Thermodynamics of Activated Phase Transitions of 8CB: DSC and MC Calorimetry

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The present paper reports the heating rate effect on the phase transitions of a pure liquid crystal octylcyanobiphenyl (8CB) with use of Differential Scanning Calorimetry (DSC) and Modulation Calorimetry (MC) techniques. The DSC runs were taken at various temperature ramp rates from 20 to 0.5 K/min for heating and cooling scans. Well-defined endothermic/exothermic peaks were found at the melting/crystallization, smectic-A to nematic (SmA−N), and nematic to isotropic (N−I) transitions on heating/cooling scans, respectively. All transitions shift in temperature significantly with different ramp rates. The temperature shift of Cp peaks between heating and cooling scans indicates the order of the transitions. In addition, all transitions follow an Arrhenius behavior. The activation energy of a transition increases as the total energy involved in the transition decreases. The respective enthalpy and entropy change of each transition provides information on the Gibbs free energy. The significance of the results is discussed in terms of the order of transitions. A comparative analysis of MC and DSC techniques highlights the significance of the two techniques. MC is a practicable tool for observing the phase dynamics whereas DSC is a good tool for studying the rate kinematics of the transitions.

I. Introduction

Liquid crystals exhibit unique phase transitions and thermal properties that make them useful for a number of potential applications. Liquid crystals commonly are used to manufacture LCD screens for displays in computers, TVs, and watches. Liquid crystals commonly are used to manufacture LCD screens for displays in computers, TVs, and watches. They are attractive materials for fundamental research because of their structural, transitional, thermal, orientational, optical, and photoacoustic properties.

One of the liquid crystals, octylcyanobiphenyl (8CB), has been used in numerous studies due to its smectic-A to nematic (SmA−N) and nematic to isotropic (N−I) transitions of 8CB have been studied for decades.14,16,20–23 Only a few reports on the melting and crystallization transitions can be seen explaining enthalpies etc.,16,24–26 and no detailed study has been found on the heating rate effects of melting and crystallization of 8CB liquid crystal. Therefore, we have undertaken a detailed calorimetric study of a bulk 8CB using Differential Scanning Calorimetry (DSC) to show rate kinetics and activated dynamics of the various transitions of 8CB using Arrhenius theory. We also present a comparative study of DSC and traditional modulation calorimetry (MC) as a function of temperature to show the difference between the two techniques.

DSC has been used widely to study various transitions (glass transitions, crystallization, other first- and second-order transitions) of different research materials (glasses, polymers, liquid crystals, etc.),16,20,22,24,27–32 whereas alternating current (AC) or AC has been used recently to study phase transitions of the liquid crystals near equilibrium, using high-precision measurements.17,33–37 The DSC technique is particularly convenient due to the following facts: (1) it requires little sample preparation, (2) it is quite sensitive, (3) it is relatively independent of sample geometry, (4) it takes little time to run samples, (5) it has a wider temperature range, and (6) it can be operated for various ramp rates (e.g., from 0.5 to 20 K/min). Whereas the MC technique is particularly useful due to the following facts: (1) it uses a modulating heating frequency to heat the sample, (2) it provides better sensitivity to the results, (3) it provides a direct measure of heat capacity, (4) it uses lower ramp rates to observe high-precision results near equilibrium, and (5) it provides phase dynamics as well as dynamic complex heat capacity results.

Therefore, we have used the DSC technique to study rate kinetics of various transitions of 8CB and the MC technique to show phase dynamics of 8CB showing a comparative study of both techniques in the present work.

Here we report the detailed study of the thermodynamics of the activated phase transitions of bulk 8CB using DSC and MC techniques. This study reports the rate kinetics and the activation energy dynamics of all transitions of bulk 8CB using Arrhenius theory. The heating rate dependent study of all transitions of 8CB was performed with the DSC technique for heating and cooling scans at six different ramp rates. A comparison between DSC and MC was performed to show the significance of the two techniques. Sample preparation and experimental setup details of calorimetric spectroscopy are described in Section II. The results of rate dependent studies are shown in Section III, with discussion and conclusions drawn in Section IV.

II. Experimental Details

Pure octylcyanobiphenyl (8CB) liquid crystal was used to study the activated thermodynamics of its phase transitions. A sample of 8CB, obtained from Frinton Laboratories, having...
molecular weight 291.44, was degassed for about 1 h under a vacuum unit at room temperature (293 K) and then used in the study.

For the DSC technique, a MDSC model 2920 (TA instruments) was used to obtain DSC thermograms of the sample at different heating scan rates of 20, 15, 10, 5, 1, and 0.5 K/min without using any modulating frequency. The sample of 8CB (5 mg) was loaded into aluminum pans (dimensions: ~8 mm diameter and ~0.5 mm thick) and placed into a differential scanning calorimeter (DSC) along with an empty reference pan. The sample was first annealed at 323 K for 5 min and then immediately quenched to 243 K and the sample was equilibrated for 15 min. The sample was heated from 243 to 333 K at 20 K/min ramp rate and then cooled to 243 K with the same ramp rate. The respective heat flow of the sample was recorded along with temperature change during heating and cooling scans. The DSC equipment was well calibrated at each scanning rate. The DSC thermograms showed well-defined endothermic peaks in heating scans and well-defined exothermic peaks in cooling scans. The peak temperature of the transitions was taken as representative because it shows the maximum change in enthalpy. Heating and cooling the sample at the same ramp rate for a second time gave identical results and confirmed that the phase transitions of the liquid crystal 8CB are reversible. The same measurements were made for other heating scan rates, too. All experimental and environmental conditions were kept identical for all runs so that a comparison of the phase transition parameters could be made to understand the rate effect on phase transitions of the sample.

For the last few decades, a high-resolution AC calorimetry or MC technique has been used to understand the phase transitions of liquid crystals. Normally, SmA–N and N–I transitions were studied with it. To compare DSC and MC techniques, the thermal properties of 8CB were also studied with the MC technique.

High-resolution MC was performed with a home-built calorimeter at WPI. This MC is a traditional AC calorimeter with one cell used for samples, normally run at much slower ramp rates (10 to 500 mK/h) near equilibrium with use of low modulating frequencies (15 to 50 mHz). In this range of heating rate, no temperature shift can be observed because it measures heat capacity of the sample near equilibrium. But it measures the phase dynamics in terms of phase shift. The sample cell consisted of a silver sheet crimp-sealed in an cup shaped container with a lid (dimensions: ~12 mm diameter and ~0.5 mm thick) closely matching the dimensions of the heater sealed under pressure with the sample after being exposed to the vacuum for 2 h. After it was sealed, a 120-Ω strain-gauge heater and a 1-MΩ carbon-flake thermistor were attached to the cell and then the cell was mounted into the calorimeter, the details of which have been described elsewhere.38 In the ac-mode, power is put into the cell as $P_{ac}e^{i\omega t}$ resulting in temperature oscillations with amplitude $T_{ac}$ and a relative phase shift of $\phi \equiv \Phi + \pi/2$, where $\Phi$ is the absolute phase shift between $T_{ac}$ and the input power. The same sample (25 mg) was studied with MC. The respective heat capacity of the sample was measured as a function of temperature for heating and cooling scans at 6 K/h ramp rate. The temperature of the sample was varied from 300 to 333 K for the heating scan and then cooled from 333 to 300 K at a fixed heating frequency of 15 mHz at the same ramp rate. An empty silver cell was also measured to obtain the heat capacity of silver keeping all experimental conditions identical with the previous experiment. To calculate the heat capacity of the sample, the heat capacity of the empty cell was subtracted from the sum of the sample and cell heat capacities.

III. Results

A. DSC Technique. 1. Heating and Cooling Scans. Figure 1 shows the heating and cooling scans of bulk 8CB liquid crystal at a 10 K/min heating rate spanning the isotropic and crystal phases. Well-defined endothermic peaks were found on heating scan, and exothermic peaks were found on cooling scans at K–SmA–N, SmA–N, and N–I transitions. The transitions on heating scan represent absorption of heat whereas the transition on cooling scan represents release of heat. The K–SmA has the largest peak or enthalpy, and SmA–N has the smallest peak or enthalpy. The positions of the transitions, in the cooling scan, are found a little lower than those in the heating scan.

2. Rate Effect on Transitions. A heating rate dependent study of all transitions of 8CB was performed for various heating scan rates. Significant shifts in temperature were observed in transition temperature for all transitions.

Figure 2 shows that the heating rate effect on various transitions of bulk 8CB on heating scan at different ramp rates varies from 20 to 1 K/min. As the ramp rate decreases, all transitions shift toward lower temperature. The rate of shifting in the melting transition is more than either of the other SmA–N, N–I transitions whereas the rate of shifting is least in the SmA–N transition. Transitions on cooling scan also show a rate effect with the change of ramp rates. They shift toward higher temperature as the ramp rate decreases. Crystallization shows the maximum enthalpy with highest shifting rate and SmA–N shows the smallest enthalpy with least shifting rate. For simplicity, these plots are not shown here but all results are considered in the data analysis.

To see a clear shift in the peak temperature of each transition in the heating scan, the excess specific heat capacity versus temperature graphs are plotted for each transition after subtracting a baseline to the experimental value of the heat capacity of each transition. The specific heat capacity (J/gK) can be
calculated by taking the ratio of heat flow (W/g) and heating rate (K/s). The blowups of such plots are shown here.

Figure 3 shows the blowup of the melting transition at heating rates that vary from 20 to 0.5 K/min. It is clear that as the heating rate decreases, the peak shifts toward lower temperature significantly. The peak size and shape also changes and becomes sharper and larger but the area covered by the peak is almost the same for all ramp rates and found to be independent of heating rates. Figure 4 shows the blowup of the N–I transition. The peak becomes sharper and larger and shifts toward lower temperature as ramp rate decreases but its shifting rate is less than the melting transition rate. The enthalpy of this transition is smaller than the melting transition. Figure 5 shows the blowup of the SmA–N transition. It is clear that the peak is very shallow for faster rates and changes to a clear peak as rate decreases, shifting toward lower temperature. In this case, the peak shifting rate is found to be the lowest and the enthalpy of the transition is smallest.

Hence all transitions show a clear shift in temperature with different heating ramp rates and shift toward lower temperature as ramp rate decreases. The enthalpy of the melting/crystallization is maximum ~26 kJ/mol, whereas the enthalpy of SmA–N transition is minimum ~0.2 kJ/mol and the N–I transition has an intermediate enthalpy of ~0.9 kJ/mol. These ΔH values compare favorably to those in the literature.16,20 The enthalpy is found to be independent of ramp rate and follows the energy conservation law.

3. Evolution of Activation Energy. The significant shift observed in transitions of 8CB for heating and cooling scans follow Arrhenius behavior. According to Arrhenius behavior,39–42 the heating rate can be given by

\[ \beta = \beta_o \exp \left( \frac{-\Delta E}{RT} \right) \]  

where \( \beta \) is the effective heating rate (in K/min), \( \beta_o \) is a constant (in K/min), \( \Delta E \) is the activation energy (in joules/mole), \( R \) is universal gas constant (in J/mol K), and \( T \) is the absolute temperature (in kelvin). This equation can also be shown as:

\[ \ln \beta = \ln \beta_o - \left( \frac{\Delta E}{RT} \right) \]  

where \( \Delta E \) is determined from the slope of the graph, which is plotted between \( \ln \beta \) and \( 1/T \), and \( \ln \beta_o \) is the intercept on the y axis.
kinetics of liquid crystals. This technique is particularly
has recently been started to be used to study phase transition
intercept (0 K) and represents a second-order transition.
first-order transition whereas the SmA
intermediate intercept of 0.5 K and hence represents a weak
a strong first-order transition. The N
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heat of transition at equilibrium. Melting/crystallization has the
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transitions. Both heating and cooling scans follow straight lines
ramp rate for heating and cooling scans where (a) represents
Arrhenius behavior and indicate the required activation energy
for the transitions in the form of the slope of the lines. The
transitions on heating scan show negative slope due to the
absorption of heat because the endothermic peaks found on the
heating scan shift toward lower temperature with the decrease
of ramp rate. And the transitions on the cooling scan show
positive slope due to the release of heat because the exothermic
peaks found on the cooling scan shift toward higher temperature
with the decrease of ramp rate. The slope of the melting
transition is least and the slope of the SmA–N transition is
maximum whereas the slope of N–I is found to be intermediate.
4. Determination of the Transitional Order. If the peak
temperature of each transition is plotted versus ramp rate, the
intercept found at rate zero ramp rate presents the equilibrium
transition and when compared to heating and cooling scans,
offers evidence of the order of the transitions. Such plots are
plotted as follows:
Figure 6 shows a plot between the ln of the heating scan
versus 1/T for all transitions of 8CB for heating and cooling
scans, respectively. All transitions form a straight line following
Arrhenius behavior and indicate the required activation energy
for the transitions in the form of the slope of the lines. The
transitions on heating scan show negative slope due to the
absorption of heat because the endothermic peaks found on the
heating scan shift toward lower temperature with the decrease
of ramp rate. And the transitions on the cooling scan show
positive slope due to the release of heat because the exothermic
peaks found on the cooling scan shift toward higher temperature
with the decrease of ramp rate. The slope of the melting
transition is least and the slope of the SmA–N transition is
maximum whereas the slope of N–I is found to be intermediate.

Figure 7 is plotted as peak temperature of the transition versus
ramp rate for heating and cooling scans where (a) represents
K–SmA, (b) represents N–I, and (c) represents SmA–N
transitions. Both heating and cooling scans follow straight lines
and give an intercept at zero ramp rate for each transition. This
intercept represents a clear indication of the presence of latent
heat of transition at equilibrium. Melting/crystalization has the
largest intercept of 22 K at zero ramp rate and hence represents
a strong first-order transition. The N–I transition shows an
intermediate intercept of 0.5 K and hence represents a weak
first-order transition whereas the SmA–N transition shows no
intercept (0 K) and represents a second-order transition.
B. Comparison with MC Technique. The MC technique
has recently been started to be used to study phase transition
kinetics of liquid crystals. This technique is particularly
important due to its dynamic results. We, therefore, present the
MC technique along with the DSC results to compare these two
techniques in the present work.
A heating scan was performed for bulk 8CB in MC at a 0.1
K/min heating rate. A comparative study of MC and DSC results
is shown under Figure 8, which is plotted as specific heat
capacity (J/gK) versus temperature (K) for the heating scan
of SmA–N and N–I transitions of 8CB. The DSC results are
plotted for a 10 K/min heating rate. The DSC results show nicer,
sharper, and bigger peaks than the MC results. The MC
measures the phase dynamics in terms of the complex heat
capacity of the sample, which can be represented as real ($C_p'$
= $C_p$ cos $\phi$) and imaginary ($C_p''$ = $C_p$ sin $\phi$) parts of the
complex heat capacity ($C_p$) where $\phi$ represents the corresponding
phase shift. The real and imaginary parts represent the storage
and lost heat capacities. The storage heat capacity shows smaller
enthalpy with smaller peaks than the results found in DSC for
SmA–N and N–I transitions whereas the lost part $C_p''$ shows
a small dip at both transitions along with negative enthalpies
in MC. But the total enthalpy added by storage and lost parts is
the same as the enthalpy found in the DSC results. This indicates
that the total enthalpy of both transitions (SmA–N, N–I) is
independent of the techniques used. In Figure 8, the storage
and lost heat capacity of 8CB with the MC technique show the
enthalpy of SmA–N as 0.41 and 0.18 J/g, respectively, whereas
the enthalpy of the respective transition found in DSC is 0.59
J/g, which is the sum of the above two. Furthermore, the storage
and the lost part of enthalpies for the N–I transition are 2.36

\begin{align*}
\Delta T &= 22 \text{ K} \\
\Delta T &= 0.5 \text{ K} \\
\Delta T &= 0.01 \text{ K}.
\end{align*}
and 0.57 J/g, respectively, whereas in DSC it is 2.93 J/g, which is the sum of the above two enthalpies. This indicates that the MC gives phase dynamics in terms of the complex heat capacity and phase shift of the transitions. Both techniques provide clear and sharper peaks for SmA–N, N–I transitions where their enthalpies are found independent of the techniques used.

IV. Discussion and Conclusions

A. Activated Dynamics of Transitions. The phase transitions of bulk 8CB show activated rate kinetics which can be studied by using the rate dependent theory of Arrhenius. By using this theory, the activation energy of molecular motion and rearrangement of the sample near the transition temperature can be calculated by the slope obtained from the graph plotted between \( \ln \beta \) versus \( 1/T \) as shown in Figure 6.

It is clear from Figure 6 that each transition requires some activation energy and Figure 1 shows that different transitions have different enthalpies. The change found in enthalpy and activation energy indicates a relationship between the enthalpy and the activation energy of the transitions. Figure 9 shows a comparative plot for enthalpy and activation energy of each transition of 8CB for heating scans. It is clear that as the enthalpy of the transition decreases, the activation energy increases. The strong first-order transition, melting or crystallization, has maximum enthalpy of ~26 ± 0.10 kJ/mol and hence needs the least activation of ~1.6 ± 0.10 kJ/mol, whereas the weak first-order transition, N–I, has less enthalpy of ~0.9 ± 0.10 kJ/mol than the melting and needs intermediate activation of ~3.2 ± 0.08 kJ/mol. The second-order SmA–N transition shows the least enthalpy of ~0.2 ± 0.04 kJ/mol and hence needs maximum activation energy of ~3.4 ± 0.03 kJ/mol. This can be explained in terms of latent heat present in the transitions. Because of the presence of latent heat, the first-order transitions show bigger enthalpy than the second-order transitions and need less activation energy. The data details for energy dynamics are given in the Tables 1 and 2 for heating and cooling scans, respectively.

From these tables it is clear that the cooling transitions need more activation energy than heating transitions because the cooling transitions show less enthalpy than heating and hence need more activation as shown in Figure 10.

![Figure 8](image_url) Comparative specific heat versus temperature plot for DSC and MC techniques for 8CB liquid crystal at two different heating ramp rates of 10 and 0.1 K/min rates, respectively, where \( C_p' \), \( C_p'' \), and \( C_p \) represent real (storage), imaginary (lost), and total heat capacities, respectively.

![Figure 9](image_url) Comparative results of enthalpy and activation energy of each transition of 8CB for heating scans. Vertical lines show the error bars in the enthalpy and the activation energy, respectively. The size of the error is smaller than the symbol size.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>( \Delta E )</th>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
<th>( \Delta G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>melting</td>
<td>1.59±0.10</td>
<td>-26.91±1.00</td>
<td>-91.41 nonspont (-ve)</td>
<td></td>
</tr>
<tr>
<td>SmA–N</td>
<td>3.43±0.08</td>
<td>-0.16±0.04</td>
<td>-0.52 nonspont (-ve)</td>
<td></td>
</tr>
<tr>
<td>N–I</td>
<td>3.27±0.03</td>
<td>-0.91±0.10</td>
<td>-2.91 nonspont (-ve)</td>
<td></td>
</tr>
</tbody>
</table>

* Shown are the transitions, activation energy of the transition \( \Delta E \) (in kJ mol\(^{-1}\)), enthalpy of the transition \( \Delta H \) (in kJ mol\(^{-1}\)), the entropy of the transition \( \Delta S \) (in J mol\(^{-1}\) K\(^{-1}\)), and the Gibbs energy \( \Delta G \) (in kJ mol\(^{-1}\)) with nonspontaneous changes with negative sign for heating scans.

**Table 1: Summary of the Rate Effects on Heating Scan of Bulk 8CB**

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**Table 2: Summary of the Rate Effects on Cooling Scan of Bulk 8CB**

<table>
<thead>
<tr>
<th>Transitions</th>
<th>( \Delta E )</th>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
<th>( \Delta G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>crystallization</td>
<td>0.27±0.10</td>
<td>23.38±1.00</td>
<td>87.21 spont (+ve)</td>
<td></td>
</tr>
<tr>
<td>N–SmA</td>
<td>5.96±0.80</td>
<td>0.14±0.03</td>
<td>0.45 spont (+ve)</td>
<td></td>
</tr>
<tr>
<td>I–N</td>
<td>3.56±0.60</td>
<td>0.90±0.08</td>
<td>2.88 spont (+ve)</td>
<td></td>
</tr>
</tbody>
</table>

* Where \( \Delta E \) and \( \Delta H \) are in kJ mol\(^{-1}\) and \( \Delta S \) is in J mol\(^{-1}\) K\(^{-1}\), and the Gibbs energy \( \Delta G \) in kJ mol\(^{-1}\) shows spontaneous changes with positive sign.

B. Discussion of MC vs DSC. Usually MC is used to study phase dynamics of liquid crystals at much slower heating ramp rates (50 to 200 mK/h) to obtain more sensitive and dynamic results near equilibrium with modulated heating frequency. The MC shows the phase dynamics of the transitions by measuring complex heat capacity and phase shift of the sample. DSC is used to study rate kinematics of the samples with a wider range of heating ramp rates (from 0.5 to 20 K/min), using much higher scan rates than MC. Here a comparison is shown between two techniques in Figure 5, and data details are shown in Tables 1 and 2. It is difficult to compare these two techniques at the same ramp rates because of their own qualities, but both techniques provide nice and clear peaks for SmA–N and N–I transitions. The peak height observed in MC is divided into its storage and lost parts and appears smaller in size than the DSC results, but the sum of storage and lost peaks is the same as DSC results. This indicates that total area covered under peaks found in either transition SmA–N or N–I is independent of the technique used. Hence the MC technique is found as a practicable tool for observing dynamics of the transition in terms of phase shift and complex heat capacity whereas DSC provides rate kinematics details of the transitions of the system.
C. Conclusions. The activated dynamics of the phase transitions of bulk 8CB have been performed with DSC and MC techniques and reveal interesting results. Well-defined endothermic and exothermic peaks were found in heating and cooling scans, respectively. The rate dependent study of each transition shows significant shift in each transition temperature with different heating ramp rates. The transition temperature of various transitions shifts toward lower temperature as ramp rate decreases in heating scans. This rate shift follows Arrhenius behavior and provides the activated dynamics of the transitions of bulk 8CB. As the enthalpy of the transition decreases from either first-order transitions melting or N → I to the second-order transition SmA → N, the required activation energy of the respective transition increases. This can be explained in terms of the order of transitions. The second-order transition has smaller enthalpy of the order of ~0.2 kJ/mol with no latent heat and hence needs more activation energy (>2 times) than either of the first-order transitions which contain latent heat and have bigger enthalpies. The strong first-order transition-melting or crystallization has maximum enthalpy (~26 kJ/mol) with maximum latent heat and hence needs a lower activation energy (~2 times) than the weaker first-order transition N → I. The comparative analysis of DSC and MC shows that the enthalpies found for either first- or second-order transitions SmA-N or N-I are independent of techniques used as well as independent of heating ramp rate too. Hence, the MC technique is a practicable tool for observing dynamics of the transition in terms of phase shift and complex heat capacity whereas DSC is a good tool for studying the rate kinematic details of the transitions of the system where enthalpies are independent of heating ramp rates and techniques used.

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References and Notes