Chapter 5

Photoacoustic analysis of phase transitions in liquid crystals

Application of photoacoustic technique for the detection of phase transitions in a variety of liquid crystals is discussed in this chapter. Investigations are carried out in 7OCB and 8OCB liquid crystals and in multi-component BL001, BL002, BL032 and BL035 nematic mixtures. The novelty of the present method is that the experiment is performed at a wavelength at which the liquid crystal samples do not absorb the optical radiation. Photoacoustic signal generation is achieved from such a non-absorbing sample by mixing it with a very small amount of an organic dye which absorbs the incident radiation. By employing this approach both first order and second order phase transitions have been detected. A qualitative evaluation of the heat capacity profile during phase transitions is also made by using a simple analysis based on the Rosencwaig-Gersho theory.
5.1 Phase transitions

A phase is a form of matter that is uniform throughout in chemical composition and physical properties and can be distinguished from other phases by these definite properties and composition. A substance in the solid phase has a definite shape and rigidity, but the liquid phase has no definite shape, but has a definite volume. The gaseous phase has no definite shape or volume, but has a shape and volume determined by the shape and size of the container. Usually, phase transitions are associated with a sudden change in the physical properties of the system when temperature, pressure, or other thermodynamic variable changes [1-5]. For a given thermodynamical conditions a phase is said to be stable when its energy called the Gibb's free energy, given by \( G = U - TS + PV \), is minimum. During a phase transition, if the Gibb's function varies discontinuously with respect to pressure and temperature, such transitions are said to be of first-order. But, if \( \left( \frac{\partial G}{\partial T} \right)_P \) and \( \left( \frac{\partial G}{\partial P} \right)_T \) changes continuously and \( \left( \frac{\partial^2 G}{\partial T^2} \right)_P \), \( \left( \frac{\partial^2 G}{\partial P^2} \right)_T \) and \( \left( \frac{\partial^2 G}{\partial T \partial P} \right) \) changes discontinuously during a transition, then it is said to be a second-order phase transition [1-4]. Being a material showing both first order and second order phase transitions, liquid crystals are exploited widely for phase transition studies [5-10].

5.1.1 Phase transitions in liquid crystals

We have seen in chapter 4 that liquid crystalline materials can exist in a number of mesophases between the crystalline solid and the isotropic liquid state. Consequently, these materials exhibit a rich variety of phase transitions each having its own unique identities. Transition from one mesophase to another state can be brought about by pure thermal processes, i.e. by changing the temperature of the sample. Liquid crystals belonging to this group are known as thermotropic materials [5-8,11]. There is another class of liquid crystals called the lyotropic liquid crystals, the details of which are given in the previous chapter. Of these two classes, the former type finds applications in technological devices such as display systems while the latter has great significance in biological systems. The present chapter deals with the studies on thermotropic liquid crystals

Though a detailed description of the different mesophases and their properties are given in chapter 4, it would be appropriate to recall the significant properties of the phases that are discussed in this chapter to facilitate the understanding of the results of the investigation. As we know, an essential requirement for mesomorphism to occur is that the molecule must be highly
geometrically anisotropic in shape, like a rod or a disc and on an average their long axis should point in a preferred direction, called the director. The nematic phase carries only long-range orientational order of the director and there is no correlation between the centers of gravity of the molecules. Consequently, the molecules are quite mobile in this particular phase. Typically, nematic viscosities are of the order of 0.1 Poise. Smectic liquid crystals are layered systems with varying degrees of order within each layer and with differing angular relations between the director $\vec{n}$ and the normal to the layers. When there is no order within a layer and when $\vec{n}$ is perpendicular to the plane of the layers, we have the case of smectic-A liquid crystal. Compared to nematics, smectics are very viscous and the typical value of viscosity are of the order of 10 Poise. Because of higher symmetry, the nematic phase usually occurs at a higher temperature than the smectic-A phase [5-8]. Apart from these mesophases, all liquid crystals transform to the totally disordered isotropic phase at elevated temperature, i.e. after the mesophases. Cooling down to a lower temperature, i.e. prior to the mesophases, will result in the crystallisation of these materials. The transition between these phases can be either first order or second order where critical fluctuations play an important role. Regarding the theoretical models used to describe various phases and phase transitions, Maier and Saupe have proposed a molecular theory of the nematic phase in which the alignment of the molecules parallel to a preferred axis is described by an orientational order parameter [12]. Kobayashi and McMillan extended this model to the smectic-A phase by introducing another order parameter, namely, the amplitude of a density wave in the direction of the nematic preferred axis [13-15].

In order to determine the order of different kinds of transitions and to fully characterise the nature of the fluctuations at critical and multi-critical points, different types of high-resolution experimental techniques are usually employed. During the last couple of decades an impressive amount of calorimetric results have been obtained and in many cases a better understanding of several phase transitions in liquid crystals have been reported. These results have been obtained with measuring techniques such as differential scanning calorimetry (DSC), ac calorimetry, steady state calorimetry and the recently introduced photoacoustic and photopyroelectric methods [16-24]. In early days, many of these experimental efforts have largely been devoted to the study of static thermal quantities such as heat capacity and enthalpy. In the last decade, however, a number of high-resolution studies on thermal transport properties during phase transitions are reported. This is achieved by extending ac calorimetry to the high-frequency regime and by applying laser induced photoacoustic or photopyroelectric methods [23-35]. Zammit et.al have used the photoacoustic technique for the simultaneous measurement of thermal conductivity, diffusivity and heat capacity during smectic-A to nematic transition in
certain cyanobiphenyl liquid crystals [32]. They are also able to evaluate the critical exponents of these thermal parameters during the phase transition. Apart from these calorimetric studies there exists a number of experimental methods to study the phase transitions in liquid crystals and a few of such methods are light scattering, IR and optical absorption, fluorescence, inelastic neutron scattering, dielectric measurements, electron paramagnetic resonance, ultrasonic studies and x-ray studies [36-47].

Laser induced photoacoustic studies on phase transitions in 4-cyano-4'-heptyloxy biphenyl (7OCB), 4-cyano-4'-octyloxy biphenyl (8OCB) liquid crystals and on certain multi-component nematic liquid crystal mixtures are discussed in the following sections. Regarding 7OCB and 8OCB, phase transition data obtained from investigations using many other methods are available in the literature [48-56]. However, the nematic mixtures investigated here are some of the recently developed compounds by Merck Inc. [57]. BL001, BL002, BL032 and BL035 are the trade names assigned by the manufacturer. Each of these low molecular weight mixtures contains four to nine cyanobiphenyl components. These mixtures possess a wide nematic range around the room temperature and hence they find a lot of applications in display technology.

5.2 Experimental details

Laser induced photoacoustic technique is used to monitor various phase transitions in liquid crystalline materials. A schematic diagram of the experimental set-up is shown in figure 1. The radiation source used to produce the PA signal is a water-cooled argon ion laser (Liconix 5000). The laser emission at 488nm wavelength is used for the investigations. The laser beam having a 1/e² diameter of 1.2mm is intensity modulated at 344Hz using a mechanical chopper (Ithaco HMS 230). The beam is then passed through a convex lens of focal length 5cm. The distance between the lens and the sample surface is adjusted in such a way that the entire surface of the sample gets illuminated. All the measurements are performed at an incident laser power of 20mW. Defocused laser beam at low power level is used to reduce the localised heating at any point in the sample. Investigations are carried out by heating the sample from the room temperature to elevated temperatures. Temperature scanning rate of 0.2 °C per minute is adopted throughout the measurements. The output of the microphone (Knowles BT1834) is recorded at regular intervals of temperatures using a single phase analog lock-in-amplifier (Stanford Research Systems SR 510).
Figure 1: Schematic diagram of the experimental set-up used for the phase transition studies.

Cross-sectional view of the resonant PA cell used for the investigations is shown in figure 2. The sample chamber is 3mm in radius and 6mm in depth. Top of the sample compartment is closed with a glass window which allows the optical radiation to impinge on the sample. In order to protect the microphone from damage due to heating of the sample, the microphone compartment is positioned away from the sample chamber. The two chambers are then acoustically coupled through a thin-walled stainless steel tube of inner diameter 1mm and of length 19cm. This resonant PA cell has an acoustic resonance peak at 440 Hz. The cell has provision to operate in the temperature range from 77K to 400K. For subzero-temperature measurements, liquid nitrogen can be used to cool down the sample temperature. Meanwhile, the heater coil (60W) wound over the sample chamber serves as the heat source for above-room-temperature studies. The heater coil together with a stabilised DC power supply and a chromel-alumel thermocouple forms the temperature controller unit. The thermocouple is inserted into the body of the sample chamber through a narrow bore of diameter 1mm which is drilled from one side of the cell body and ends up very close to the sample in the chamber.
5.3 Results and discussion

5.3.1 Phase transitions in 7OCB and 80CB

The liquid crystals 7OCB and 80CB are obtained from Merck Inc. UK and are used without further purification. These compounds are white powder in the crystalline state at room temperature, while in the smectic-A and nematic phases they are white viscous fluids and finally in the isotropic phase they appear like an ordinary, colourless liquid. Similar to most of the other liquid crystals, 7OCB and 80CB do not absorb the optical radiation in the visible region \([5-8,36]\). Hence, in order to generate the photoacoustic signal, these materials are mixed with a very small amount (0.5 % weight) of an organic dye Eosin (Merck) which has a very good absorption at the excitation wavelength (488nm). High thermal stability as well as the good photostability of the dye has been taken into account while selecting it as the colouring substance. The liquid crystal sample taken in the photoacoustic cell has a thickness of about 2 millimetre. The photoacoustic signal amplitude is recorded during the heating of the sample, starting from the crystalline phase. Great care is taken in the choice of the laser beam intensity as well as the heating rate to make sure that the photoacoustic signal profile is not affected by too high a laser intensity or by a high heating rate. Though a thick layer of the sample is used for the investigations, the photoacoustic signal is mainly contributed by the light absorbed within the first thermal diffusion length of the material \([58]\). The thermal diffusion length \(\mu\) is equal to

\[
\sqrt{\frac{2a}{\omega}},
\]

where \(a\) is the thermal diffusivity and \(\omega\) is the modulation frequency. Usually, the
thermal diffusion length is only a few micrometer in liquid crystals [5-8,31,36]. Consequently, the alignment and other properties of the surface layer will reflect in the photoacoustic signal.

Since the PA signal profile varies with pressure and temperature inside the cell and depends on the thermal properties of the gas (air), calibration of the experimental system is necessary. For this purpose, the temperature response of the PA cell is recorded using carbon black as the sample. The observed signal amplitude profile is shown in figure 3. This data is used to normalise the PA signals obtained from the liquid crystal samples.

Figure 3: Response of the PA cell with respect to temperature, recorded using carbon black sample.

The normalised PA signal amplitude variation during heating of the liquid crystal 8OCB, starting from the crystalline phase, is shown in figure 4. From this plot it can be seen that there is a remarkable variation in the PA signal amplitude at three distinctly different temperatures. This anomalous behaviour of the signal is obviously due to the sudden changes in the thermal parameters like heat capacity, thermal conductivity etc of the sample. Such changes occur normally during transition from one phase to another phase of the material. In the case of 8OCB, the observed transition temperatures are 54.3 °C, 66.9 °C and 80.8 °C. These values are in agreement with the reported phase transition temperatures 54 °C, 67.2 °C and 80.2 °C of this particular liquid crystal [18,49-52]. These transition temperatures are assigned to crystalline to smectic-A, smectic-A to nematic and nematic to isotropic transitions respectively.
From the thermodynamical point of view, the large decrease in the PA signal profile during melting, *i.e.* the crystalline to smectic-A transition, can be explained as follows. During melting, all the available heat is absorbed by the melting process. Or in other words the sample acts a heat sink for the entire heat, including the heat generated by the photoacoustic process. Consequently the PA signal amplitude drops markedly, as visible in figure 4. It is worthwhile to note that, in figure 4, the crystalline to smectic-A and nematic to isotropic transitions are marked by a dip in the PA signal profile followed by a small peak structure. These two transitions are reported to be first order in nature [49-52]. On the other hand, during the smectic-A to nematic transition, the dip in PA signal profile has smaller depth compared to the other two transitions. Also in this case, the PA signal profile does not carry any peak structure in the vicinity of transition temperature. Further more, in the case of smectic-A to nematic transition, the sudden change in PA signal amplitude is restricted to a relatively small temperature range while for the other two transitions the change in the signal amplitude is visible over a much larger temperature range. These facts attributes a different nature for the smectic-A to nematic transition in 8OCB, which is reported to be essentially a second order transition [15,50,51].

Similar results have been observed in the case of the liquid crystal 7OCB as well. The normalised PA signal variation with temperature for 7OCB is shown in figure 5. In this case, only two transitions are observed and the corresponding transition temperatures are 55.6 °C and 74 °C. These values are in agreement with the earlier reported values of 55 °C and 73.5 °C,
which corresponds to crystalline to nematic and nematic to isotropic liquid transitions respectively \([48,59,60]\). Both the transitions are first order in nature. In the case of both the liquid crystals, no major change in the transition temperatures has been observed in comparison with the earlier reported values. This clearly indicates that the transition temperatures of 7OCB and 8OCB remain almost unaffected by the addition of a small amount of the organic dye. It has already been reported that the very low concentrations of dyes in the liquid crystals will not affect their thermal properties or transition temperatures in any appreciable manner \([61]\).

![Figure 5: PA signal amplitude versus temperature plot for 7OCB.](image)

**5.3.2 Phase transitions in nematic liquid crystal mixtures**

The nematic liquid crystal mixtures, namely BL001, BL002, BL032 and BL035, used for the investigations are obtained from Merck Inc. UK \([57]\). All these compounds are in the nematic phase at room temperature and transform to isotropic liquid phase at elevated temperatures. These mixtures also do not absorb the optical radiation in the visible region and hence as in the case of previous measurements, organic dye Eosin (0.5\% by weight) is added to enhance the light absorption at the excitation wavelength (488nm). The liquid crystal samples kept inside the photoacoustic cell have a thickness of around 2mm. The samples are then thermally thick and optically transparent. Again, the measurements are carried out by heating the sample, starting from the nematic phase.
The photoacoustic signal recorded in the case of the liquid crystals BL001 and BL002 during the heating process is shown in figure 6. From these plots it is clear that as the temperature crosses the transition point, the photoacoustic signal amplitude changes from a maximum to a minimum. Similar observations have been made in the case of liquid crystals BL032 and BL035 and the photoacoustic signal profile during the nematic to isotropic transition of these liquid crystals are shown in figure 7. The observed values of transition temperatures are 60.8 °C and 71.8 °C for BL001 and BL002 respectively. The transition temperature of BL032 and BL035 are located at 86.7 °C and 95.7 °C respectively. These values are in good agreement with the thermal data provided by Merck Inc. [57]. According to the manufacturer the nematic to isotropic transition temperatures are 61 °C, 72 °C, 87 °C and 96 °C, respectively, for BL001, BL002, BL032 and BL035. Hence the present observations also confirm that the addition of a trace amount of a dye to the liquid crystals does not affect the transition temperature in any significant manner.

From figures 6 and 7, we can see that there is a gradual increase in photoacoustic signal in the nematic phase as the temperature approaches the transition temperature. It is a well known fact that the elastic properties such as the surface tension and viscosity vary gradually with rise of temperature in the nematic range itself [5—8,31,36]. This may have some influence on the gradual increase of photoacoustic signal in the nematic phase itself as the temperature approaches the transition point. However, this is a special case associated with liquid crystals alone and hence the available general theories for photoacoustic effect are not sufficient to give a satisfactory explanation for this observation.

Another important point that has to be noticed from figures 6 and 7 is that the signal amplitudes in the nematic and isotropic phases differ by a large value. Eventhough the dependence of density on the photoacoustic signal is clearly explained in the Rosencwaig-Gersho theory, the change in volume and hence the change in density during nematic to isotropic transition is less than 0.5% in most of the liquid crystals [5-8,31,36]. Hence density change cannot account for such a large difference in photoacoustic signals in the two phases. But, it is a well-known fact that the nematic phase possesses strong light scattering property compared to the isotropic phase. In the present case, the sample is optically transparent at the excitation wavelength and hence the absorption and scattering processes will take place along the entire thickness of the sample. Under the present experimental condition such a multiple scattering effect in the nematic phase will increase the effective path length of the light beam inside the sample, leading to an increased light absorption and correspondingly an enhanced photoacoustic signal in the nematic phase. In fact this difference in signal amplitudes between
the ordered nematic phase and the isotropic liquid phase is clearly visible in the case of 7OCB also (figure 5), but in the case of 8OCB this difference (figure 4) is not as large as in the other cases. It must be noted here that 8OCB has an additional smectic-A phase and it is not clear whether the presence of this mesophase will influence any of the physical properties in the nematic phase.

![Graph 1](image1)

![Graph 2](image2)

**Figure 6:** PA signal amplitude versus temperature plot for BL001 and BL002.
![Graphs showing PA signal amplitude versus temperature for BL032 and BL035.](image)

**Figure 7:** PA signal amplitude versus temperature plot for BL032 and BL035.
5.3.3. Analysis of the PA signal profile using R-G theory

Rosencwaig and Gersho developed the theory for photoacoustic effect in 1976 [58]. This one-dimensional heat flow model is valid in most of the cases and a complete discussion regarding this is given in chapter 2. For the complex photoacoustic signal $Q = q \exp(-i\psi)$, with amplitude $q$ and phase $\psi$ (with respect to the incident radiation), the following equation holds:

$$Q = \frac{\eta I_0 r_g P_0}{2\sqrt{2}T_0 k_l g a_g (\beta^2 - \sigma^2)} \left[ \frac{(r - 1)(b + 1)e^{\sigma_l} - (r + 1)(b - 1)e^{-\sigma_l} + 2(b - r)e^{-\beta}}{(g + 1)(b + 1)e^{\sigma_l} - (g - 1)(b - 1)e^{-\sigma_l}} \right]$$

where, $I_0$, $P_0$ and $T_0$ are respectively, the incident light intensity, the ambient pressure and temperature; $\gamma_g$ the ratio of heat capacities of the gas, $k$ and $\beta$ are the thermal conductivity and optical absorption coefficient of the sample, $l$ the sample thickness, $l_g$ the thickness of the gas column in the cell, and $\sigma = (1+i)a$, with $a = 1/\mu$ the thermal diffusion coefficient. $\eta$ is the light to heat conversion efficiency. One further has $b = \left( \frac{k_b a_b}{k_g} \right)$, $g = \left( \frac{k_g a_g}{k_f} \right)$, $r = (1-i)\beta/2a$. Here, the subscripts $g$ and $b$ refer to the gas and the backing material. When the sample is optically transparent and thermally thick, we can set $e^{-\beta} \equiv 1 - \beta$, $e^{-\sigma_l} \equiv 0$ and $|r| \ll 1$, then the expression for acoustic signal will reduce to the form,

$$Q \approx \frac{-i\gamma P_0 I_0}{4\sqrt{2}T_0 l_g} \frac{\beta \mu_s^2}{a_g k_s}$$

In this case, only the light absorbed within the first thermal diffusion length contributes to the signal, in spite of the fact that light is being absorbed throughout the length of the sample. Also, since the thermal diffusion length of the sample is smaller than the sample thickness, the backing material would not have any contribution to the PA signal. The above equation can be written as

$$Q = K \left( \frac{\mu_g}{T_0} \right) \left( \frac{\mu_s^2}{k_s} \right)$$

where the proportionality constant $K$ includes all the constant terms in equation (2). For air, $\left( \mu_g / T_0 \right)$ is a slowly varying function of temperature, which can be evaluated from the thermal parameters of air. The term $\left( \mu_s^2 / k_s \right)$ is equal to $\left( 2/\omega p_s C_s \right)$ where $\omega$ is the chopping
frequency, $p_S$ and $C_S$ are the density and heat capacity of the sample. Hence the reciprocal of the PA signal amplitude multiplied by $\left( \frac{\mu_g}{T_0} \right)$ will be a quantity proportional to the heat capacity of the sample. The variation of $\left( \frac{\mu_g}{T_0} \right)$ with temperature is shown in figure 8 [62].

![Figure 8: Variation of $\left( \frac{\mu_g}{T_0} \right)$ of air with temperature.](image)

The behaviour of $\left( \frac{1}{PA \text{ signal}} \right) \times \left( \frac{\mu_g}{T_0} \right)$, which is proportional to specific heat capacity, with respect to temperature is studied for all the liquid crystals. The corresponding plot for the liquid crystals 7OCB and 8OCB are shown in figure 9. From this plot, we can see that the quantity proportional to the heat capacity of both liquid crystals exhibits a sharp peak structure across the transition regions. It is worthwhile to note here that the sharp increase in heat capacity is occurring in a narrow temperature range during the second order smectic-A to nematic transition. But, in the case of the other two first order transitions, namely crystalline to smectic-A and nematic to isotropic transitions, the increase in heat capacity occur in a much broader temperature range. Also, the intensity of the peak during the smectic-A to nematic transition of 8OCB is less than that during nematic to isotropic transition. This is in good agreement with the earlier high-resolution ac calorimetric measurement on 8OCB made by Garland et.al. [51].
Figure 9: $\left(1 / \text{PA signal}\right) \times \left(\mu_g / T_0\right)$ versus temperature plot for 8OCB and 7OCB.
Figure 10: \[
\left(\frac{1}{PA \text{ signal}}\right) \times \left(\frac{\mu_B}{T_0}\right)
\] versus temperature plot for the nematic mixtures BL001, BL002, BL032 and BL035.

The typical behaviour of \[
\left(\frac{1}{PA \text{ signal}}\right) \times \left(\frac{\mu_B}{T_0}\right)
\] with respect to the temperature, for the nematic liquid crystal mixtures is shown in Figure 10. Typically, the specific heat capacity of liquid crystals shows only a sharp peak structure across the transition temperature [5-8,31,36,48-56]. The present observation of a dip structure prior to the transition peak is resulting from the gradual increase in the PA signal in the nematic phase as the temperature approaches the transition temperature. This dip in the heat capacity profile may be due to some surface effects as discussed in the previous section. Again, the difference in the signal amplitudes in the nematic and isotropic phases are attributed to the difference in bulk light scattering properties in these two phases. However, any reports regarding the phase transition studies on these nematic liquid crystal mixtures are not available in the literature for a comparative study. Though, the present measurement is only a qualitative one, the same method can be used to evaluate the absolute values of static and dynamic thermal parameters of the liquid crystals if the material under investigation is optically opaque at the excitation wavelength [32].
5.4 Conclusions

The application and advantages of photoacoustic technique for determining the phase transition temperatures in a variety of liquid crystals are discussed. First order as well as a near second order phase transition in two alkoxy-cyanobiphenyl liquid crystals, 7OCB and 8OCB, have been studied using a gas-microphone photoacoustic technique. The observed phase transition temperatures are found to be in good agreement with the earlier reported values. It is confirmed that the addition of a very small quantity of an organic dye to the liquid crystals will not affect the transition temperatures in any significant manner. Results obtained from the nematic liquid crystal mixtures are also very promising. The difference in the measured signal amplitude in the nematic and isotropic phases is attributed to the difference in the light scattering properties associated with the degree of order of these phases. Decrease in signal amplitude during phase transitions is mainly due to the increase in the heat capacity of the liquid crystal.

Present investigations show that the PA technique is a powerful analytical tool for the study of variations in thermal parameters associated with phase transitions in liquid crystals and in the identification of the order of transition. This method is very simple, less time consuming and can be performed using an optical radiation at any wavelength by properly selecting the dye and hence is a very promising tool for the thermal characterisation of liquid crystals.
References

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