Differential Scanning Calorimetric Study of the Nematic Liquid Crystal 5CB

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A power compensated differential scanning calorimeter was used to make several thermodynamic measurements of the nematic liquid crystal 5CB (4-pentyl-4´-cyanobiphenyl). 1.1 mg, 3.6 mg, and 6.3 mg samples were heated from -20°C to 70°C at 10°/minute. The observed temperatures for the solid-liquid crystal and liquid crystal-liquid transitions were quite precise and generally close to literature values, but consistently high. For more advanced thermodynamic data, such as the latent heat and heat capacity of the sample, standards could not be found. Latent heat values for the solid-liquid crystal and liquid crystal-liquid transitions demonstrated good precision. However, experimental values for determining heat capacity in each phase at an arbitrary temperature were generally imprecise.

INTRODUCTION

Differential scanning calorimetry is one of the most widely used analytical instruments because of the ease with which it can provide large amounts of thermodynamic data. Properly used, information on the phase transitions of a sample, such as transition temperature, enthalpy, heat capacity, specific heat, and latent heat, can all be calculated from a single data run. Enthalpy, a term often used in physical chemistry, is a measure of the energy of a system that includes the energy due to the volume that the system occupies. Heat capacity is the proportionality constant between the amount of head added to an object and the resulting temperature change of the object, and specific heat is the heat capacity per unit mass. Latent heat is the amount of heat per unit mass that must be transferred to a sample when it completely undergoes a phase change. This experiment was an attempt to use DSC to examine the phase transitions and thermodynamic properties of the nematic liquid crystal 5CB.

The liquid crystal 5CB (4-pentyl-4´-cyanobiphenyl) has simple phase transitions. It changes from a solid to a nematic liquid crystal at 22.5°C, and melts to an isotropic liquid at 35°C[1]. On a microscopic level, the rodlike 5CB molecules are locked in place and aligned when the sample is a solid. When the sample becomes a liquid crystal, the molecules are free to translate and can rotate somewhat. However, the molecules remain roughly aligned. The aligned but mobile molecules are what give liquid crystals their unique properties. When the sample finally melts to a liquid, all orientation is lost. Because melting from a solid to a liquid crystal involves breaking intermolecular bonds, it is endothermic, though not as much as a straight transition from solid to liquid. The liquid crystal-liquid transition involves disrupting orientation, so it is also endothermic, but it requires much less energy.

EXPERIMENT

The Perkin-Elmer DSC-4 used in the experiment is a power compensated calorimeter[2]. The instrument has two pans: one for a sample and one for a reference. Each pan has an independent electrical heater. The diminutive size of the heaters, sample holders, and samples allow for rapid heating, cooling, and equilibration. Platinum resistance thermometers sit immediately below the sample holders and are used to measure the temperature of each holder separately. The heaters are close below the thermometers and are in thermal contact with a heat sink, allowing them to cool easily. Refrigeration units allow for even quicker cooling and for analysis below room temperature. Sample and reference temperatures are fed into a differential amplifier, which then adjusts the power to the heaters so that the two temperatures are identical. A signal that is proportional to the difference in the power input from the two heaters is transmitted to the data

acquisition system. The power difference is measured as a temperature program scans the sample and reference through a range of temperatures. Thus, the corresponding time and temperature for each power are known.

The DSC used in the experiment was controlled by a 386 IBM-compatible computer running the Perkin Elmer instrumental software (version 6.00) from DOS. The computer was connected to the instrument via GPIB. The software collected data and provided graphical analysis tools to determine transition temperatures and peak areas.

The DSC was set to heat and cool at 10°C per minute, a moderately slow rate for DSC. The slower the scan rate, the less hysteresis affects measurements, but slow scan rates also lead to low, wide thermogram peaks. Generally, faster rates are used for samples with quick, simple transitions to produce sharp thermogram peaks and save time. The range of the instrument was set to 10 mcal/s, meaning that a power signal of 10 mcal/s would register full displacement on a chart recorder. Because the software was not a chart recorder, this was not a practical limitation. However, the sensitivity controls the size of the peaks. 10 mcal/s was chosen because it provided good sensitivity while not being overwhelmed by large transitions. The program was set to take data every 0.1°C, approximately 100 points per minute.

Before use, the DSC was calibrated. Calibration is accomplished by running a standard material, usually indium, and comparing the experimental melting point and enthalpy of transition (or latent heat) to standard values. Two screws in the instrument, one for adjusting temperature readings, one for adjusting enthalpy readings, were turned until the temperature and enthalpy values were reproducibly within desired tolerance of the standard values.

Before any analytical or calibration samples were run, the instrument was run under analytical conditions with both the sample and reference pans empty. For the indium calibration temperature range, no transitions were seen with empty pans. However, in the range for the liquid crystal samples, a second-order transition appeared at about 40°C. This indicated that the sample holder was contaminated. When several solvents failed to remove the contaminant, the DSC was heated to 400°C for 20 hours with a nitrogen flow through the sample chamber. This eliminated the contaminant.

DSC samples were prepared by encapsulation in aluminum sample holders. A small amount of sample was placed in a thin aluminum pan, which was then placed on the stage of a piston-like sample crimper. An aluminum lid was placed on the pan and the hammer of the crimper was gently brought down on the capsule. The end product resembled two thin discs of aluminum rolled together at the edge. The encapsulation process ensures that the sample is spread thinly and evenly, providing good thermal contact with the capsule and the sample holder. A blank capsule (one with nothing in the aluminum pan) was made and placed into the reference pan.

The final step before collecting sample data was to run blanks. An empty capsule was placed in the sample pan and the instrument was run under analytical conditions. The thermogram showed no transitions and was reproducible, so the instrument was ready for analysis.

Three samples of 5CB were prepared, each of a different mass. The DSC was initially cooled to -20°C, and each sample was left in the sample pan for approximately ten minutes to ensure that thermal equilibrium was reached. Then the temperature was run from -20°C to 70°C at 10°/min and back down at the same rate. Later runs consisted of only heating.

ANALYSIS AND INTERPRETATION

The output of a power compensated DSC is a plot of the power difference to the two sample holders plotted versus temperature (or occasionally time). Such a plot is called a thermogram. The typical thermogram peak is not Gaussian. First order transition peaks appear to be a Gaussian curve leaning forward, while second-order transitions appear as a curved rise in the baseline. For first-order transitions, the leading edge is linear, with a slope independent of such factors as sample size[2]. Where a line extrapolated from the leading edge of the curve intercepts the baseline is taken to be the temperature of the transition.

One curious aspect of thermograms is that the freezing point of a sample is often much lower than its melting point. This is due to an effect called hysteresis. In this case, hysteresis has two principal causes. The thermal history of a sample plays a large role. As these samples were heated and cooled repeatedly, hysteresis was obvious. Hysteresis is also an inherent physical property, as solid are more oriented than liquids. Orienting, especially into complex crystalline structures, is more difficult and unpredictable than disordering. Analogously, anyone can break apart a jigsaw puzzle quickly, and most people will take about

the same amount of time to do it. However, those people probably cannot assemble identical puzzles either as quickly as breaking them apart or in the same time that others do. Because of hysteresis, melting data are preferred for temperature determinations instead of freezing data.

Many physical properties of a sample can be determined from the thermogram. The power axis indicates the change in energy of the sample with respect to time (dQ/dt). Under constant pressure, the energy Q is identical to the enthalpy H. For an endothermic process, the plotted energy and enthalpy changes will be positive, because more energy must be supplied to the sample to keep it at a constant temperature. This is seem as a positive spike on the thermogram.

Integrating a thermogram peak over a range of temperatures (and therefore times) gives the sample's total enthalpy for that transition. Dividing this by the sample mass gives the enthalpy per unit mass for the transition, also known as the latent heat of transition. The constant pressure heat capacity of the sample is given by

$$C_p = \frac{dH}{dT} = \frac{dQ}{dT} = \frac{dQ}{dt}\left(\frac{dT}{dt}\right)^{-1} = P\left(\frac{dT}{dt}\right)^{-1} \quad (1)$$

where (dT/dt) is the temperature scanning rate, which is a constant, and P is the power difference (read from the thermogram), which varies with temperature. The specific heat of a sample is simply its heat capacity divided by its mass.

A typical thermogram, with the power curve from the blank run numerically subtracted, is shown in Figure 1. As expected, the solid-liquid crystal transition was endothermic and involved much more energy than the liquid crystal-liquid transition. Interestingly, the sample did not recrystallize by the end of data runs. If the sample was immediately run again, multiple heating peaks appeared around 20-25°C. However, if the sample was allowed to sit for ten minutes before being run again, a normal thermogram was seen. The conclusion, then, is that the sample needs a certain amount of time to crystallize, and that this time is greater than the amount of time at the end of the data run.

Using previously described relations, the heat capacity, specific heat, and transitional latent heat were determined for the five data runs taken. However, all data from run five except for transition temperature and enthalpy were lost due to computer failure.
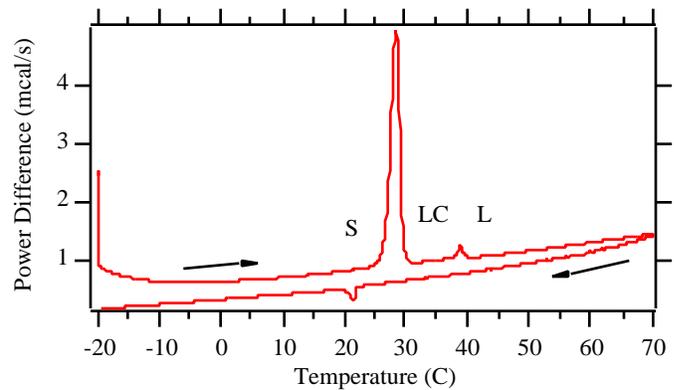
FIG. 1. Thermogram for heating and cooling of 5CB sample. Arrows indicate direction of time. On the heating portion, the large solid-liquid crystal transition peak is apparent, as is the smaller liquid crystal-liquid peak.. While the cooling peak has a liquid-liquid crystal transition (shifted due to hysteresis), there is no recrystallization peak. The step appearance of the baseline is a digital drawing effect, not a property of the data.

Rather than try to pick a value on the thermogram peak to analyze heat capacity during a transition, the heat capacity was instead calculated for each of the three phases, Modifying Equation 1 gives

$$C_p = \alpha + \beta T \quad (2)$$

where T is temperature and the constant is 6.0 s/K. Power is taken to be linearly related to temperature, where α (in mcal/s) is the intercept of power plotted versus temperature for a given phase, and β (in mcal/s*K) is the slope. The values of α and β were determined by performing a least-squares linear fit to the thermogram baseline in each phase region. Temperature ranges common to a phase in all runs were chosen for analysis.

For the solid phase (2.6°C to 20.8°C), α was calculated to be 0.41±0.13 mcal/s, and β to be 0.0077±0.0036 mcal/s*K. For the liquid crystal phase (31.7°C to 36.7°C), the values were determined to be 0.27±0.16 mcal/s and 0.0142±0.0023 mcal/s*K. For the isotropic liquid phase (41.2°C to 51.1°C), they were 0.30±0.17 mcal/s and 0.0128±0.0015 mcal/s*K. These are the averages of the values from the four full data sets followed by one standard deviation. For any given temperature, the heat capacity can be calculated from Equation 2 and these constants. The specific heat can be calculated by dividing the heat capacity by the mean sample mass for these four runs (2.35mg).

The literature values of the solid-liquid crystal and liquid crystal-liquid transition temperatures are 22.5°C and 35.0°C respectively[3]. The mean experimental solid-liquid crystal

transition temperature was 25.0±2.9°C, which differs from the literature value by 11%, but includes it within one standard deviation. The mean experimental liquid crystal-liquid transition temperature was 37.5±0.3°C, which is within 7% of the literature value, but several standard deviations away. With one exception, transition temperature readings were consistently high, indicating a systematic error. Sample defects may be responsible. Another possibility is that although the instrument was calibrated for indium at ~150°C, there may be a calibration shift or drift for much lower temperatures.

The mean latent heat value for the solid-liquid crystal transition was 13.36±0.53 cal/g, and the liquid crystal-liquid value was 0.418±0.032. These values, which should be constant for a substance, have standard deviations of 4% and under 8%, respectively. No standard values for specific heat or latent heat of 5CB transitions could be found. However, the liquid crystal-liquid transition generally has a latent heat of about[4] 0.5 cal/g. The mean value for the transition is 8% away from this, so the data are generally close to what is expected.

CONCLUSION

While differential scanning calorimetry is a powerful method for analyzing phase transitions and physical properties of materials, only a glimpse of this power was seen in the experiment. Three samples of the nematic liquid crystal 5CB were run on a Perkin-Elmer DSC-4. The precision of phase transition temperatures was good, but the accuracy, while satisfactory for a first attempt, could be much better. Calculated heat capacity values were generally imprecise, while latent heat calculations had standard deviations as low as 4%. Although more data with more fresh samples over a wide range of instrument settings would give a clearer picture of the abilities of the DSC, time constraints limited the amount of data and range of parameters for the experiment.

ACKNOWLEDGMENTS

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[3] G Vertogen and W.H. de Jeu, Thermotropic Liquid Crystals, Fundamentals, 1st ed. (Springer-Verlag, New York, 1988), p.9.

[4] Perkin-Elmer DSC-4 Users Manual, p. 5-12.