Use of photoacoustic effect for the detection of phase transitions in liquid crystal mixtures

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Abstract. We report on a laser induced photoacoustic study of the nematic-to-isotropic transition in certain commercial nematic liquid crystal mixtures, namely BL001, BL002, BL032 and BL035. A simple analysis of the experimental data using the Rosencwaig–Gersho theory shows that the heat capacities of all these compounds exhibit a sharp peak as the temperature of the sample is varied across the transition region. Also, substantial differences in the photoacoustic signal amplitudes in nematic and isotropic phases have been noticed for all the mixtures. The increased light scattering property of the nematic phase may be the reason for the enhanced photoacoustic signal amplitude in this phase.

1. Introduction

In recent years, considerable efforts have been made in the synthesis and characterization of liquid crystals and their mixtures with a wide nematic range [1–7]. The unique properties, such as lower viscosity, increased temperature range, larger birefringence and dielectric anisotropy, of low-molecular weight nematic compounds segregate them from other liquid crystals. The wide range of a particular phase, especially the nematic phase, is an essential requirement in device fabrication. Apart from their applications in display devices, nematic liquid crystals are few among the most attractive nonlinear optical materials [8–11]. Furthermore, the addition of organic dyes to nematic liquid crystals has been shown to be the source of myriad very interesting and complex nonlinear optical properties [12–15]. The dye molecules added to the liquid crystals would become orientated along particular directions due to the long range orientational order and intricate hydrodynamic properties of liquid crystals. One of the major advantages of dye-doped nematic liquid crystals is that we can control the nonlinear optical properties of the liquid crystals at any wavelength by an appropriate dye selection. From an application viewpoint, dye-doped liquid crystals have been investigated as possible candidates for optical cavities as well as for spatial filtering, photothermal self-phase modulation, holograms and for optical recording [15–19].

Thermal measurements play an important role in locating and characterizing the different phases and phase transitions in liquid crystal compounds. Among the various characterization methods, the ac calorimetric method is the most powerful and commonly used technique for the thermal characterization of liquid crystals [20–22]. Photoacoustic effect, mirage effect and photon transmission methods are some of the very recently introduced methods for the phase transition studies in liquid crystals [23–25].

The photoacoustic (PA) technique, being highly sensitive, less time consuming and applicable over a wide spectral region, has produced numerous interesting results in liquid crystal characterization [25–27]. The PA technique is based on the periodic heating of a sample illuminated by the absorption of modulated optical radiation. In a gas-microphone configuration, the sample is contained in a gas-tight cell. In addition to a steady-state temperature gradient, a thermal wave will also be produced in the sample. The thermal wave in the sample couples back to the gas above the sample and this will result in a periodic fluctuation of the temperature of a thin layer of gas close to the sample surface. This thin layer of gas will act as an acoustic piston, which will result in the production of a periodic pressure change in the cavity. A sensitive microphone coupled to the sample chamber can be used to detect this pressure fluctuation. Actually, the PA signal produced by the sample originates from a thin surface layer with thickness characterized by the thermal diffusion length μ, given by $\mu = (2\alpha/\omega)^{1/2}$ where $\alpha = (k/\rho C)$ is the thermal diffusivity, k is the thermal conductivity, ρ is the density, C is the heat capacity and ω is the modulation frequency of the incident optical radiation.

In this paper, we report on the PA measurements carried out during nematic-to-isotropic transition in some commercial nematic liquid crystal mixtures, namely, BL001, BL002, BL032 and BL035, provided by Merck Ltd, UK [4].

Liquid crystals of this series are well known for their wide range of nematic phase, ranging from –20 °C to above 60 °C, which is a major factor contributing to their practical applications, especially in display devices. Even for quite low modulation frequencies, μ is usually in the micrometre range for liquid crystals, and hence just a few milligrams of the sample confined in a small cavity are sufficient for the investigation.

2. Theory

The theory for the PA effect was developed by Rosencwaig and Gersho in 1976 [33]. Basically, it is a one-dimensional heat flow model valid in most cases. For the complex PA signal $Q = q \exp(-i\psi)$, with amplitude q and phase ψ (with respect to the incident radiation), the following equation holds:

$$Q = \frac{\eta \beta I_0 \gamma_g P_0}{2\sqrt{2} T_0 k l_g a_g \left(\beta^2 - \sigma^2\right)} \quad (1)$$

$$\times \left[\frac{(r-1)(b+1)e^{\sigma l} - (r+1)(b-1)e^{-\sigma l} + 2(b-r)e^{-\beta l}}{(g+1)(b+1)e^{\sigma l} - (g-1)(b-1)e^{-\sigma l}}\right]$$

where I_0, P_0 and T_0 are the incident light intensity, the ambient pressure and temperature in the cell, respectively, γ_g is the heat capactiy ratio of the gas, β is the optical absorption coefficient of the sample, l is the sample thickness, l_g is the thickness of the gas column in the cell, and $\sigma = (1 + i)a$, with $a = 1/\mu$ the thermal diffusion coefficient. η is the light to heat conversion efficiency. Furthermore, one has

$$b = \left(\frac{k_b a_b}{ka}\right) \qquad g = \left(\frac{k_g a_g}{ka}\right) \qquad r = (1-i)\frac{\beta}{2a}.$$

Here, the subscripts g and b refer to the gas and the backing material, respectively. When the sample is optically transparent and thermally thick, we can set $e^{-\beta l} \cong 1 - \beta l$, $e^{-\sigma l} \cong 0$ and $|r| \ll 1$. The liquid crystals investigated here are optically transparent and thermally thick under our experimental conditions. The acoustic signal then becomes

$$Q \cong \frac{-i\gamma P_0 I_0}{4\sqrt{2} T_0 l_g} \frac{\beta \mu_s^2}{a_g k_s}. \quad (2)$$

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. If we treat β as a constant term, which is a valid approximation for liquid crystals, then the PA signal amplitude is given by

$$Q = K \left(\frac{\mu_g}{T_0}\right) \left(\frac{\mu_s^2}{k_s}\right) \quad (3)$$

where the proportionality constant K includes all the constant terms including β. For air, $\left(\frac{\mu_g}{T_0}\right)$ is a slowly varying function of temperature, which can be evaluated from the thermal parameters of air. The term $\left(\frac{\mu_s^2}{k_s}\right)$ is equal to $\left(\frac{2}{\omega \rho_s C_s}\right)$ where ω is the chopping frequency, ρ_s and C_s are the density and heat capacity of the sample, respectively. 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.
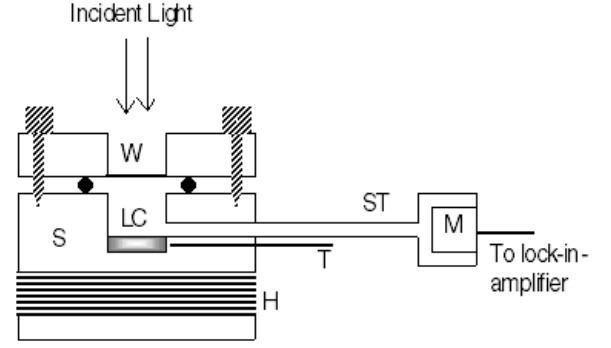

Figure 1. Cross-sectional view of the photoacoustic cell: W, the glass window; LC, the liquid crystal; T, the thermocouple; S, the stainless steel body; H, the heater coil; ST, the stainless steel tube; M, the microphone.

3. Experimental set-up

The experimental set-up used for the present investigation consists of an argon ion laser operating at 488 nm as the excitation source. A home-built resonant PA cell with a gas-microphone configuration was used for the studies. The cross-sectional view of the PA cell is shown in figure 1. To protect the microphone from damage due to the increased temperature of the sample chamber, the microphone chamber was kept away from the sample compartment and both the chambers were acoustically coupled through a thin walled stainless steel reservoir. The laser beam at a power level of 20 mW was mechanically chopped at 344 Hz and defocused so as to illuminate the entire surface of the sample kept inside the highly polished cavity of the PA cell. Defocusing was carried out to reduce the local heating effect on the sample surface and to ensure that the signal is contributed by the entire sample. A chromal–alumel thermocouple, together with an electrical heating element attached to the cell body and a temperature controller, were used to measure and control the temperature of the sample. A scanning rate of 200 millikelvin per minute was used throughout the measurements. The signal was then detected using an electret microphone (Knowles BT1834) and the microphone output was processed using a lock-in amplifier (Stanford Research Systems-SR 510). As the behaviour of the PA signal profile was found to be affected by too high a laser intensity and by a high heating rate, great care was taken in the choice of the laser beam intensity as well as the heating rate.

The samples used for the investigations were specially synthesized, wide nematic range liquid crystal mixtures meant for device fabrication. Since all these materials are optically transparent at 488 nm wavelength, we added an organic dye Eosin (0.5% by weight) to enhance the light absorption at this wavelength. High thermal stability, as well as the good photostability of the dye, has been taken into account in the selection of Eosin as the dopant. It has already been reported that the very low concentrations of dyes in the liquid crystals will not affect the thermal properties or transition temperatures to any significant extent [27]. The liquid crystal samples kept inside the PA cell have a thickness of around 2 mm. Under these conditions, the sample is thermally thick and optically thin. Measurements were carried out by heating the sample starting from the nematic phase.
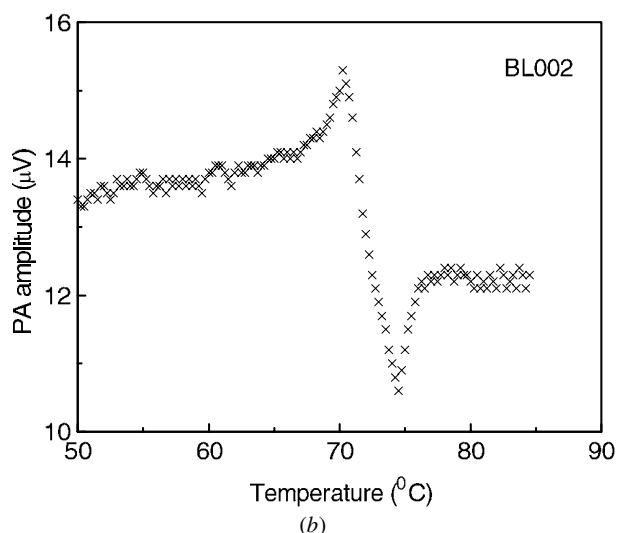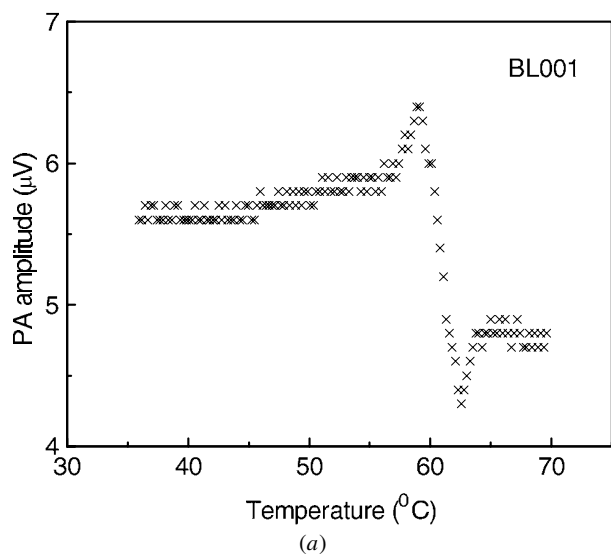
Figure 2. Photoacoustic signal amplitude versus temperature for the liquid crystals (*a*) BL001 and (*b*) BL002.

Figure 3. Photoacoustic signal amplitude versus temperature for the liquid crystals (*a*) BL032 and (*b*) BL035.

4. Results and discussion

Photoacoustic measurements were made on four nematic liquid crystal mixtures, namely BL001, BL002, BL032 and BL035, which are the trade names provided by Merck Ltd. All the above liquid crystals were in the nematic phase at room temperature and transform to the isotropic liquid phase at elevated temperatures. The PA signal response of the liquid crystals BL001 and BL002, recorded during the heating process, is shown in figures 2(*a*) and 2(*b*). From these plots it is clear that, as the temperature crosses the transition point, the PA signal amplitude changes from a maximum to a minimum. The exact values of the transition temperatures were determined from the derivative plot of the PA signal amplitude. The derivative plots show minima at 60.8 °C and 71.8 °C for BL001 and BL002, respectively. The observed transition temperatures are in close agreement with the thermal data provided by Merck Ltd [4].

Similar observations have also been made in the liquid crystals BL032 and BL035, and the PA signal profiles during the nematic-to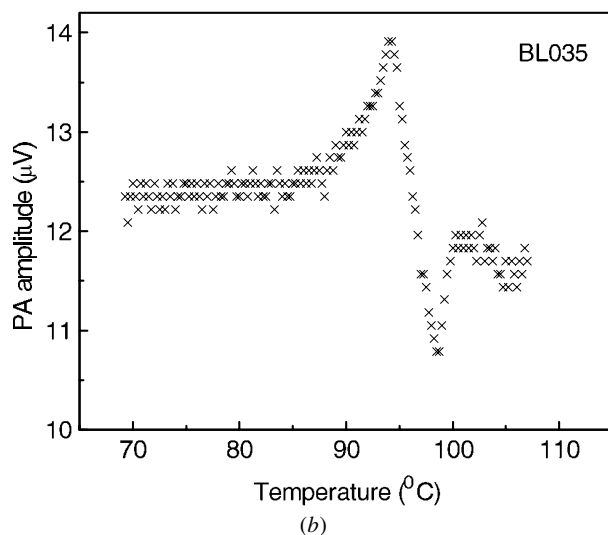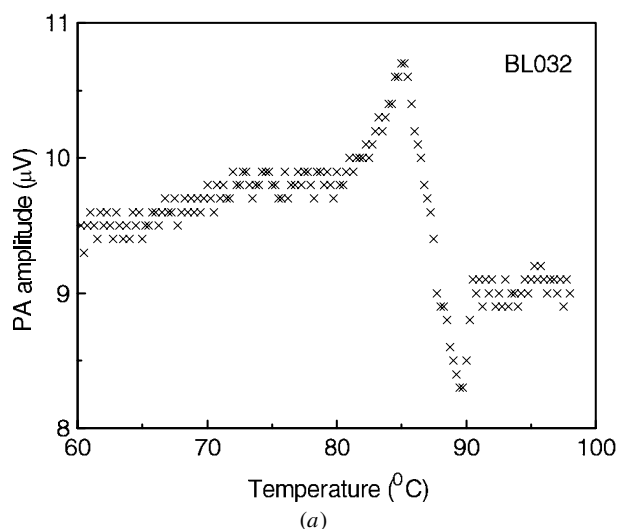-isotropic transition of these liquid crystals are shown in figures 3(*a*) and 3(*b*). The nematic-to-isotropic transition temperatures of these liquid crystals were also determined from the derivative plots and are located at 86.7 °C and 95.7 °C for BL032 and BL035, respectively. These values are also in close agreement with the thermal data provided by the manufacturer [4]. The present observations also confirm that the addition of trace amounts of dye to the liquid crystals has not affected the transition temperature in any significant manner.

From figures 2 and 3, it is clear that there is a gradual increase in the PA signal in the nematic phase as the temperature approaches the transition temperature. It is a well-known fact that the elastic properties, such as surface tension and viscosity, vary gradually with temperature rise in the nematic range itself [28–29]. This may have some indirect influence on the gradual increase of the PA 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 general theories available for the PA effect are not sufficient to
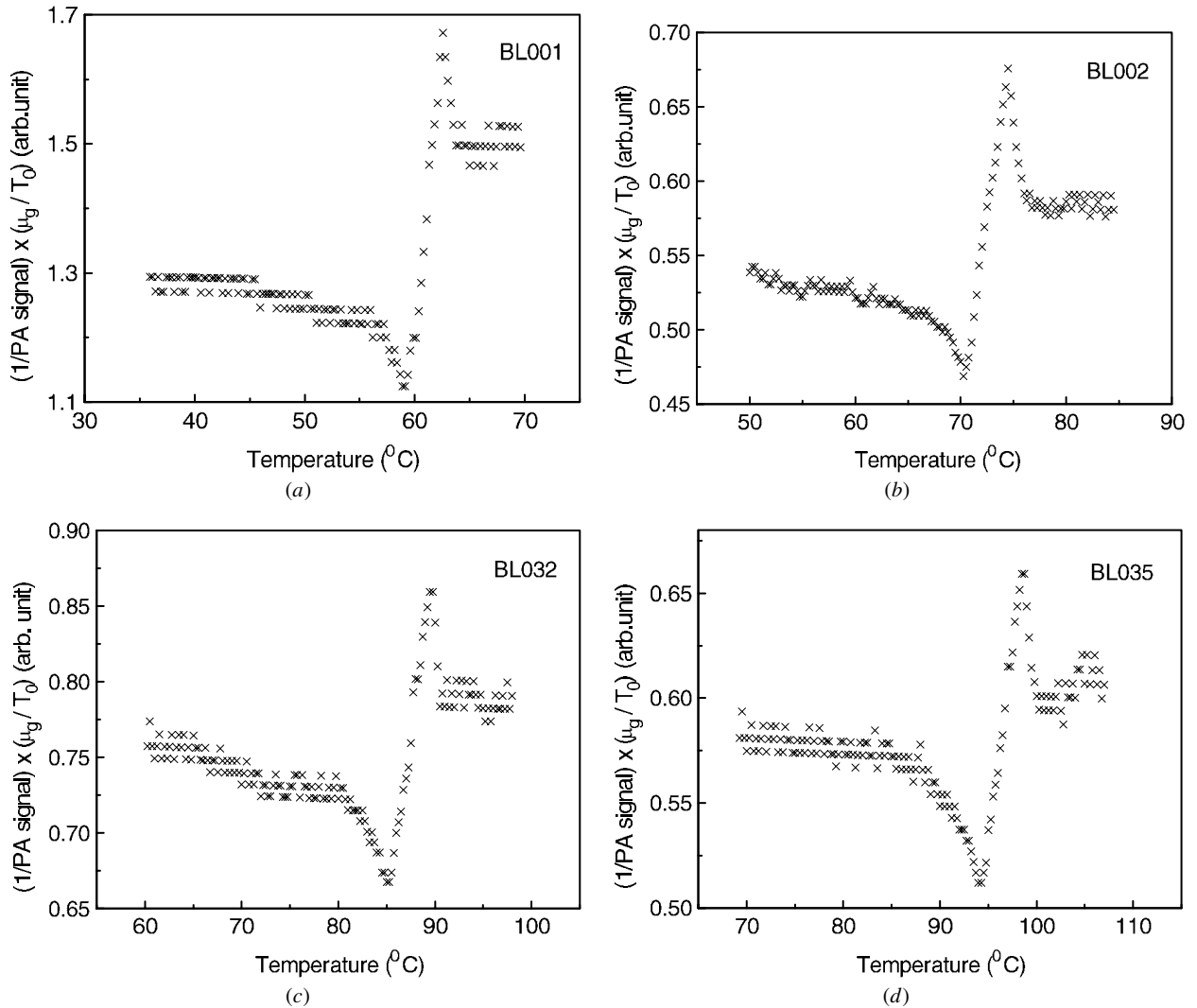
Figure 4. The (1/PA signal) $\times (\mu_g/T_0)$ versus temperature plots for (*a*) BL001, (*b*) BL002, (*c*) BL032 and (*d*) BL035.

give a satisfactory explanation for the present observations. Another important result is that the signal amplitudes in the nematic and isotropic phases differ by a large value, as can be seen from figures 2 and 3. Even though the dependence of density on the PA signal is clearly explained in the Rosencwaig–Gersho theory, the change in volume, and hence the change in density, during nematic-to-isotropic transition will be less than 0.5% in most of the liquid crystals [29–32]. Thus, density change cannot account for such a large difference in PA signals in the two phases. But, it is a well-known fact that the nematic phase possesses a 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 conditions, 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 PA signal in the nematic phase compared to the isotropic phase, where the scattering is very weak.

The typical behaviour of $[(1/\text{PA signal}) \times (\mu_g/T_0)]$, which is proportional to the heat capacity, derived from the experimental data using equation (3), is shown in figure 4. A comparison of the present results with the heat capacity profile during the nematic-to-isotropic transition of many other liquid crystals shows that the present observation of a sharp dip structure prior to the transition point is not in perfect agreement with earlier reported high-resolution calorimetric data [20, 22]. One reasonable argument for this observation is that the Rosencwaig–Gersho model is purely a one-dimensional thermodynamical model in which the roles of physical parameters, such as viscosity, surface tension etc, have not been considered. Even if we used bulk samples for the studies, the PA signal is mainly contributed by a small thickness, called the first thermal diffusion length, within the sample. The thermal diffusion length in liquid crystals will be only a few tens of micrometres at the modulation frequency which we used. Hence, the present observation of anomalous behaviour may be due to some surface effects or due to a pre-transitional ordering or changes in physical parameters occurring prior to the transition point. However, under the present experimental conditions, the evaluation of

the absolute value of heat capacity is rather difficult. One major advantage of the present method is that the experiment can be performed at any excitation wavelength by properly selecting the dye added to the liquid crystals.

To conclude, the application and advantages of the photoacoustic technique for determining the phase transition temperatures in nematic liquid crystal mixtures is discussed. The difference in the measured signal amplitude in the nematic and isotropic phases is attributed to the difference in the light scattering properties in the ordered and disordered phases. The present method is very simple, less time consuming and can be performed using optical radiation at any wavelength, and hence this is a very promising tool for the thermal characterization of liquid crystals

Acknowledgment

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