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EXPERIMENTAL CONSIDERATIONS FOR TEMPERATURE MODULATED DSC AT LOW TEMPERATURE

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Abstract

Temperature modulated DSC (TMDSC) at low temperatures requires attention to the selection of experimental parameters that are within the capability of the instrumentation as well as special care in calibration of heat capacity measurement when high precision is required. Data are presented to facilitate selection of appropriate modulation periods and amplitudes at low temperature when using a mechanical cooling accessory. The standard error of the mean heat capacity measurement for a sapphire standard increased with decreasing temperature, decreasing period, and increasing pan mass. For ice in hermetically sealed pans, the standard error of the mean heat capacity measurement was larger than for sapphire and did not follow a predictable trend with changes in temperature and period of modulation. This was attributed to changes in sample geometry between successive measurements due to melting and resolidification. A simple one-point temperature calibration by TMDSC may be unsuitable for precise measurement of heat capacity because of the random error caused by sample placement and the systematic error caused by cell asymmetry, temperature dependence of the calibration constant, and different sample thermal conductivities. An alternative calibration procedure using standard DSC and either a linear or second order fit of the calibration constant over the temperature range of interest is proposed.

Keywords: freeze-drying, glass transitions in frozen systems, heat capacity calibration, Lissajous figures, sucrose

Introduction

TMDSC is a technique whereby a periodically varying temperature is overlaid on a linear heating rate. With a Fourier transformation of the modulated heat flow output, the heat flow signal can be deconvoluted into its periodic and underlying components, the theoretical details of which have been provided by Wunderlich [1], Schawe [2], and Reading [3]. Often, the temperature is varied with a sinusoidal modulation. Regardless of the form of the temperature modulation, the data are treated with the

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assumptions that the heat flow responses of the sample and calorimeter are linear responses, with second and higher order harmonics of the Fourier transformation considered as negligible effects [4]. These assumptions are not entirely appropriate for many types of thermal responses, but have been useful in the characterization of glass transitions, crystallization and melting events in many materials.

Given the importance of these types of thermal events in the characterization of pharmaceutical and food materials, TMDSC has the potential to contribute greatly to these fields as the technique continues development. For example, the frequency dependence of the glass transition may offer evidence for its identification using thermal analysis and a means to measure material properties such as fragility that may be difficult to measure in frozen systems. Additionally, direct measurements of crystallization rates may be possible either from phase data [5] or through isothermal heat capacity changes [6].

The advantage of TMDSC over conventional DSC lies in the direct measurement of the frequency dependent heat capacity. Unfortunately, the calibration of heat capacity by TMDSC is in general both frequency and temperature dependent. For example, in a temperature range with no frequency dependent thermal events, the frequency independent sample heat capacity, C_s, is given by:

$$C_s = K(\omega, T)\frac{A_{HF}}{A_{Ts}\omega} \tag{1}$$

where the calibration constant, K, will deviate from unity, and the modulated heat flow amplitude, A_{HF}, will be a function of frequency, ω, and temperature. A_{Ts} in the above equation is the temperature amplitude.

Several researchers have verified the applicability of the theoretical model for the measurement of heat capacity by TMDSC [6–8]. High precision (1%) of the standard error of the mean has been reported with the use of standards in encapsulated aluminum pans, nitrogen purge gas, thin samples, and an auto-sampler which reproducibly places sample pans in the TMDSC cell [7]. Of particular importance to the proper application of TMDSC is the use of modulation conditions and an underlying heating rate that gives a fast approach to steady state of the sinusoidal temperature variation and maintenance of steady state throughout an experiment. This has been studied by Wunderlich for liquid nitrogen cooling and air cooling by measuring the maximum available amplitudes and assessing steady state by Lissajous figures [7]. The same data for cooling with a mechanical cooling accessory have not been published.

Calibration constants for heat capacity measurement using standards have been shown to vary with temperature as well as frequency [7]. In addition to the temperature and frequency effect, the sample mass and thermal conductivity have been shown to influence the calibration constant when there are significant temperature gradients within the sample [8, 9]. Cell imbalance due to the calorimeter itself or unequal sample and reference pan masses can apparently also have an effect [10]. A simple and practical method of accounting for all of these effects has not been published.

Our interest has been in the use of TMDSC to characterize frozen aqueous solutions intended for freeze-drying. The objective of this study was to assess the reproducibility, calibration, and modulation parameter selection issues for TMDSC at low temperature. The specific questions that have been considered are

1. What are the limits on amplitudes and frequency using a mechanical cooling accessory at low temperature?
2. How reproducible are the measurements of heat capacity for sapphire and ice standards?
3. Does the type of sample pan influence the reproducibility and, if so, why?
4. Are the calibration constants for the heat capacity similar for sapphire and ice standards?
5. Does a linear or second order calibration of the heat capacity measurement by TMDSC using a standard DSC calibration run improve the accuracy and reproducibility of the TMDSC measurements compared to one-point methods?

The principle goal was to determine if a simple method of calibration of the heat capacity measurement by TMDSC with a set of standard DSC experiments on the sample of interest is useful and practical to minimize many of the uncertainties in heat capacity calibration.

Materials and methods

These studies were done using a temperature modulated DSC (Model 2920, TA Instruments, New Castle, DE) equipped with a mechanical cooling accessory (RCS®, TA Instruments, New Castle, DE) and helium cooling gas. The temperature and cell constant were calibrated with the appropriate type of aluminum pans at 1°C min^{-1} using the melting temperature of mercury (–38.83°C) and either a helium or nitrogen cell purge at a flow rate of 25 ml min^{-1}. The value for the heat capacity calibration constant was set to unity so that its value could be accurately calculated for the standards.

Evaluation of maximum modulation amplitude

The maximum amplitudes at temperatures of –60, –40, –20 and 50°C using empty crimped aluminum pans were evaluated at periods of 40, 60 and 80 s by increasing the amplitude and determining when the modulating temperature cannot follow the temperature program.

Determination of maximum cooling rate

The maximum cooling rate of the mechanical cooling accessory was determined with a nitrogen purge of 25 ml min^{-1} and helium cooling gas. The cooling rate was set to 100°C min^{-1} and the actual cooling rate was measured at temperatures ranging from the initial temperature of 55 to –70°C.

These data were used to calculate the theoretical maximum amplitudes as a function of temperature and period using the derivative of Eq. (2) with respect to temperature, the fact that the maximum occurs at $\omega t=\pi/2$, and the assumption that the cooling rate is limiting.

$$T_s - T_o = qt - \frac{qC_s}{k} + A_{Ts}\sin(\omega t) \tag{2}$$

This equation describes the steady state temperature at the sample position, T_s, where T_o is the initial temperature, q is the underlying heating rate, C_s the sample heat capacity, A_{Ts} is the amplitude of the modulation, and ω is the frequency of the modulation. The heat transfer coefficient is denoted by k.

Preparation of standards and 80% (m/m) sucrose solution

A sapphire disk (0.145 cm diameter, 0.025 cm thickness and 22.2 mg) was used both in encapsulated and hermetically sealed aluminum pans. An 8–10 mg sample of double distilled water was used to prepare the ice standard by spreading the liquid evenly in the bottom of the hermetically sealed pans.

Sucrose (analytical grade) was obtained from Mallinckrodt Baker (Paris, KY). The 80% (m/m) solution was prepared by stirring a weighed amount of sucrose and double distilled water until a clear solution was obtained with gentle heating over a hot plate. Water lost by evaporation was added back after dissolution.

Standard DSC calibration of heat capacity

In order to assure the accurate measurement of the sample heat capacity by standard DSC, the standard DSC experiments were calibrated for heat capacity with either the sapphire standard or ice by baseline subtraction of empty pans. The measured heat capacity as a function of temperature at a scanning rate of 5°C min^{-1} was adjusted by comparison to standard literature values for the heat capacity of the materials. A linear fit of the measured temperature dependence of the standard DSC calibration factor was used to correct the standard DSC measurement for both the sapphire standard and the ice standard. The calibration function for the ice standard was used to correct the heat capacity for an 80% (m/m) solution of sucrose in water measured at 5°C min^{-1} since the properties of ice more closely resemble the sample properties compared to the sapphire standard.

Determination of the reproducibility of the TMDSC measurement of heat capacity

For the sapphire and ice standards, the heat capacity was measured in triplicate at temperatures of –60, –40, –20, 20, and 50°C at periods of 40, 60, 80, and 100 s and an amplitude of 0.2°C. The low amplitude was chosen to assure that the capabilities of the instrument were not exceeded over the temperature range. In addition, data during heating at 1°C min^{-1} were recorded over the same temperature range from –60 to 50°C. Reproducibility is reported as the standard error of the mean for the sapphire standard using no pan, an encapsulated pan, and a hermetically sealed pan, while the reproducibility of the ice standard is reported only for the hermetically sealed pan. It was not possible to prepare an ice sample in crimped aluminum pans because the liquid is not amenable to the crimping process. Sample and reference pans were matched within ±0.1 mg to avoid a cell asymmetry contribution to the standard error.

TMDSC calibration of heat capacity for standards

Heat capacity calibration constants were calculated using the known heat capacities of sapphire [11] and ice [12] as a function of temperature. Theoretical calculations of the calibration constants as a function of heat transfer coefficient and period [8] were compared to experimental results.

Sample TMDSC measurement of an 80% (m/m) sucrose solution

For the sucrose solution, a 14.0 mg sample was cooled to –65°C at 0.5°C min^{-1} and then heated at the same rate after a 20 min isothermal hold time to allow for steady state. The amplitude was held constant at 0.2°C and the period was varied from 40 to 100 s.

Results and discussion

An important consideration in TMDSC experiments is the selection of modulation conditions. While it has been suggested that relatively large amplitudes and short periods give the highest precision in TMDSC experiments [7], the accuracy can be compromised if the sample temperature does not follow the temperature program. We report results with the use of a mechanical cooling accessory to guide the selection of modulation parameters with this instrumental set-up.

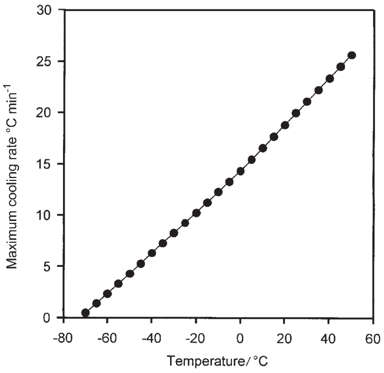

Fig. 1 Maximum cooling rate as a function of temperature using the RCS mechanical cooling accessory

Figure 1 illustrates the maximum cooling rate as a function of temperature using the mechanical cooling accessory. It is apparent that the maximum cooling rate decreases with temperature down to the lowest temperature achievable with the instrument of approximately –70°C. Since the maximum cooling rate required at any given period during modulation is a function of the amplitude, the maximum amplitude as a function of period and temperature can be calculated using Fig. 1 and the derivative of Eq. (2), assuming that the cooling rate is the limiting factor. Other factors such as heat transfer lags or temperature control issues were not considered. The calculations are shown in Fig. 2 along with some experimental values. The experimental values lie approximately parallel to the calculated curves, which verifies, as expected, that the maximum amplitudes are correlated with the maximum cooling rate. The shift most likely is due to the heat transfer lags that were mentioned above. Most important from the Fig. is the recognition that at temperatures of –60°C and below, the maximum amplitude is always less than approximately 0.5°C with empty pans. A sample decreases the maximum amplitude even further, such that for most experiments down to –60°C the maximum amplitude can typically be as small as 0.3°C. While such small amplitudes are desirable in maintaining the assumptions of linearity during thermal transitions, the precision of the measurements may be compromised.

Table 1 Reproducibility of heat capacity (expressed in %); measurement with sapphire standard

Temperature/°C	Period/s				
	40	60	80	100	Average
		No pan			
50	0.2	0.1	0.1	0.1	0.1
20	0.3	0.2	0.3	0.1	0.2
–20	0.4	0.3	0.3	0.3	0.3
–40	0.0	0.0	0.1	0.0	0.0
–60	0.1	0.3	0.4	0.4	0.3
Average	0.2	0.2	0.2	0.2	0.2
		Standard pan			
50	0.7	0.7	0.4	0.8	0.6
20	1.4	1.2	1.0	1.1	1.2
–20	3.0	2.5	1.8	1.9	2.3
–40	3.0	2.3	1.9	1.7	2.2
–60	3.9	3.1	3.0	2.7	3.2
Average	2.4	2.0	1.6	1.6	1.9
		Hermetic pan			
20	2.6	1.7	1.4	1.3	1.7
–20	3.4	2.5	2.2	1.7	2.4
–40	4.8	3.7	3.2	0.2	3.0
–60	5.1	3.8	3.2	2.9	3.8
Average	4.0	2.9	2.5	1.5	2.7

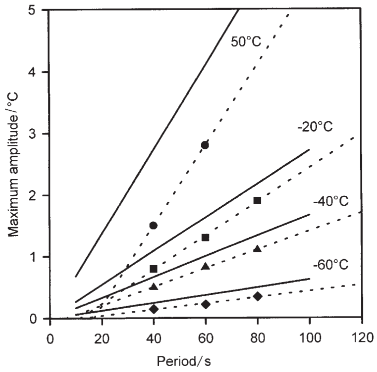

Fig. 2 Maximum amplitude as a function of period at four temperatures. Solid lines are calculated values, symbols refer to data at the indicated temperatures

Another important factor in determining the precision of TMDSC measurements is the pan type. Wunderlich *et al.* have observed that the use of hermetically sealed aluminum pans results in less precision compared to crimped aluminum pans [13]. This is important considering that only hermetically sealed pans can be used to prepare liquid samples. Data for the standard error of the mean heat capacity measurement for a sapphire standard using an amplitude of 0.2°C are reported in Table 1. Since the sample pans were placed manually in the DSC cell, the random error is most likely the result of small changes in sample placement in the calorimeter between experiments. Even with the use of such a small amplitude as 0.2°C, the precision of the data using no pans is excellent down to temperatures as low as –60°C. With encapsulated pans, the precision is comparable to previous observations at ambient and higher temperatures using a sapphire standard and an automatic sample loader that gives good reproducibility of the sample pan position between experiments [7]. At lower temperatures, the error increases such that the average error with the use of encapsulated pans with sapphire is approximately 2%.

Table 2 Reproducibility of heat capacity (expressed in %); measurement with ice standard

Temperature/°C	Period/s				
	40	60	80	100	Average
		Hermetic pan			
20	3.0	4.3	4.2	4.5	4.0
–20	0.3	4.1	6.0	7.0	4.3
–40	3.2	1.6	4.1	5.6	3.6
–60	4.6	1.1	4.2	5.7	3.9
Average	2.8	2.8	4.6	5.7	4.0

The second observed trend is an increase of the standard error as the period of the modulation is decreased. These same trends are also observed in hermetically sealed pans. The standard error is always higher in this case such that the average standard error is approximately 3%. For ice samples, the standard error increases to 4% as shown in Table 2. The trend with temperature and period is not as clear with ice. This could be because of changes in liquid geometry between experiments due to melting and resolidification.

A dramatic effect of pan type is observed in the calibration constants for the heat capacity as a function of temperature and period in Figs 3a-c for sapphire. With no pan, the calibration constants are close to unity for the four chosen periods and hence show only a modest frequency and temperature dependence. For crimped aluminum pans the dependence of the calibration constants on temperature and period are comparable to previous observations [7]. For both of these cases, the calibration constant measured at a heating rate of 1°C min^{-1} is within the limits of precision of the technique measured under quasi-isothermal conditions. This implies that at heating rates of 1°C min^{-1} and less, cross-over effects [14] are not important for sapphire samples under these conditions. Cross-over effects are violations of the assumptions used in the mathematical treatment

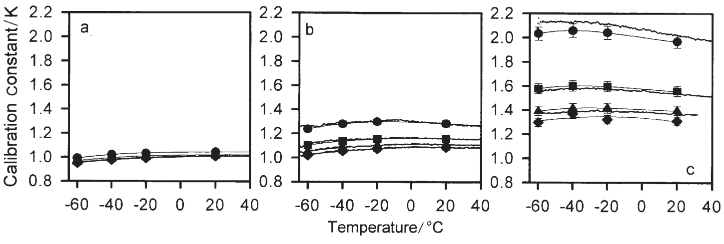

Fig. 3 Calibration constant as a function of temperature for the sapphire standard as a function of temperature at periods of 40 s (circles), 60 s (squares), 80 s (triangles) and 100 s (diamonds). Symbols are connected by smooth trendlines for clarity. Heating data at 1°C min^{-1} at each period are also included.
a – no pans; b – encapsulated pans; c – hermetically sealed pans

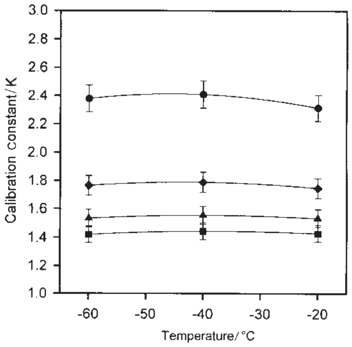

Fig. 4 Calibration constant as a function of temperature for the ice standard as a function of temperature at periods of 40 s (circles), 60 s (diamonds), 80 s (triangles) and 100 s (squares). Symbols are connected by smooth trendlines for clarity

of TMDSC data that the heat capacity does not change over one period. This idea is the basis for the recommendation by instrument manufacturer to include at least six modulation cycles throughout a thermal transition. For hermetically sealed pans, the frequency effect and temperature dependence of the heat capacity calibration are more pronounced. In addition, for a period of 40 s the data at a heating rate of 1°C min^{-1} are outside the limits of precision of the measurement under quasi-isothermal conditions. In this case, it appears that cross-over effects may be more important, although the shape of the calibration curves with temperature are similar to the quasi-isothermal measurements. For ice in hermetically sealed pans (Fig. 4), the shape of the curves are similar to sapphire, but the actual values of the calibration constant as a function of temperature and period are significantly different at the p=0.05 level.

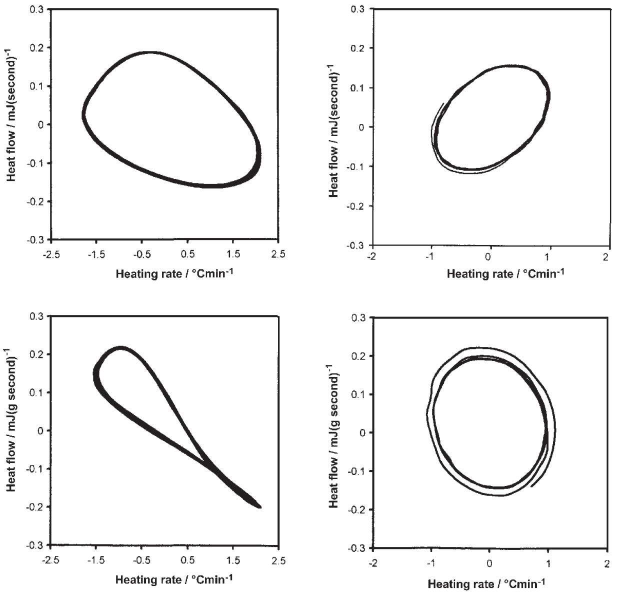

Fig. 5 Lissajous figures for a sapphire sample with a period of a – 40 s; b – 80 s and an ice sample at c – 40 s and d – 80 s at a temperature of –60°C

The geometry, thickness, and thermal conductivity of sapphire and ice samples are quite different. While it is expected that these differences along with the pan type may effect the calibration constant [8, 9], it is not immediately apparent how they can affect the precision of the measurement. Some variation may be attributed to inadequate experimental design if enough time is not allowed to reach the steady state [15]. Since steady state was assured for these data, another explanation may be attributed to the deviation from a 'symmetrical' steady state where the heat flow response retraces itself with respect to the instantaneous heating rate. Lissajous plots that illustrate this relationship have been shown to be valuable in assessing steady state because of the formation of a retraceable ellipse in the fully controlled case. Since the heat capacity is determined from the slope of the positive axis of the ellipse, any deviation from a symmetrical steady state can create a bias in the calibration constant. This occurs at low temperature and short periods in the sapphire and ice sample. The fact that it is more prevalent in the ice sample (Fig. 5) is evidence of greater heat transfer effects for that sample. Variation of the Lissajous figures between consecutive experiments (caused by changes in heat transfer conditions) can cause variability in the measurement. A large observed change with ice samples is further evidence for a change in sample configuration between experiments and may explain why the trends of precision with ice are not as clear as with sapphire.

Additional insight into the variation of the precision of the heat capacity measurement with respect to period, sample, and pan type can be gained from the mathematical model developed by Schawe [8]. Schawe has developed a simple theory for the prediction of the dependence of the heat capacity calibration constant on the heat transfer coefficient, *k*, which includes effects from the instrument, pan, sample, and geometry [8].

The measured heat flow signal, $\Phi(t)$, has been shown to be of the form:

$$\Phi(t)=A_{\mathrm{HF}}\,(A\cos\omega t+B\sin\omega t)=KA_{\mathrm{HF}}\cos(\omega-\varphi_{\mathrm{g}}) \tag{3}$$

where,

$$A=\frac{4}{\pi}\sum_{n=0}^{\infty}(-1)^{n}\frac{(2n+1)^{3}}{(2n+1)^{4}+\alpha^{2}} \tag{4}$$

$$B=\alpha\frac{4}{\pi}\sum_{n=0}^{\infty}(-1)^{n}\frac{(2n+1)^{3}}{(2n+1)^{4}+\alpha^{2}} \tag{5}$$

$$\alpha=\frac{4\omega k}{\pi^{2}} \tag{6}$$

and the phase calibration function, φ_{g}, is the difference between the measured, φ_{m}, and instrumental baseline, φ_{b}, phase lags. The heat transfer coefficient, *k*, along with the modulation frequency ω determines the constants *A* and *B*.

The heat capacity calibration constants, *K*, defined as the inverse of the value defined by Schawe to be consistent with the definition used in (1), is then determined through the relationship:

$$K=\frac{1}{\sqrt{A^{2}+B^{2}}} \tag{7}$$

Using Schawe's model for the heat capacity calibration, the heat transfer coefficients for a sapphire standard at 20°C were calculated for experiments at four periods with the sapphire disk alone, in an encapsulated pan, and in a hermetically sealed pan. These data are shown in Fig. 6. With no pans, the heat transfer coefficient was small and was found to vary only slightly with period. In the case of encapsulated pans and hermetically sealed pans, the heat transfer coefficient varies more dramatically with period compared to the experiments using no pans. Unfortunately, this observation

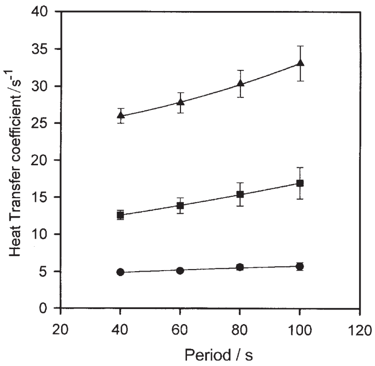

Fig. 6 Heat transfer coefficient as a function of period for the sapphire standard in no pans (circles), crimped pan (squares) and hermetically sealed pan (triangles)

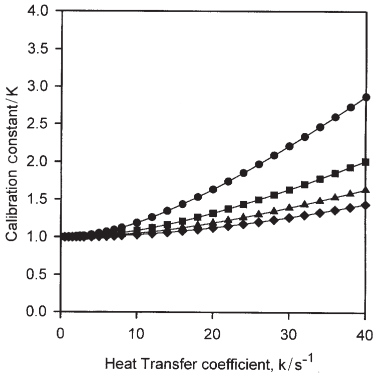

Fig. 7 Theoretical relationship between the calibration constant and the heat transfer coefficient at periods of 40 s (circles), 60 s (squares), 80 s (triangles) and 100 s (diamonds)

means that Schawe's model can not in general be used to calibrate the heat capacity as a function of period, since a constant heat transfer coefficient is required by the model.

The calculations can, however, provide some insight into the variability of the heat capacity measurement. Figure 7 shows the theoretical variation of the calibration constant as a function of heat transfer coefficient using Schawe's model for four selected periods. The figure illustrates that the calibration constant increases faster with heat transfer coefficient as the period decreases. The practical implication is that a small percentage change in the heat transfer coefficient, potentially caused by random sample placement, can result in relatively large standard error in the heat capacity measurement by affecting the calibration constant more significantly in heavier pans than in lighter pans. This is due to the fact that small percentage changes in the heat-transfer coefficient are more significant as the heat-transfer coefficient increases (Fig. 7).

Common sources of systematic error in TMDSC such as cell asymmetry and dependence of the calibration constant on temperature have been identified and can be corrected. These observations of random error and the dependence of the calibration on sample properties, however, make it uncertain to use a calibration method that is based on TMDSC. It may be better to accept the TMDSC measurement of the heat capacity as a relative measurement at low temperature and to calibrate the heat capacity measurement with standard DSC. A linear or second order temperature dependent calibration for the sample of interest based on the heat capacity by standard DSC at temperatures where there are only frequency independent effects is an alternative procedure that can eliminate the random error associated with sample placement. The systematic error caused by cell asymmetry and heat transfer can also be minimized if these errors can be approximated by the calibration function over the temperature range of the experiment. The procedure is to first measure the heat capacity of the sample by standard DSC at a sufficiently high heating rate (i.e. 5°C min^{-1}) to give adequate precision (<1%). Next, a TMDSC measurement is made at the desired frequency using an appropriate underlying temperature ramp rate and modulation parameters. Since the heat capacity is frequency independent at the low and high temperature extremes, calibration of the heat capacity measurement can be made using these temperature ranges. The calibration constant can be calculated within these ranges as the ratio of the standard DSC measurement and the TMDSC measurement of the heat capacity. From this combined range of the calibration constant at the extreme low and high temperature end of the data, a linear or second order polynomial fit can be constructed from the data. TMDSC heat capacity data at intermediate values between the two ranges can be corrected by the calibration function that is now specific for the material analyzed.

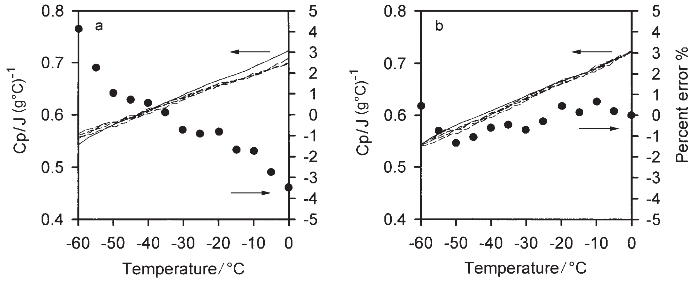

Fig. 8 Comparison of a one-point temperature calibration (8a) with a linear calibration (8b) of the heat capacity of a sapphire standard at periods of 40–100 s. Circles refer to the percent error associated with the experiment at a period of 100 s

A comparison of a linear calibration method with the standard one-point calibration recommended by the instrument manufacturer for a sapphire standard is shown in Fig. 8. The error in the one point calibration at the temperature extremes is four times the error that is observed when using the linear calibration method. This error does not include the random error that would be associated with the measurement if the heat capacity were calibrated by TMDSC.

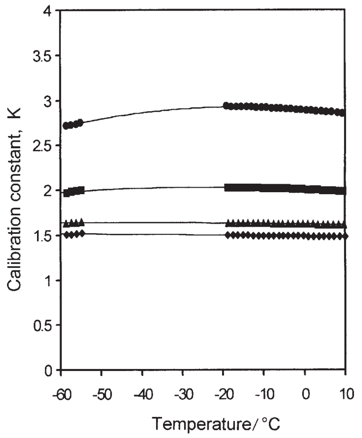

Fig. 9 Calibration constant *vs*. temperature for the 80% (m/m) sucrose sample at periods of 40 s (circles), 60 s (squares), 80 s (triangles) and 100 s (diamonds)

The heat capacity change of the sapphire standard over the temperature range of interest was small compared to the change observed in an 80% sucrose glass. A linear calibration with temperature was inadequate for the sucrose solution, but a second order fit of the heat capacity was adequate at four frequencies (Fig. 9). A significant benefit in calibrating by standard DSC is that it is possible to compare the frequency dependence of transitions using material specific calibration functions. This is illustrated with Fig. 10, representing the frequency dependence of the storage heat capacity of an 80% (m/m) solution of sucrose in water. The shift of the heat capacity step to a higher temperature with an increase of the period identifies the thermal transition as the glass transition of the freeze-concentrated solution.

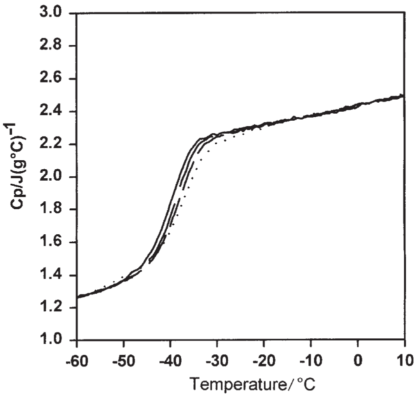

Fig. 10 Frequency dependent storage heat capacity of the 80% (m/m) sucrose sample as a function of temperature at periods of (from left to right) 100, 80, 60 and 40 s respectively

Conclusions

It is clear that using TMDSC at low temperature involves many special considerations, especially when using frozen aqueous samples. Care must be taken when choosing modulation conditions and heating rate to insure that the instrument is capable of controlling the sample according to the chosen program. Often this means small amplitudes (<0.3°C) and small heating or cooling rates (≤1°C min^{-1}). At low temperature, heat transfer effects dominate such that the heat capacity calibration constant can be a strong function of temperature, sample mass, sample configuration, and sample placement. It is questionable to rely on a single temperature calibration of the heat capacity with a standard when so many other systematic and random errors can affect the measurement. From a practical standpoint, it may be better to accept the TMDSC measurement of the heat capacity as a relative measurement at low temperature. Calibrating each sample 'internally' with itself using a simple comparison with a set of standard DSC measurements of the heat capacity in regions where there are no frequency dependent events may be a more meaningful way to compare TMDSC experiments at different modulation periods.

References

1 B. Wunderlich, Y. Jin and A. Boller, Thermochim. Acta, 238 (1994) 277.
2 J. Schawe and G. Hohne, Thermochim. Acta, 287 (1996) 213.
3 A. Lacey, C. Nikolopoulos and M. Reading, J. Thermal Anal., 50 (1997) 279.
4 B. Wunderlich, A. Boller, I. Okazaki and S. Kreitmeier, Thermochim. Acta, 282/283 (1996) 143.
5 A. Toda, T. Oda, M. Hikosaka and Y. Saruyama, Thermochim. Acta, 293 (1997) 47.
6 S. A. Knopp, S. Chongprasert and S. L. Nail, J. Thermal Anal., 54 (1998) 659.
7 A. Boller, Y. Jin and B. Wunderlich, J. Thermal Anal., 42 (1994) 307.
8 J. Schawe and W. Winter, Thermochim. Acta, 298 (1997) 9.
9 B. Schenker and F. Stager, Thermochim. Acta, 304/305 (1997) 219.
10 A. Boller, I. Okazaki, K. Ishikiriyami, G. Zhang and B. Wunderlich, J. Thermal Anal., 49 (1997) 1081.
11 D. Ditmars, S. Ishihara, S. Chang and G. Bernstein, J. Res. Nat. Bureau of Standards, 82 (1982) 159.
12 C. Angell, in Water – A Comprehensive Treatise, ed. F. Franks, Plenum Press, New York 1982, Vol. 7, Chapter 1.
13 M. Varma-Nair and B. Wunderlich, J. Thermal Anal., 46 (1996) 879.
14 J. Shawe, Thermochim. Acta, 304/305 (1997) 111.
15 B. Wunderlich, A. Boller, I. Okazaki and S. Kreitmeier, J. Thermal Anal., 47 (1996) 103.