HEAT CAPACITY STUDY ON THE MODEL LIQUID CRYSTAL 8CB: ASC vs DSC

INTRODUCTION

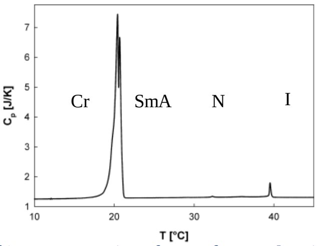
8CB is a model compound for the study of phase transitions, since it exhibits three distinct types of phase transitions: a strong first-order melting transition, a continuous transition between the liquid crystalline phases smectic A and nematic, and weakly first-order transitions from the nematic phase to the isotropic liquid. Peltier-element based ASC was applied to 8CB. In this technique, a constant power *P* is applied to the sample, while the temperature is measured as a function of time. From these data, both heat capacity and enthalpy can be calculated as

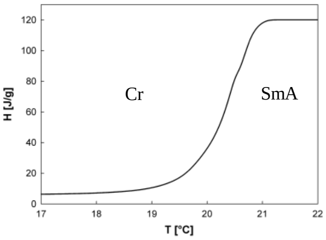
$$C_p = \frac{dQ}{dT} = \frac{dQ/dt}{dT/dt} = \frac{P}{\dot{T}} \qquad H(T) = P\left[t(T) - t(T_0)\right]$$

This approach contrasts to that of a DSC, where a constant temperature rate is applied to the sample and a known reference sample. The heat capacity is obtained from a comparison between the power absorbed by sample and reference, while the enthalpy can only be obtained from an integration of the heat capacity.

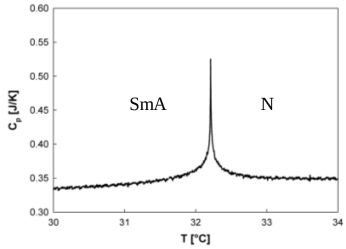
ASC

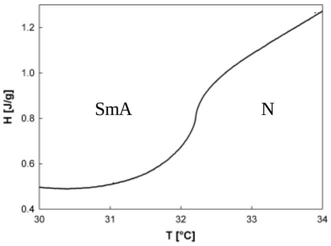
Sample: 70 mg 8CB. Data are presented as total heat capacity of sample, cell and addenda. Enthalpy is reduced to sample mass and a linear background is subtracted for better display.



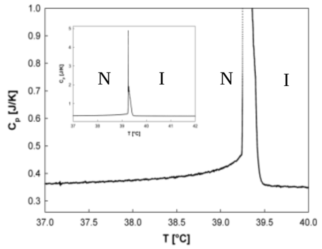


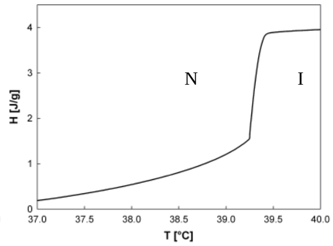
(left) Heat capacity of 8CB from a heating run over a broad temperature range as measured by a Peltier-based ASC with an average rate of about 6 K/h. The melting transition around 20 °C is the dominant feature, with a somewhat double peak structure. The smectic A to nematic (AN) transition at ~33.7 °C and the nematic to isotropic liquid (NI) transition at ~40.5 °C can still be distinguished.
(right) Enthalpy curve for the melting transition of 8CB, showing the steep increase (latent heat) as well as the rounding at lower temperatures due to pretransitional melting of the alkyl chains of the 8CB molecules.





(left) AN transition from a Peltier-element based ASC with an average rate of about 0.3 K/h. The heat capacity shows as a sharp, symmetric peak. From the range outside the transition, the noise level can be asserted as much less than 1% of the signal.
(right) Enthalpy at this transition, showing the absence of a steep increase, indicating the absence of latent heat within the resolution. This confirms the second-order continuous nature of the AN transition in 8CB.

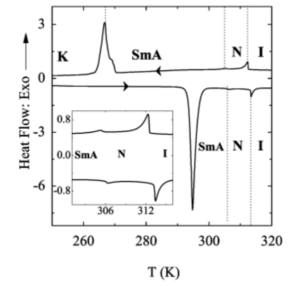




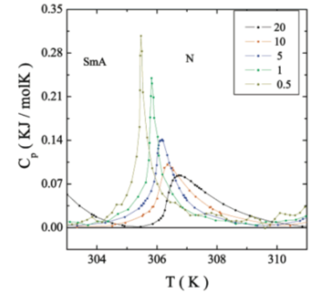
(left) At the NI transition the figure clearly shows the pretransitional increase from about 38 °C, followed by a very steep increase at the phase transition, as determined by ASC. The inset shows how the heat capacity attains a very high effective value, a consequence of the first-order nature of the transition and the presence of latent heat. The high temperature wing is somewhat widened due to the presence of impurities in the sample. The width of this two-phase region is a measure of the purity of the sample.
(right) Enthalpy curve for the NI transition, showing the steep increase (latent heat) as well as the rounding at lower temperatures due to pretransitional effects associated with weakly first-order transitions.

DSC

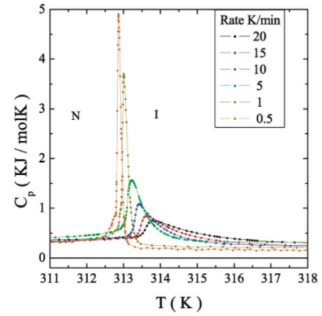
Sample: 5 mg, 10 K/min or as indicated in D. Sharma, J.C. MacDonald, G. S. Iannacchione. Thermodynamics of activated phase transitions of 8CB: DSC and MC calorimetry. J. Phys. Chem. B 110, 16679 (2006).



DSC heat flow curves for 8CB in cooling and heating runs. The melting transition does not show the double feature, whereas the NA and NI transitions are visible, but appear broadened compared to the ASC results.



Rate dependence for the AN transition determined by DSC. The transition appears as asymmetric and is much broader than in the ASC results. Even at the slowest rates achieved, the AN transition shows some broadening towards the higher temperatures, something absent in the ASC results. This experimental artifact is a consequence of the DSC constant rate operation principle.



The heat capacity at the NI transition as determined by DSC here shows as a clear peak only at the lowest rates. Some pretransition is visible, but the sharp onset of the ASC data is missing. The peaks are in all cases broadened with respect to the ASC data, and no two-phase region due to the latent heat can be distinguished in any of the runs, indicating that the rate-dependent broadening is a consequence of the technique.

CONCLUSION **ASC allows to obtain high resolution heat capacity data on all the transitions in 8CB with a detail that exceeds that of DSC curves. At the same time the enthalpy *H*(*T*) is obtained directly from the measurement of *P* and *T*(*t*). In addition, the width and exact shape of the heat capacity curve may allow for determination of purity of the samples.**