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Note

Baseline construction for determination of transition enthalpies by differential scanning calorimetry

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The problem of baseline interpolation for integration of differential scanning calorimetry (DSC) first-order phase transition peaks has been a subject of interest for a number of years[1–8]. The method for construction of the baseline becomes of particular importance when the transition enthalpy (latent heat) is very small and the baseline level shift (due to a change in heat capacity) is large, as is frequently the case for certain liquid crystal transitions. Some baseline construction techniques involve iterative procedures which may prove slow and cumbersome. Others require computer analysis. Still others involve assumptions which are admittedly arbitrary. Thus the need for a rapid—yet reasonably accurate—analytical method for baseline construction is apparent. This note describes a method possessing the advantages of both speed and reproducibility when applied to the determination of enthalpies for nematic–isotropic transitions of liquid crystalline materials.

The method is based on the assumption that the DSC temperature scan rate is sufficiently slow that the baseline in the transition region is proportional to the following expression for heat capacity[1, 2]:

$$C_p(T) = X(T)\, C_{p2} + [1 - X(T)]\, C_{p1} \tag{1}$$

where $X(T)$ is the fraction of sample converted from phase 1 to phase 2 at temperature T and C_{p1} and C_{p2} are the heat capacities (constant pressure) in phases 1 and 2.

If the true baseline is known, $X(T)$ can be calculated from the expression[1]

$$X(T) = \frac{\int_{T_1}^{T} g(T)\mathrm{d}T}{\int_{T_1}^{T_2} g(T)\mathrm{d}T} \tag{2}$$

where $g(T)$ is the magnitude of the DSC signal (measured with respect to the true baseline) and T_1 and T_2 are temperatures in phases 1 and 2, far from the transition

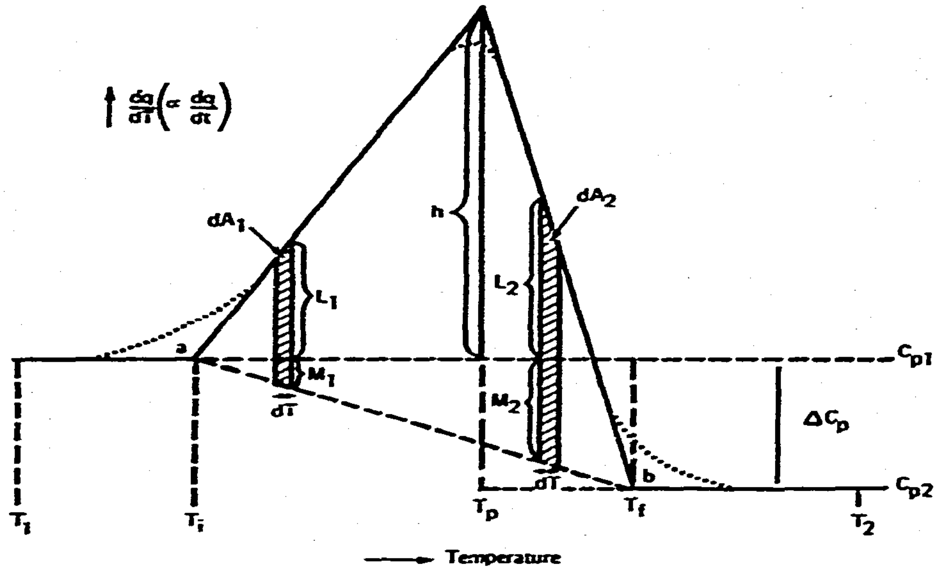


Fig. 1. Approximation to DSC lineshape.

region. In other words $X(T)$ is equal to the ratio of the area under the DSC peak between temperatures T_1 and T, to the total area under the peak.

It is known that DSC transition peaks are often roughly triangular in shape[9]. Triangular shape is a second assumption in our derivation of an analytic expression for the approximate baseline. In Fig. 1, a DSC peak is represented schematically. The solid lines represent the best triangular approximation to the true peak shape (dotted curve). In the figure T_i and T_f are the initial and final temperatures for the transition peak as determined by extension of the straight line portions of the leading and trailing edges of the line shape to their intersection with the lines C_{p1} and C_{p2}, the baselines extrapolated from well below and well above the transition region. T_p is the temperature at the maximum of the transition peak; h is the peak height above the initial baseline (C_{p1}); L_1 and M_1 (L_2 and M_2) are two segments, the sum of which give the altitude of area increment dA_1(dA_2), and $\Delta C_p = C_{p1}$-C_{p2}. A first approximation to the baseline is given by a straight line joining points (a) and (b) in Fig. 1. A second (and usually sufficiently accurate) approximation is then obtained by computing $X(T)$ using the first approximation baseline in eqn (2) and substituting in eqn (1).

For a straight line approximation to the baseline area increments are given by:

$$dA_1 = (L_1 + M_1)\,dT = \left[\frac{h}{T_p - T_i} + \frac{\Delta C_p}{T_f - T_i}\right](T - T_i)\,dT. \qquad T_i \le T \le T_p \qquad (3)$$

$$dA_2 = (L_2 + M_2)\,dT = \left[\frac{h + \Delta C_p}{T_f - T_p} - \frac{\Delta C_p}{T_f - T_i}\right](T_f - T)\,dT. \qquad T_p \le T \le T_f \qquad (4)$$

Integrating eqns (3) and (4) gives

$$A_1 = \int_{T_i}^{T} \mathrm{d}A_1 = \frac{1}{2}\left[\frac{h}{T_p - T_i} + \frac{\Delta C_p}{T_f - T_i}\right](T - T_i)^2 \qquad (5)$$

$$A_2 = \int_{T_p}^{T} \mathrm{d}A_2 = \frac{1}{2}\left[\frac{h + \Delta C_p}{T_f - T_p} - \frac{\Delta C_p}{T_f - T_i}\right][(T_f - T_p)^2 - (T_f - T)^2] \qquad (6)$$

The total integrated area up to any temperature such that $T \leq T_p$ is given by eqn (5). However, the total integrated area up to any temperature such that $T > T_p$ is given by:

$$A = \int_{T_i}^{T_p} \mathrm{d}A_1 + \int_{T_p}^{T} \mathrm{d}A_2$$

$$= \frac{1}{2}\left\{h(T_f - T_i) + \Delta C_p(T_p - T_i) - \left[\frac{h + \Delta C_p}{T_f - T_p} - \frac{\Delta C_p}{T_f - T_i}\right](T_f - T)^2\right\}.$$

$$(T_p \leq T \leq T_f) \qquad (7)$$

The total integrated area (i.e., over the entire temperature range T_i to T_f) is therefore

$$A_{tot} = \int_{T_i}^{T_p} \mathrm{d}A_1 + \int_{T_p}^{T_f} \mathrm{d}A_2 = \frac{1}{2}\{h(T_f - T_i) + \Delta C_p(T_p - T_i)\} \qquad (8)$$

From eqns (2), (5), (7) and (8) we now calculate $X(T)$:

$$X(T) = \frac{A_1}{A_{tot}} = \frac{(T - T_i)^2}{(T_p - T_i)(T_f - T_i)}. \qquad (T_i \leq T \leq T_p) \qquad (9)$$

$$X(T) = \frac{A}{A_{tot}} = 1 - \frac{(T_f - T)^2}{(T_f - T_i)(T_f - T_p)}. \qquad (T_p \leq T \leq T_f) \qquad (10)$$

Conveniently neither eqn (9) nor (10) contain h or ΔC_p as a parameter.

The expression for the second approximation to the baseline (from eqns (1), (9), and (10) is thus a quadratic:

$$C_p(T) = C_{p1} + \frac{\Delta C_p(T - T_i)^2}{(T_p - T_i)(T_f - T_i)}. \qquad (T_i \leq T \leq T_p) \qquad (11)$$

$$C_p(T) = C_{p2} + \frac{\Delta C_p(T - T_f)^2}{(T_p - T_i)(T_f - T_i)}. \qquad (T_p \leq T \leq T_f) \qquad (12)$$

The straight line first approximation is, of course, given by:

$$b(T) = \frac{C_{p2}(T - T_i) - C_{p1}(T - T_f)}{T_f - T_i} \qquad (13)$$

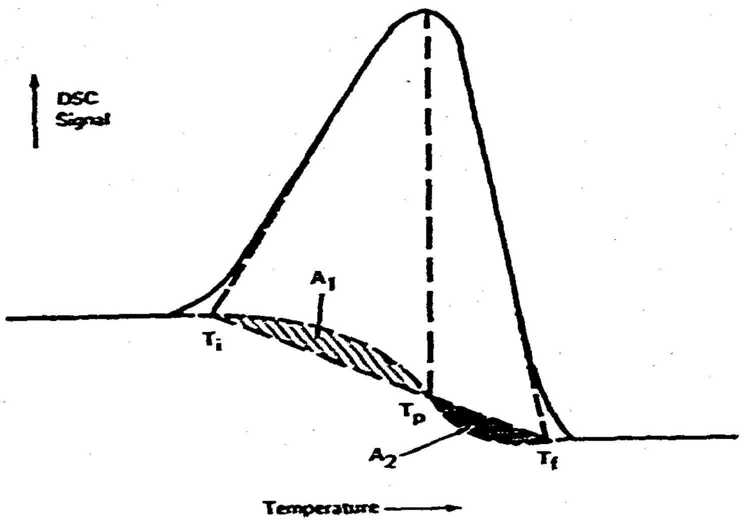


Fig. 2. Area differences in the two approximations.

By differentiating eqns (11)–(13) and comparing the equations and their derivatives it is easy to verify the following relations:

$$\text{At } T = T_i\text{: } C_p(T) = b(T); \frac{dC_p}{dT} = 0 \tag{14}$$

$$\text{At } T = T_p\text{: } C_p(T) = b(T); \frac{dC_p}{dT} = 2\frac{db}{dT} \tag{15}$$

$$\text{At } T = T_f\text{: } C_p(T) = b(T); \frac{dC_p}{dT} = 0 \tag{16}$$

Thus it is easy to approximate a true baseline by constructing the straight line baseline and then drawing a smooth curve which passes through the straight line at T_i, T_p, and T_f with zero slope at T_i and T_f and twice the straight line slope at T_p.

The two approximate baselines are shown in Fig. 2. The area differences found in using the two different baselines are indicated A_1 and A_2. Since one is additive and the other subtractive, the net areal error introduced by use of the straight line baseline is proportional to the difference of A_1 and A_2 which can be shown to be

$$A_1 - A_2 = \frac{\Delta C_p(2T_p - T_f - T_i)}{6} \tag{17}$$

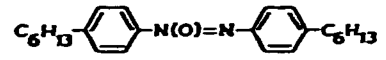
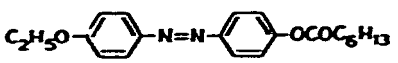
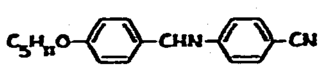
The error is, of course, zero if $\Delta C_p = 0$ or if T_p is halfway between T_i and T_f. The fractional error is thus:

$$\frac{A_1 - A_2}{A_{tot}} = \frac{\Delta C_p(2T_p - T_f - T_i)}{3[h(T_f - T_i) + \Delta C_p(T_p - T_i)]} \tag{18}$$

For a typical nematic to isotropic phase transition $\Delta C_p \approx 0.2h$, T_p—$T_i \approx 1.2$K, and

TABLE 1

SCAN DIRECTION INDEPENDENCE OF NEMATIC–ISOTROPIC ENTHALPIES DETERMINED USING PRESENT BASE-LINE CONSTRUCTION TECHNIQUE

Compound	*Transition enthalpy (kJ mol^{-1})*		*Literature*
	Increasing scan	*Decreasing scan*	
	0.653	0.636	0.57[a]
	0.624	0.636	
	1.08	1.05	
	0.448	0.456	

[a] J. van der Veen, W. H. de Jeu, M. W. M. Wanninkhof and C. A. M. Tienhoven, *J. Phys. Chem.*, 77 (1973) 2153.

$T_f—T_p \approx 0.7$K, so that the calculated error is 0.016 or 1.6%. Actual measurements yielded discrepancies of only 1–2% between the two methods. The error is of the order of the uncertainty in the use of a planimeter, so a straight line baseline seems a reasonable approximation to the true baseline. For greater accuracy the second approximation can, of course, be used.

The validity of the method can be tested by determination of transition enthalpies for phase changes in which polymorphism and supercooling do not play a role. For such transitions, e.g., nematic–isotropic phase changes of liquid crystals, the measured transition enthalpies are expected to be independent of temperature scan direction. We have applied the methods of this note to a number of liquid crystals and find excellent reproducibility of results, independent of scan direction (Table 1). We conclude therefore that the methods are useful for such systems.

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