
**Molecular Crystals and Liquid Crystals**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

# Some Comments on the Determination of Enthalpies of Liquid Crystalline Transitions by Differential Scanning Calorimetry

B. R. Ratna[a]; S. Chandrasekhar[a]
[a] Raman Research Institute, Bangalore, India

First published on: 01 January 1988

**To cite this Article** Ratna, B. R. and Chandrasekhar, S.(1988) 'Some Comments on the Determination of Enthalpies of Liquid Crystalline Transitions by Differential Scanning Calorimetry', Molecular Crystals and Liquid Crystals, 162: 2, 157 — 159
**To link to this Article: DOI:** 10.1080/00268948808084456
**URL:** http://dx.doi.org/10.1080/00268948808084456

*Mol. Cryst. Liq. Cryst.*, 1988, Vol. 162B, pp. 157–159
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

# Some Comments on the Determination of Enthalpies of Liquid Crystalline Transitions by Differential Scanning Calorimetry

B. R. RATNA and S. CHANDRASEKHAR

*Raman Research Institute, Bangalore 560080, India*

(*Received June 1, 1987; in final form September 28, 1987*)



We demonstrate a simple practical method of improving the accuracy of determination of enthalpies of liquid crystalline transitions by differential scanning calorimetry. The method involves measurements at different heating rates and interpolation to zero heating rate.

*Keywords: liquid crystalline transitions, differential scanning calorimetry, transition enthalpy*

Commercially available differential scanning calorimeters (DSC) are now very commonly used for determining the latent heats ($\Delta H$) of transitions in liquid crystals.[1] The usual procedure is to measure the area under the curve in the DSC thermogram, and to calibrate it against a transition in a standard material (such as indium). However, caution is necessary in applying this procedure to liquid crystalline transitions because of pronounced pretransition effects, which the DSC does not separate from the true $\Delta H$. The purpose of this note is to illustrate a practical and convenient method of overcoming this difficulty and extracting a reasonably accurate value of $\Delta H$ from DSC measurements. We present data that we have obtained on two compounds using a Perkin Elmer DSC-4 in conjunction with a Thermal Analysis Data Station (TADS).

DSC runs were taken at ten different rates, ranging from 1.0°C/min to 0.1°C/min, the lowest rate possible with the DSC set up. The total area under the endothermic peak was calculated using the com-

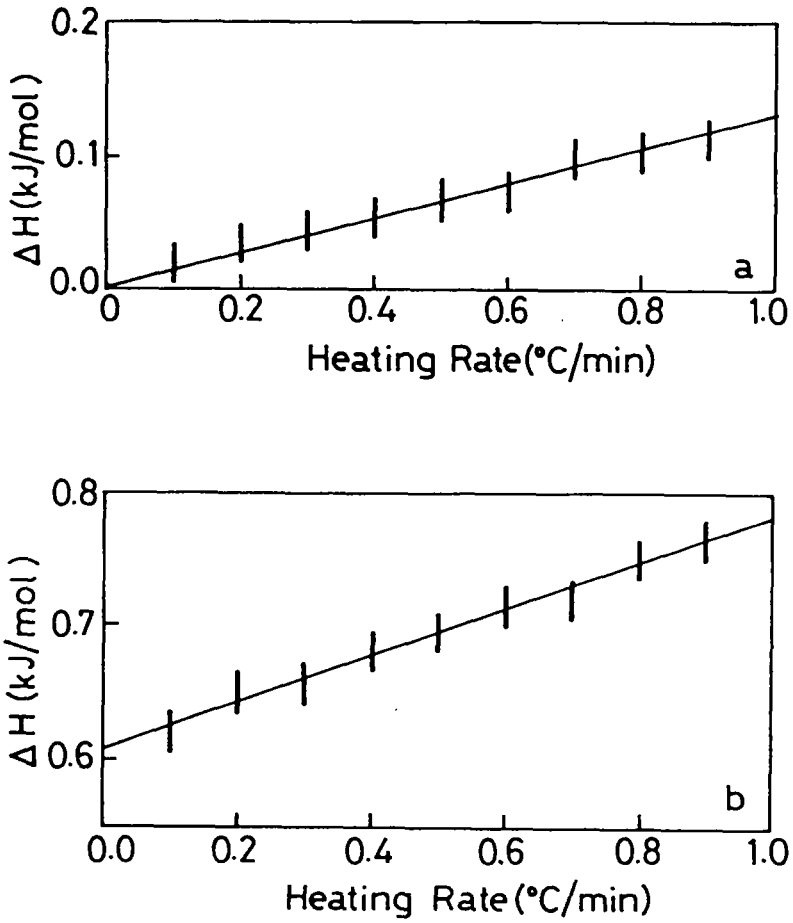


FIGURE 1 Apparent latent heat (ΔH) as determined by DSC of (a) the A–N transition and (b) the N–I transition in 8CB versus heating rate.

puterized TADS system and the corresponding enthalpy (ΔH) which includes both the latent heat and the specific heat contributions was evaluated for each heating rate. The ΔH value obtained in this manner is plotted in Figure 1 as a function of the heating rate for the A–N and N–I transitions in 4-*n*-octyl-4′-cyanobiphenyl (8CB). A least square fit of the ΔH data to a straight line gave the enthalpy at zero heating rate, which is compared below with the high precision adiabatic calorimetric data of Marynissen *et al.*[2] The agreement can be seen to be satisfactory.

TABLE I

Latent heats (in kJ/mol) of transitions in 8CB

| | Present study | Marynissen *et al.* |
|---|---|---|
| A–N | ~0 (2nd order) | <0.0004 (2nd order) |
| N–I | 0.60 | 0.612 |

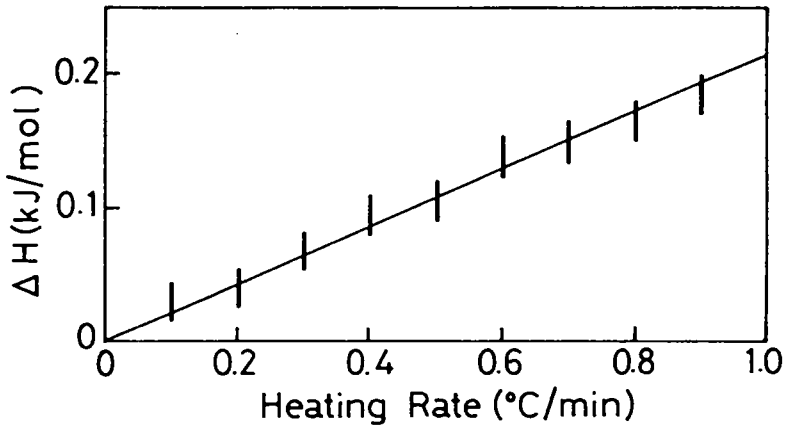


FIGURE 2 Apparent latent heat (ΔH) as determined by DSC of the A–N transition in 80CB versus heating rate.

A similar plot for the A–N transition in 4-*n*-octyloxy-4′-cyanobiphenyl (80CB) is shown in Figure 2. Again the interpolated value of $\Delta H \sim 0$ is in agreement with the very precise AC calorimetric measurements of Garland *et al.*[3] who found this transition to be of second order. Thus the method appears to be a fairly satisfactory way of correcting for precursor effects in DSC measurements on weakly first order and second order transitions in liquid crystals.

## References

1. See e.g., A. Beguin, J. Billiard, F. Bonamy, J. M. Buisine, P. Curelier, J. C. Dubois and P. Le Barny, "Sources of Thermodynamic Data on Mesogens." Special Topic XIV, *Mol. Cryst. Liq. Cryst.*, **115**, 1–326 (1984).
2. H. Marynissen, J. Thoen and W. Van Dael, *Mol. Cryst. Liq. Cryst.*, **97**, 149 (1983).
3. C. W. Garland, G. B. Kasting and K. J. Lushington, *Phys. Rev. Lett.*, **43**, 1420 (1979).