

# Pressure Modulated Differential Scanning Calorimetry (PMDSC)

A new approach to the continuous, simultaneous determination of heat capacities and expansion coefficients

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## Supporting Information

### Theory

#### Derivation of eq. 4:

Using an arbitrary experimental pressure modulation, the equation for the experimentally observed heat capacity  $C_f$  of a (T,P<sub>f</sub>,N) ensemble is<sup>1</sup>:

$$C_f = C_p - \left( T \cdot \alpha_p^* \cdot \left( \frac{\partial p}{\partial T} \right)_f \right) \quad (\text{S-1})$$

This general equation describes the heat capacity behavior of the solute and solvent respectively, under simultaneous temperature and pressure variation.

Applying the classical equation for the analysis of the apparent heat capacity difference  $\Delta C_{\text{app}}$  between sample and reference cell in a DSC experiment gives:

$$\frac{\Delta C_{\text{app}}}{m_{\text{solute f}}} = C_f^{\text{solute}} - C_f^{\text{solvent}} \frac{\bar{V}_{\text{solute}}}{\bar{V}_{\text{solvent}}} \quad (\text{S-2})$$

The experimental heat capacities of solute  $C_f^{\text{solute}}$  and solvent  $C_f^{\text{solvent}}$  in eq.S-2 can be each replaced by the expression given in eq.S-1 with the appropriate expansibilities. The eq.4 given in the paper can be obtained directly from eq.S-3.

$$\begin{aligned} \frac{\Delta C_{\text{app}}}{m_{\text{solute}}} &= C_p^{\text{solute}} - T \cdot \left( \frac{\partial p}{\partial T} \right)_f \alpha_p^*, \text{solute} - \left( C_p^{\text{solvent}} - T \cdot \left( \frac{\partial p}{\partial T} \right)_f \alpha_p^*, \text{solvent} \right) \cdot \frac{\bar{V}_{\text{solute}}}{\bar{V}_{\text{solvent}}} \\ \frac{\Delta C_{\text{app}}}{m_{\text{solute}}} &= C_p^{\text{solute}} - C_p^{\text{solvent}} \frac{\bar{V}_{\text{solute}}}{\bar{V}_{\text{solvent}}} - T \cdot \left( \frac{\partial p}{\partial T} \right)_f \left[ \alpha_p^*, \text{solute} - \alpha_p^*, \text{solvent} \cdot \frac{\bar{V}_{\text{solute}}}{\bar{V}_{\text{solvent}}} \right] \end{aligned} \quad (\text{S-3})$$

The sign and magnitude of the pressure dependent part of the  $C_f$  signal relative to the  $C_p$  signal at constant pressure is determined by two factors: by the difference between the expansibilities in eq.S-3, marked by square brackets, and by the rate and direction of the pressure change, given by the term  $\left(\frac{\partial p}{\partial T}\right)_f$ . If the expansibility difference is positive an increasing pressure results in a positive-, decreasing pressure in a negative contribution to the relative shift of the experimental heat capacity as  $dT$  is always positive in an upward temperature DSC experiment.

## Data analysis

In the present study the pressure modulation was of saw-tooth type as shown in the lower part of Fig.S-1A.

If the response of the calorimeter was instantaneous without relaxation phenomena, the saw-tooth like pressure modulation would result in constant larger or smaller  $C_f$  signals, below and above the  $C_p$  signal at constant pressure. This is indicated in the upper part of Fig.S-1A as black step function pattern. The magnitude of the positive and negative deviations from  $C_p$  is determined by the expression  $\pm T\alpha_p^* \frac{\Delta p}{\Delta T}$ .

The ideal signal expected on the basis of eq.S-3 is distorted by non-ideal response of the calorimeter. To a good approximation the response of the calorimeter is of first order, i.e. an exponential function. The output signal,  $f(t)$ , is therefore obtained by a convolution of the ideal signal,  $g(t)$ , with an exponential function,  $h(t)$ , that is characterized by the response time  $\tau=1/k$ .  $\tau$  is equal to 9s for our instrument.

$$f(t) = g(t) \otimes h(t) = \int_0^t g(\tau) h(t-\tau) d\tau \quad (S-4)$$

In the expression for  $g(t)=\pm T\alpha_p^* \frac{\Delta p}{\Delta T}$  in eq.S-4 the term  $\Delta T$  can be replaced by the product of the calorimetric heating rate  $r$  and the duration of a pressure ramp  $d$ . This results in  $\Delta T=r \cdot d$ . To normalize the integral in eq.S-4 the rate constant  $k$  must be introduced. The contribution to the experimental heat capacity signal  $f(t)$  resulting from the pressure ramp is then:

$$f(t) = \int_0^t g(\tau) k \exp(-k(t-\tau)) d\tau \quad (\text{S-5})$$

This folded output signal is shown as green curve in Fig. S-1A.

The number of ramps is given by the ratio  $\frac{t}{d}$  where  $t$  refers to the duration of the PMDSC experiment and  $d$  to the total duration of each pressure ramp.

After solving the integral for each ramp and summation over all ramps the equation used for fitting of the PMDSC-signal is as follows:

$$f(t) = \frac{\alpha_p^* T \Delta p}{r} \cdot \left( \frac{(-1)^{\left[\frac{t}{d}\right]}}{d} \left\{ \frac{1 - 2 \exp\left(kd \left[\frac{t}{d}\right] - kt\right)}{1 + \exp(-kd)} \right\} - \left( \frac{\exp(-kt)}{d} \cdot \frac{1 - \exp(kd)}{1 + \exp(kd)} \right) \right) \quad (\text{S-6})$$

The first order rate constant used was  $k=1/9 \text{ s}^{-1}$  and the amplitude  $\pm T \alpha_p^* \frac{\Delta p}{\Delta T}$  was normalized to a value of one. The square bracket in the expression  $[t/d]$  is the Gauss bracket. The duration  $d$  of the pressure ramp was 65 s for the salt solutions. The value of the product  $(d \cdot k) \approx 7.2$  causes the exponential term in the denominator of the part of eq. S-6 in braces to become negligible. The last term in eq. S-6 in round brackets plays only a role at small values of  $t$  that, however, usually coincide with the settling time of the calorimeter and are therefore not relevant to the data analysis.

For the analysis of a pressure modulated DSC experiment using a heating rate  $r$  the time  $t$  is given by eq. S-7.  $\Delta T = T - T_0$ , with  $T_0$  being the start temperature of the experiment and  $T$  being the actual temperature.

$$t = \frac{\Delta T}{r} \quad (\text{S-7})$$

The apparent heat capacity signal resulting from pressure modulation as a function of temperature can be simulated by eq. S-8. The expression  $f^*(t)$  is analogous to that in eq. S-6 except for the exclusion of the expansibility  $\alpha_p^*$ .

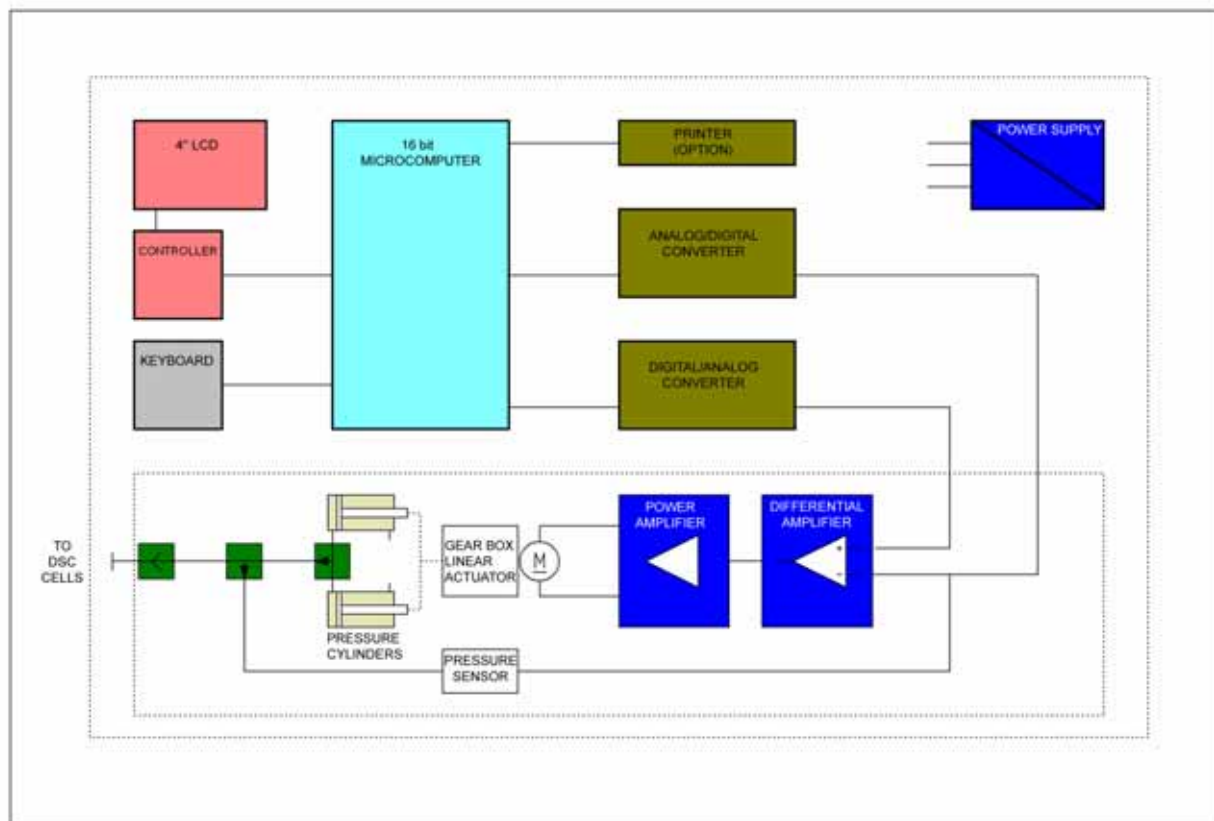
$$\frac{\Delta C_{app}}{m_{solute}} = C_p^{solute} - C_p^{solvent} \cdot \frac{\bar{v}_{solute}}{\bar{v}_{solvent}} - f^*(t) \cdot \left[ \alpha_p^{*,solute} - \alpha_p^{solvent} \cdot \bar{v}_{solute} \right] \quad (S-8)$$

The equation used for the fitting of the DSC-power output difference signal  $P_f - P_{ref}$ , with  $P_{ref}$  as power signal of the reference scan (in this case water-water), turns then out as follows:

$$P_f - P_{ref} = \frac{\Delta C_{app}}{m_{solute}} \cdot r \cdot \frac{V_{DSC-Cell}}{\bar{v}_{solute}} \cdot c_{solute} \quad (S-9)$$

Fig.S-1B visualizes eq. S-9, the power signal as dotted curve. In addition the individual contributions of  $\Delta C_{app}/m$  (see eq. S-8) to the power signal are shown in the figure, i.e. the difference in isobaric heat capacity as blue curve (constructed as mean value of the dotted curve) and the expansibility term in the upper part as red curve oscillating around zero  $\mu W$ -are shown in the graph.

## Block Diagram of Pressure Control Unit



The pressure control unit is a separate instrument that has been constructed in collaboration with the head of the electronic workshop of the Institute of Physical Chemistry of the WWU Münster, Herrn Jürgen Kröninger. It permits application of various kinds of pressure formats to an instrument, in this case a Nano DSC. Provided the calorimeter is equipped with a pressure sensor that can be read out together with the heat capacity values, any DSC instrument can be employed for the simultaneous measurement of expansibility and heat capacity data on the basis of the equations given in the two papers. The pressure control unit is fully programmable with regard to the various pressure formats. The present unit is limited for safety reasons (calorimeter damage) to pressure generation between 0 and 6.5 bars. The

pressure is applied to the DSC cells via teflon tubings as used for example in HPLC instrumentation.

## References

- (1) Rösger, J.; Hinz, H.-J.: Pressure Modulated Differential Scanning Calorimetry (PMDSC): Theoretical Background. (accompanying paper)

## Figure Captions

**FIGURE S-1:** Simulation of the PMDSC-signal.

A: Bottom: Saw-tooth like pressure input signal;

Top: Ideal normalized output signal(black) and folded signal (green) with  $\tau = 1/k=9s$ ;

B: PMDSC-signal (green) and separated contributions of heat capacity  $C_p$  (blue) and expansibility  $\alpha_p^*$  (red).



## Figures

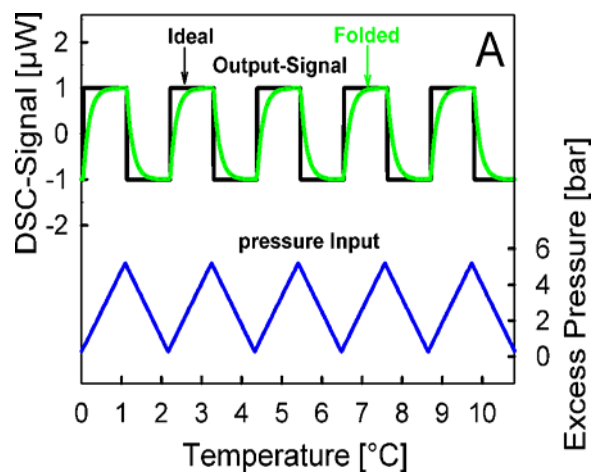


Figure S-1A

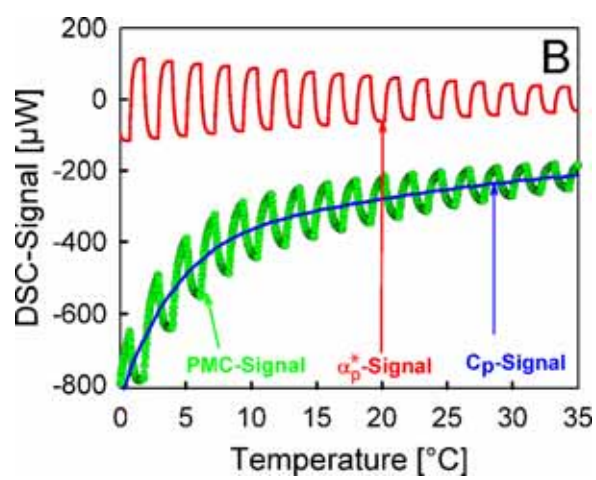


Figure S-1B