.

Keywords: compounds with low vapour pressure, DSC calibration, subambient temperature

Introduction

For our thermoporometry measurements of porous sorbent materials, DSC experiments must be performed from room temperature to −100°C. This demands calibration of temperature and DSC signal in this temperature region. A first calibration of the DSC signal can be obtained by heating and cooling runs with a piece of sapphire, with well-known specific heat. Further a more precise calibration of the DSC signal and also of the measured temperature, can only be performed using compounds with well-known heat and temperature of transition in the relevant temperature region. For this temperature region, however, only few compounds are reported in literature. These compounds are summarized in Table 1.

For most of the samples (a–e) weight loss will be observed during the DSC runs, caused by the high vapour pressure, even when the samples are contained in "hermetically sealed" pans. Only mercury keeps a constant weight.

It is possible to reduce the evaporation of a volatile sample by keeping it under its own vapour pressure in a container with a piece of wadding, wetted with the fluid itself. Then it is possible to reuse the sample several times, but of course, weight loss during the DSC experiment cannot be prevented.

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Table 1 Compounds for DSC calibration at low temperature, mentioned in literature (a–e). Further some other possible compounds are given (f–j). The vapour pressure at 25°C (P_{25}) is calculated from Ref. [5]

	Sample	Reaction*	Temp. / °C	ΔH / J·g^{-1}	P_{25} / mm Hg	Ref.
a	Cyclopentane	tr	–135.09	–	320	[2]
		m	–93.43	–	–	[2]
b	Cyclohexane	tr	–83	–	84	[1]
		m	+7	–	–	[1]
c	1,2-Dichloroethane	m	–32	–	76	[1]
d	Mercury	m	–38.87	11.62	0.002	[3]
e	Water	m	0.00	333.78	24	[3]
f	Ethanol	m	–114.6	109.12	55	[3]
g	Methanol	tr	–115.8	20.13	115	[3]
		m	–97.9	98.95	–	[3]
h	Adamantane	tr	–64.53	24.78	(2)	[4]
i	N-Buthylbenzene	m	–88	–	1.2	[5]
j	1,3-Dimethoxybenzene	m	–52	–	0.22	[5]

*tr = solid/solid transition, m = melting.

Experiments and results

A DSC apparatus from Polymer Laboratories, with programmed cooling, was used. At the beginning of the experiments the DSC apparatus was calibrated with a sapphire run and by melting experiments with indium and mercury. During our investigation we tested several new compounds: methanol, ethanol, adamantane, N-butylbenzene and 1,3-dimethoxybenzene. The last two compounds were chosen because of their low vapour pressure at room temperature. The samples were of the highest obtainable purity: mercury 99.999%, ethanol and methanol >99.8%, cyclohexane >99.8% and the other compounds better than 99%.

It was found that ethanol does not crystallize on cooling, even when cooled down to –150°C. The same effect was observed with the other compounds N-buthylbenzene and 1,3-dimethylbenzene. In fact, we got the impression that a lot of organic compounds, with low vapour pressures and melting temperatures in the desired temperature range, will not satisfy because crystallization of the liquid compounds is practically impossible during a cooling run in the DSC apparatus.

Methanol showed different problems: on cooling crystallization occurs with only slight undercooling (about 10°C). However, the heating run shows different small peaks at about –115 and –113°C, sometimes a small peak at –104°C and a broad melting peak of methanol, starting at about –110°C, while the

measured extrapolated onset temperature is −101.48°C. The measured heat effect is also very small, compared to the literature value. This is caused by weight loss through evaporation during the DSC run. The small peaks at lower temperature are probably caused by the solid/solid transition and effects of little impurity, such as water. By that also the broadening of the melting peak could be explained.

We also did not test cyclopentane (high vapour pressure) and 1,2-dichloroethane (poisonous, high vapour pressure, melting temperature close to that of mercury). Only one of the newly tested compounds, adamantane, seems to be a good calibration compound with a fast, first order transition in the desired temperature range, having a low vapour pressure (Fig. 1).

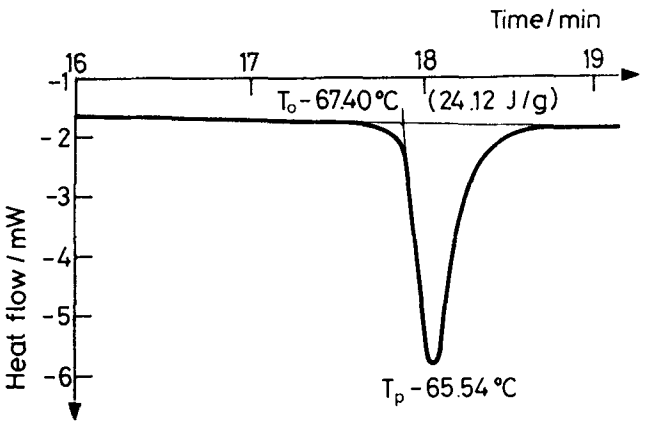

Fig. 1 DSC run of 2.732 mg adamantane, first run, $dT/dt = 10$ deg·min^{-1}

In Table 2 the results of the DSC measurements are summarized.

Except adamantane, all samples were tested in closed "hermetically sealed" cups. Still weight loss was observed for most samples. Only mercury remained at a constant weight. Adamantane was tested in a normal crimped pan. It did not lose weight during the first runs, but after it was kept during 90 days on room temperature, a weight loss of 60% was observed. So also for adamantane it is better to use hermetically sealed pans.

Conclusions

– Volatile samples like methanol and cyclohexane give problems with enthalpy calibration because of weight losses, caused by evaporation during the DSC runs, even in "hermetically sealed" pans.

– Only the application of completely tight pans will solve this problem. Control is possible by measuring the weight before and after the DSC experiment: it should be exactly the same.

– Ethanol and more complex organic molecules cannot be used in DSC experiments in pans with small sample volumes because of crystallization problems even when cooled more than 50°C below their melting temperature.

– Methanol shows a good crystallization behaviour on cooling, but although very pure methanol was used, an extra peak was observed at low temperature, maybe caused by eutectic melting, while the melting peak itself was very broad. It is possible that these effects are caused by water, introduced from the atmosphere during the sampling. So the use of methanol for temperature calibration at low temperature cannot be recommended.

– As discussed before, the high vapour pressure of methanol gives problems for the use of this compound for enthalpy calibration.

– Mercury is a good compound for calibration of temperature and heat effect. It shows sharp peaks on melting and cooling with only little undercooling. We got no problems using mercury in hermetically sealed aluminium pans, provided that the oxide layer on the aluminium metal remained intact.

– From the results in Table 2 it can be concluded, that the preceding temperature calibration with indium and mercury was not very accurate at lower temperatures: the extrapolated onset temperature of adamantane is –67.93°C, while the real transition temperature is –64.56°C, resulting into a correction of +3.37°C at this temperature.

Table 2 Results of DSC measurements

Sample	Weight / mg	Reaction*	Extrapolated onset / °C	Experimental heat / $J \cdot g^{-1}$	Heating rate / $deg \cdot min^{-1}$
Cyclohexane	(15.30)	tr	–86.58	$(75.87)^+$	+10
		m	+6.33	$(26.30)^+$	+10
Mercury	13.560	m	–42.54	12.34	–10
		m	–39.16	11.51	+10
Methanol	(6.10)	tr	(–115)	$(9)^+$	+5
			(–101.5)	$(86)^+$	+5
Adamantane	2.732	tr	–67.93	24.39	–10
		tr	–67.40	24.12	+10

*tr = solid/solid transition; m = melting.

+These values are too low, compared to literature values, because of evaporation.

– The extrapolated onset temperatures of the heating and cooling peaks of adamantane are nearly the same (–67.93°C on cooling and –67.40°C on heat-

ing, both at a rate of 10 deg·min^{-1}). This means that the transition reaction of adamantane is very fast. Nearly no undercooling is observed.

– The measured values of the heat effect are 24.39 and 24.12 J/g on cooling and heating successively. Compared to the literature value of 24.78 J/g, this will mean that the preceding calibration of the DSC signal was rather correct, also for this low temperature.

– The DSC peaks of adamantane are sharp, with a little broadening at the low temperature side. This corresponds with the observation of Westrum [4] of a pretransition heat effect at temperatures below –64.56°C. This heat effect is part of the total heat of transition.

– The vapour pressure of adamantane is low. Single melting experiments can be performed in crimped pans. For longer lasting experiments hermetically sealed pans are to be used.

– Adamantane is a good calibration compound in the low temperature region. Both the temperature and the heat of reaction can be applied for the calibration of DSC apparatus.

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Zusammenfassung — Unter Verwendung von Substanzen mit genau bekannten Umwandlungstemperaturen und -wärmen befaßte man sich mit der Kalibrierung von DSC-Geräten im Temperaturbereich von –100 bis 0°C. In der Literatur werden nur einige wenige geeignete solcher Substanzen erwähnt. Aus diesem Grunde wird als weitere Substanz Adamantan mit einem Feststoff-Feststoff-Umwandlungspunkt bei –64.56°C und einer Reaktionswärme von 24.78 J/g vorgeschlagen.