

## TEMPERATURE CALIBRATION OF HEAT FLUX DSC'S ON COOLING

*J. D. Menczel*

Hoechst Celanese, Corporate Research and Technology, 86 Morris Avenue, Summit, NJ 07901, USA

### Abstract

The temperature calibration of a TA Instruments 3200–2920 DSC has been performed on cooling using the isotropic → nematic, isotropic → cholesteric and other liquid crystal → liquid crystal transitions of thermally stable, high purity liquid crystals. The thermal stability of these liquid crystals has been verified by measuring the temperature of the mentioned transitions during cyclic heating and cooling experiments. Correspondence has been established between the real and indicated temperature during cooling for all combinations of heating and cooling rates of practical interest: correction values were determined to the indicated temperature in order to obtain the real temperature on cooling. These correction values were calculated as the average from the temperatures of four or five different liquid crystal transitions for each heating-cooling rate combination. The accuracy of the temperature calibration on cooling is ca. 0.2 °C for heating and cooling rates up to 20 °C min<sup>-1</sup>.

**Keywords:** DSC, liquid crystals, temperature calibration

### Introduction

Differential scanning calorimeters have to be calibrated with regard to both heat flux and temperature. The former is undertaken using specific heat capacity standards (most often sapphire) or melting of high purity metals, e.g. indium, tin, lead. The temperature calibration is usually performed on heating using the same metal standards that are used simultaneously for the heat flux calibration. Metal standards are used because their purity can be much higher than that of organic standards (often 99.9999%, from Johnson Matthey, Seabrook, NH: e.g. 11674 indium, 14134 tin, and 12450 lead), and also, because they do not exhibit decomposition during melting, unlike many organic substances. However, the mentioned temperature calibration is undertaken on heating, because only the melting point of metals has a definite value. Temperature calibration on cooling is not normally performed, because supercooling is a common phenomenon, therefore the crystallization temperature is not known exactly. Temperature calibration on cooling became possible as a result of widespread use of thermally stable liquid crystals. It was known that temperature of the nematic → isotropic (N → I) or cholesteric → isotropic (Ch → I) transition is identical to that of the I → N (or I → Ch). In other words, these transitions do not have a hysteresis on cooling. The absence of supercooling for these transi-

tions is explained by the fact that the nuclei of the nematic (or cholesteric) phase are always present in the isotropic melt due to density fluctuations.

The cooling calibration of a power compensation DSC has been described by Menczel and Leslie [1, 2]. In this paper, the same liquid crystals are applied to calibrate the temperature on cooling for a heat flux type TA Instruments 3200-DSC 2920 instrument.

## Experimental

### Materials

The following liquid crystals (LC) were used in this study:

1. (4-*n*-octyloxy-2-hydroxybenzal)-4'-*n*-butylaniline (LC-1, Chromofore, Inc., Huntsville, AL.), its preparation and purification is described in [1] and [2]. Purity determined by DSC method is 99.8 mol%. This liquid crystal has two transitions,

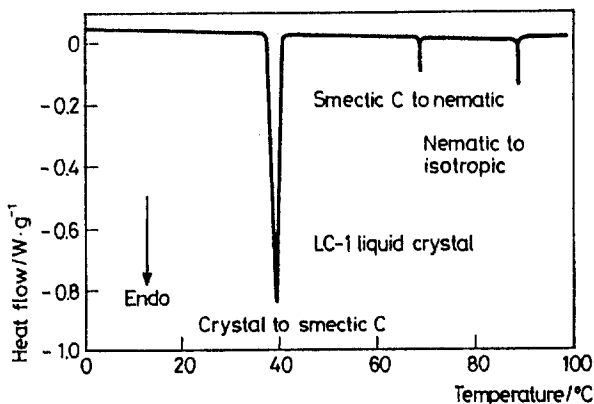


Fig. 1 The heating DSC curves of LC-1 (HR=1°C min<sup>-1</sup>)

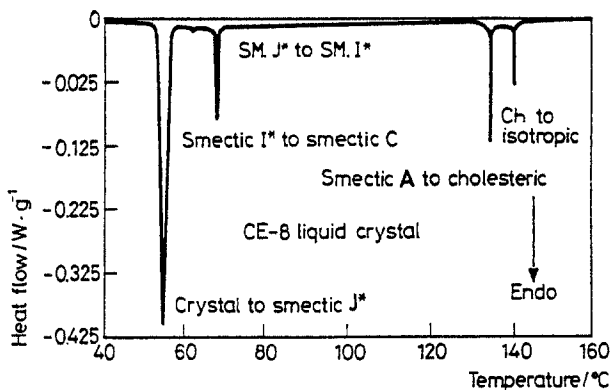


Fig. 2 The heating DSC curve of CE-8 (HR=1°C min<sup>-1</sup>)

which can be used for cooling calibration: the  $S_C \rightarrow N$  ( $69.4^\circ\text{C}$ ) and the  $N \rightarrow I$  ( $88.9^\circ\text{C}$ ).

2. (+)-(4-(2'-methylbutyl)phenyl-4'-*n*-octylbiphenyl-4-carboxylate) {commercially available as CE-8 liquid crystal from BDH Chemicals Ltd., Poole, Great Britain [3]}. Its purification is described in [2]. Purity determined by DSC is 99.7 mol%. The transition temperatures and heats of transitions are described in [1] and [2]. This liquid crystal has four transitions, which can be used for cooling calibration (from  $63.6$  to  $140.3^\circ\text{C}$ ).

### Method

A TA Instruments 3200-DSC 2920 used in this work was cooled by an FTS mechanical cooling accessory with a head temperature of ca.  $-100^\circ\text{C}$ . The 2920 DSC used in this work was calibrated on heating using indium, tin, and lead at heating rates of 1, 2, 5, 10, 20, and  $40^\circ\text{C min}^{-1}$ . Then, for each heating calibration, the instrument was calibrated on cooling at 1, 2, 5, 10 and  $20^\circ\text{C min}^{-1}$ . Higher cooling rates were not used, because for those cooling rates the temperature control was lost at relatively high temperatures. In the cooling calibration experiments the LC samples were heated up into the isotropic phase, then cooled to room temperature (cooling), and reheated again (second heating), in order to check the transition temperatures again. For the calibration purposes the transition temperatures measured on cooling and the second heating were used. A fresh sample was used for each calibration point. Since the liquid crystal transitions are very narrow (especially at low heating or cooling rates), one data point has to be recorded at every  $0.01^\circ\text{C}$ .

As described earlier [1, 2] the transition temperatures were determined as follows: for the metal standards (In, Sn, Pb) it was determined as the extrapolated onset of the melting; for the LC  $\rightarrow$  LC transitions on heating and the  $N \rightarrow I$  or  $Ch \rightarrow I$  transitions it was taken as the extrapolated onset of the transition; for the  $I \rightarrow N$  or  $I \rightarrow Ch$  transitions, and the LC  $\rightarrow$  LC transitions on cooling it was also taken as the extrapolated onset of the exothermic peaks due to reasons described in [1] and [2].

**Table 1** The transition temperatures during cyclic heating-cooling of LC-1 liquid crystal (heating rate =  $2^\circ\text{C min}^{-1}$ , cooling rate =  $2^\circ\text{C min}^{-1}$ )

|   | $T(S_C \rightarrow N)/^\circ\text{C}$ | $T(N \rightarrow I)/^\circ\text{C}$ | $\Delta T_1/^\circ\text{C}$ | $\Delta T_1/^\circ\text{C}$ |
|---|---------------------------------------|-------------------------------------|-----------------------------|-----------------------------|
| First heating                           | 69.44                                 | 88.88                               |                             |                             |
| First cooling                           | 69.15                                 | 88.63                               | 0.29                        | 0.25                        |
| Second heating                          | 69.42                                 | 88.87                               |                             |                             |
| Second cooling                          | 69.14                                 | 88.63                               | 0.28                        | 0.24                        |
| Third heating                           | 69.41                                 | 88.86                               |                             |                             |
| Third cooling                           | 69.13                                 | 88.63                               | 0.28                        | 0.23                        |
| Fourth heating                          | 69.40                                 | 88.85                               |                             |                             |
| Fourth cooling                          | 69.12                                 | 88.62                               | 0.28                        | 0.23                        |
| AVERAGE $\Delta T = 0.26^\circ\text{C}$ |                                       |                                     |                             |                             |

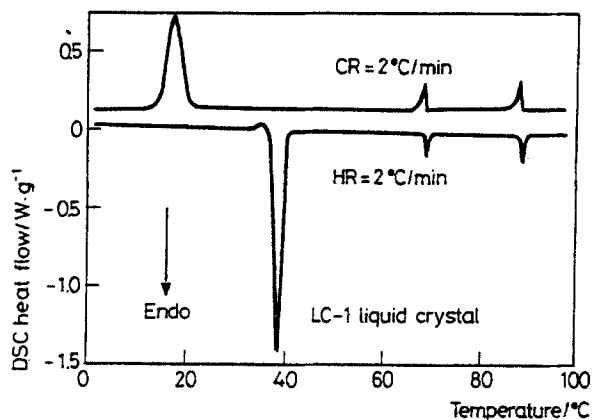


Fig. 3 The heating and cooling DSC curves of LC-1 recorded at low heating and cooling rates ( $HR=2^{\circ}\text{C min}^{-1}$ ,  $CR=2^{\circ}\text{C min}^{-1}$ )

## Results and discussion

Typical DSC traces recorded on heating for the two liquid crystals used are shown in Figs 1 and 2.

The thermal stability of these cooling standards was checked prior to the actual calibration. This is best done by measuring the transition temperatures during cyclic heating-cooling experiments. These experiments indicated that the transition temperatures are essentially unchanged in at least four heating-cooling cycles. The transition temperatures in the four consecutive heating-cooling cycles for the LC-1 liquid crystal standard are shown in Table 1. In addition to the transition temperatures the  $\Delta T$  values [Eq. (1)] are also given in this table. The data indicate that there is only a very slight decrease of the transition temperatures: the average  $\Delta T$  is  $0.26^{\circ}\text{C}$

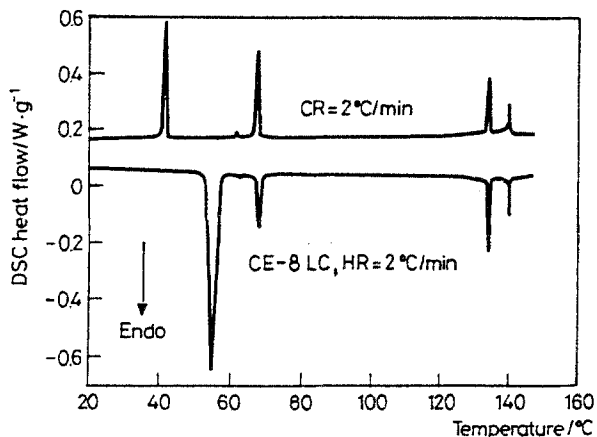


Fig. 4 The heating and cooling DSC curves of CE-8 recorded at low heating and cooling rates ( $HR=2^{\circ}\text{C min}^{-1}$ ,  $CR=2^{\circ}\text{C min}^{-1}$ )

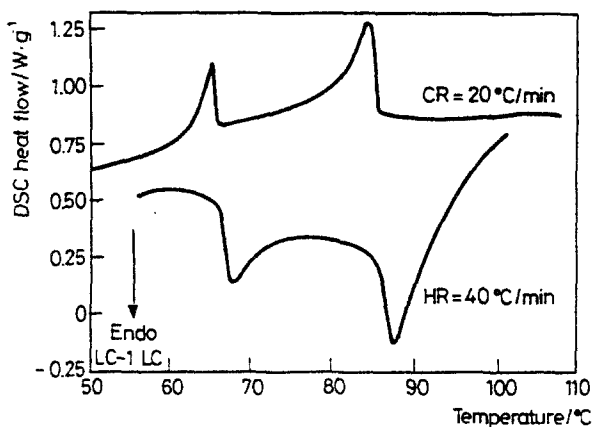


Fig. 5 The heating and cooling DSC curves of LC-1 recorded at high heating and cooling rates ( $HR=40^{\circ}\text{C min}^{-1}$ ,  $CR=20^{\circ}\text{C min}^{-1}$ )

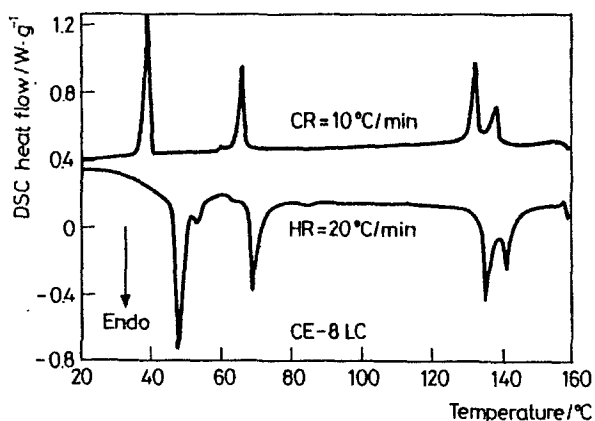


Fig. 6 The heating and cooling DSC curves of CE-8 recorded at high heating and cooling rates ( $HR=20^{\circ}\text{C min}^{-1}$ ,  $CR=10^{\circ}\text{C min}^{-1}$ )

(with a standard deviation of only  $0.03^{\circ}\text{C}$ ). Also, these data show the high precision and reproducibility of the measurement of the transition temperatures, thus, the cooling calibration proper.

The comparison of heating and cooling curves at low ( $2^{\circ}\text{C min}^{-1}$ ) for the LC standards is shown in Figs 3 and 4.

The temperature gradient in the sample was calculated: the maximum weight of the liquid crystal samples was 3 mg, the radius of the hermetically sealed sample pan is ca. 0.2 cm, and this leads to ca.  $0.1^{\circ}\text{C}$  gradient in the sample at  $40^{\circ}\text{C min}^{-1}$  [4], giving meaningful results at the heating and cooling rates used.

The results were evaluated using the following equation:

$$T_{\text{real}} = T_{\text{ind}} + \Delta T \quad (1)$$

$T_{\text{real}}$  where is the transition temperature measured on heating,  $T_{\text{ind}}$  is the transition temperature measured on cooling. All the  $\Delta T$  values calculated from the N  $\rightarrow$  I or Ch  $\rightarrow$  I and the other LC  $\rightarrow$  LC transitions for all the heating-cooling rate combinations are summarized in Table 2. The average  $\Delta T$  values together with the standard deviations of the individual points are shown in Table 3. As it can be seen from the data presented in these tables, the value of  $\Delta T$  increases with both, increasing heating and cooling rate. For most points the accuracy is better than  $\pm 0.2^\circ\text{C}$ , and this value is exceeded only at higher heating or cooling rates, obviously, due to errors arising as a consequence of increasing curvature in the leading edge of the transition peaks.

When comparing the performance of the two liquid crystals, it is more advantageous to use CE-8 than LC-1 at low heating or cooling rates, because more transitions (4 vs. 2) can be used in the same run (Figs 3 and 4). However, at high heating or cooling rates, the two high temperature transitions of CE-8 overlap, therefore the results obtained from LC-1 are more reliable (Figs 5 and 6).

Table 2 The measured  $\Delta T$  values of CE-8 and LC-1 liquid crystals at different heating-cooling rate combinations

| Cooling/ $^\circ\text{C min}^{-1}$ | $\Delta T$                               |  |  |  |                                    |
|------------------------------------|--|--|--|--|------------------------------------|
|                                    | 1  | 2  | 5  | 10                                       | 20                                 |
| Heating/ $^\circ\text{C min}^{-1}$ |  |  |  |  |                                    |
| 1                                  | 0.10; 0.12;<br>0.05; 0.11;<br>0.12; 0.15 | 0.23; 0.21;<br>0.16; 0.04;<br>0.14; 0.07 | 0.30; 0.27;<br>0.15; 0.04;<br>0.39; 0.30 | 0.57; 0.49;<br>0.31; 0.49;<br>0.36; 0.66 | 1.15; 1.12;<br>0.68; 0.74;<br>0.93 |
| 2                                  | 0.17; 0.21;<br>0.17; 0.16;<br>0.20; 0.27 | 0.28; 0.25;<br>0.11; 0.19;<br>0.24; 0.33 | 0.35; 0.45;<br>0.21; 0.28;<br>0.41; 0.50 | 0.70; 0.62;<br>0.30; 0.87;<br>0.60; 0.74 | 1.35; 1.39;<br>0.92; 1.78;<br>0.97 |
| 5                                  | 0.41; 0.33;<br>0.32; 0.32;<br>0.40; 0.46 | 0.37; 0.38;<br>0.50; 0.41;<br>0.35; 0.22 | 0.52; 0.61;<br>0.38; 0.48;<br>0.60; 0.70 | 0.74; 0.60;<br>0.53; 0.57;<br>0.74; 0.83 | 1.09; 1.20;<br>0.96; 0.95;<br>1.14 |
| 10                                 | 0.49; 0.62;<br>0.34; 0.51;<br>0.62; 0.72 | 0.75; 0.58;<br>0.56; 0.73;<br>0.92; 1.00 | 0.87; 0.69;<br>0.49; 0.63;<br>0.85; 0.94 | 0.76; 0.97;<br>0.49; 0.65;<br>0.84; 0.95 | 1.48; 1.33;<br>1.20; 1.10          |
| 20                                 | 0.64; 0.87;<br>1.05; 1.18;<br>0.74       | 0.76; 1.01;<br>1.04; 0.97;<br>0.96       | 0.88; 1.14;<br>1.01; 1.12;<br>1.2        | 1.30; 1.41;<br>1.43; 1.68;<br>1.22       | 1.94; 1.63;<br>1.65; 1.73;<br>1.44 |
| 40                                 | 1.20; 1.63;<br>1.56; 1.90;<br>2.03       | 2.35; 1.38;<br>1.89; 1.82                | 1.71; 2.65;<br>1.60; 1.36                | 2.35; 2.04;<br>2.14; 2.26                | 2.10; 2.70;<br>2.41; 1.97          |

**Table 3** The average  $\Delta T$  values of CE-8 and LC-1 liquid crystals with the standard deviations

| Cooling/ $^{\circ}\text{C min}^{-1}$<br>Heating/ $^{\circ}\text{C min}^{-1}$ | $\Delta T$  |             |             |             |             |
|--|-------------|-------------|-------------|-------------|-------------|
|  | 1           | 2           | 5           | 10          | 20          |
| 1  | 0.11 (0.03) | 0.14 (0.08) | 0.24 (0.13) | 0.48 (0.13) | 0.92 (0.21) |
| 2  | 0.20 (0.04) | 0.23 (0.08) | 0.37 (0.11) | 0.64 (0.19) | 1.08 (0.27) |
| 5  | 0.37 (0.06) | 0.37 (0.09) | 0.55 (0.11) | 0.67 (0.12) | 1.07 (0.11) |
| 10   | 0.55 (0.13) | 0.76 (0.18) | 0.75 (0.17) | 0.78 (0.18) | 1.28 (0.16) |
| 20   | 0.90 (0.22) | 0.95 (0.11) | 1.07 (0.13) | 1.41 (0.17) | 1.68 (0.18) |
| 40   | 1.66 (0.32) | 1.86 (0.40) | 1.83 (0.57) | 2.20 (0.14) | 2.30 (0.33) |

The values in paranthesis mean the standard deviation.

## References

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