Open-cell photoacoustic investigation of the thermal effusivity of liquid crystals

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Abstract. We report the use of an open photoacoustic cell configuration for the evaluation of thermal effusivity of liquid crystals. Initially, the method is calibrated using water and glycerol as transparent liquid samples, and the role of thermal conductivity of these liquids on the photoacoustic signal amplitude is discussed. To demonstrate the application of the present method for the evaluation of thermal effusivity of liquid crystals, we have used certain multicomponent nematic liquid crystal mixtures, namely BL001, BL002, BL032, and BL035. Each of these liquid crystal mixtures contains four to nine components and are primarily based on the cyanobiphenyl structure. The measured values of thermal effusivity of BL001 and BL002 were found to be almost the same, but differ from those of BL032 and BL035, which implies a difference in composition of the latter two from the former two mixtures. [DOI: 10.1117/1.1384884]

Subject terms: photoacoustic and photothermal science and engineering; nematic liquid crystals; thermal effusivity.

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1 Introduction

In recent years considerable effort has been made in the theoretical and experimental study of the thermal properties of liquid crystals. Their applications in a variety of fields such as displays, temperature sensors, etc., have stimulated vigorous research activities in this field, as can be seen from the abundance in recent literature on the subject.[1–5] Among the various mesophases of liquid crystals, the nematic phase is the most extensively studied. The nematic phase is characterized by long range orientational order, where the molecules are aligned in a preferred direction. Also, in the nematic phase the centers of mass are randomly positioned, and the molecules are free to rotate about their long axes. It has been a clearly established fact that the thermal properties, such as the thermal conductivity in the nematic phase, are highly dependent on the alignment and the structure of the molecules.[6,7] Even though the thermal parameters and the critical behavior of heat transport properties close to the phase transition regions have been studied in detail, the physical mechanism of heat transport in liquid crystals at points far away from the transition temperature has not been explained on a quantitative manner. Among the various characterization methods, the ac calorimetric method is one of the most commonly used techniques for the thermal characterization of liquid crystals.[8–11]

In the past two decades the photoacoustic (PA) technique has become very popular for various measurements of material properties. This method has also been applied for the thermal characterization of liquid crystals.[12–16] Very recently, N. A. George et al. demonstrated the use of an open PA cell configuration for the thermal characterization of certain comb-shaped polymers.[12] The principle of the PA effect is based on the light-induced heat release and consequent acoustic generation from a material when it is irradiated with a modulated optical radiation. The dependence of a PA signal on both the thermal and optical properties of the sample makes it a convenient method for the study of materials in different forms. The thermal effusivity, similar to the thermal diffusivity, is a unique thermal transport property of a material. The thermal effusivity is defined by $e_s=(k\rho C)^{1/2}$ with dimension $\mathrm{W\,s^{1/2}\,cm^{-2}\,K^{-1}}$, where k is the thermal conductivity, ρ is the density, and C is the specific heat capacity. Even though the thermal effusivity is an abstract thermal quantity and is a relevant thermophysical parameter for surface heating and cooling as well as in quenching processes, it is one of the least explored quantities in physics. Actually, the thermal effusivity is a measure of the sample's thermal impedance or its ability to exchange heat with the environment. The thermal effusivity of liquid crystals has great importance when they are used as temperature sensors or in temperature sensitive devices.

We report the thermal effusivity of certain multicomponent cyanobiphenyl liquid crystal mixtures, namely BL001, BL002, BL032, and BL035. A simple open cell PA configuration is used for the investigations. Initially, the method is calibrated using water and glycerol as the nonabsorbing samples. Special emphasis given to selecting these liquid crystals for the present study is due to the wide nematic range of these materials, which enabled them to find potential applications in a variety of advanced fields such as display technology, and to the best of our knowledge the present measurement is the first of its kind in liquid crystals.

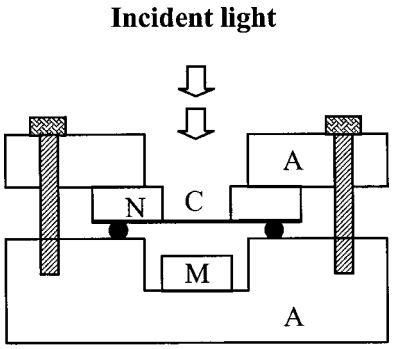

Fig. 1 Cross-sectional view of the OPC: A=acrylic frame; M=microphone; N=nylon ring; and C=copper foil.

2 Theory

The cross-sectional view of the open photoacoustic cell (OPC) is shown in Fig. 1. The liquid crystal sample holder is made of a nylon ring with a 75-μm-thick copper foil at its bottom. When the sample holder is filled with a nonabsorbing liquid sample and is irradiated with a modulated optical radiation, the copper foil absorbs the light and periodic heat is generated at the surface of the copper foil in contact with the liquid sample. The thermal diffusion equations for the OPC configuration shown in Fig. 2 are[17,18]

$$\frac{\partial^2 T_s}{\partial x^2} = \sigma_s^2 T_s$$

$$\frac{\partial^2 T_0}{\partial x^2} = \sigma_0^2 T_0 - \frac{\beta I_0}{k_0}\,\delta(x+l_0) \tag{1}$$

and

$$\frac{\partial^2 T_g}{\partial x^2} = \sigma_g^2 T_g\,,$$

where $\sigma_i=(1+j)a_i$, with $a_i=(\pi f/\alpha)^{1/2}$. Here the suffix i denotes the liquid sample ($i=s$), the copper foil ($i=0$), and the air in the PA chamber ($i=g$). Assuming that the entire light is absorbed at $x=-l_0$ and solving Eq. (1) together with the boundary conditions of temperature and heat flux continuity, one can arrive at the expression for the acoustic pressure in the OPC chamber as

$$\delta Q = \frac{\gamma P_0 \beta I_0}{T_0 l_g \sigma_g k_0 \sigma_0}\left(\frac{\exp(j\omega t)}{b\cosh(l_0\sigma_0)+\sinh(l_0\sigma_0)}\right) \tag{2}$$

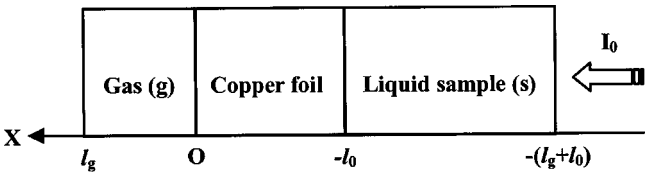

Fig. 2 Schematic diagram of the geometry of the OPC for which the calculations were made. The periodic heat is generated at $x=l_0$. For an empty sample holder, the liquid sample s is replaced with the gas g.

where

$$b=(k_s\sigma_s/k_0\sigma_0).$$

Now, if the copper foil is thermally thin ($l_0\sigma_0 \ll 1$), then the PA signal produced by the transparent liquid copper foil composite sample is given by

$$\delta Q_1 = \frac{\gamma P_0 \beta I_0 (\alpha_g \alpha_s)^{1/2}}{2\pi T_0 l_g k_s}\,\frac{\exp[j(\omega t-\pi/2)]}{f}. \tag{3}$$

Equation (3) implies that the PA signal now varies as f^{-1} and is proportional to the ratio

$$\sqrt{\alpha_s}/k_s = e_s^{-1},$$

the inverse of the thermal effusivity of the transparent liquid.

On the other hand, if the sample holder is empty, i.e., for a thermally thin copper foil alone, the pressure fluctuation δQ_2 is given by

$$\delta Q_2 = \frac{\gamma P_0 \beta I_0 \alpha_g^{1/2}\alpha_0}{(2\pi)^{3/2} T_0 l_g l_0 k_0}\,\frac{\exp[j(\omega t-3\pi/4)]}{f^{3/2}}. \tag{4}$$

Thus according to Eq. (4), the signal varies as $f^{-3/2}$ and depends on the ratio α_0/k_0. Using this as a reference signal and from the ratio of Eqs. (3) and (4), one can measure the thermal effusivity of the liquid sample by measuring the PA signals from the empty sample holder and the liquid filled sample holder, provided the thickness, density, and specific heat capacity of the absorbing layer (copper foil) are known.

3 Experimental

The experimental setup used for the present investigation is almost similar to the conventional PA setup.[19] The only difference is that instead of a closed PA cell, here we use an open cell fabricated on an acrylic sheet. This minimum volume cell has very high signal-to-noise ratio. For the present investigations we have used a sample holder made of a nylon ring with an inner diameter of 7 mm and thickness 3 mm, and its bottom is closed with a copper foil of thickness 75 μm. The liquid crystal is filled up to half of the holder, and the entire sample holder is kept over the microphone, leaving a small volume of air in-between the two. Modulated optical radiation at 488 nm from an argon ion laser (Liconix 5000 series) is used to illuminate the copper substrate. The laser power is kept constant at 100 mW with a stability of $\pm$0.005 mW/h. The periodic pressure variation produced in the chamber is detected using a highly sensitive miniature electric microphone (Knowles BT 1834). The output is processed using a lock-in-amplifier (Stanford Research Systems SR 510). The PA signal amplitude is recorded as a function of modulation frequency of the laser beam for both the empty sample holder and the one filled with the liquid (liquid crystal) samples. The measurements were carried out at 27°C in the nematic phase of the samples and in the absence of any external magnetic or electric fields.

Even though these liquid crystals are optically nonabsorbers at 488 nm, scattering loss is an important factor to

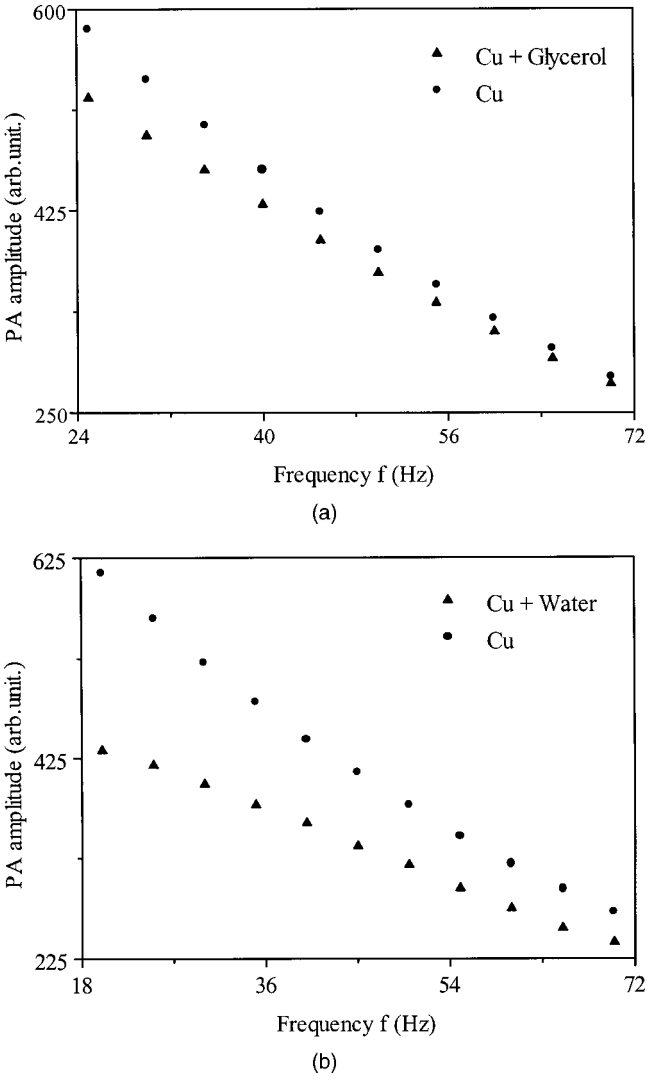

Fig. 3 The OPC signal amplitude as a function of the modulation frequency for: (a) glycerol-copper system and (b) water-copper system.

be taken into account. The same sample holder is used to measure the transmitted intensity at 488 nm. For this purpose the copper foil is replaced by a glass plate (1.5 mm thick) and its surface facing the PA cell cavity is coated with carbon black thin film. For an empty sample holder, a linear dependence of the PA signal amplitude with the incident light intensity is observed. Then the sample holder is filled with the liquid crystal and the photoacoustic signal at a constant incident light intensity is recorded. From this value we accurately estimated the percentage transmittance of each of the samples. For the same sample thickness as used for the thermal effusivity measurements (1.5 mm), the optical transmittance (at 488 nm) are 67, 66, 64, and 65%, respectively, for BL001, BL002, BL032, and BL035. Though the nematics form a different domain size when they are in contact with copper and glass, slight changes in the measured transmittance values are found to result in a small change in the thermal effusivity values.

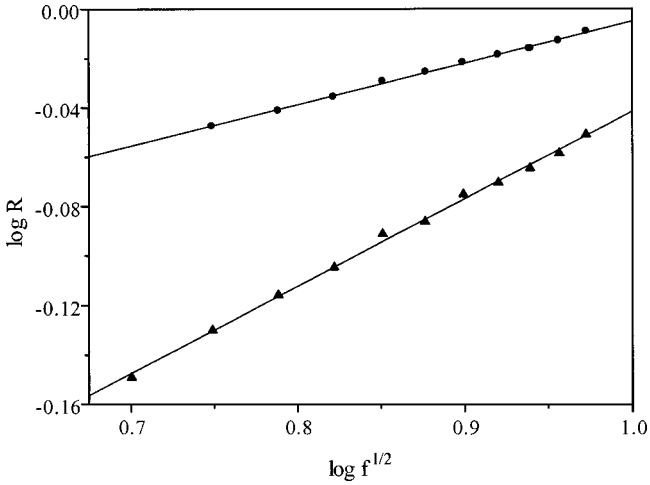

Fig. 4 Logarithmic plot connecting the square root of frequency *f* and the amplitude ratio *R* for water and glycerol with the reference sample (Cu foil). The solid circle is for glycerol and the solid triangle is for water.

4 Results and Discussion

Initially, the experimental setup was calibrated using water and glycerol, the thermal properties of which are well known. The PA signal produced by the empty sample holder and that obtained after filling it with transparent liquids are measured as a function of the modulation frequency. The observed PA signal variation with frequency from the copper foil is in perfect accordance with the Rosencwaig-Gersho theoretical model. This implies that the frequency of mechanical resonance of the copper membrane does not fall in the frequency range of our investigations. Typical variation of the PA signal amplitude for the glycerol-copper and water-copper systems are shown in Figs. 3(a) and 3(b). It is worthwhile to note that the amplitude of the signal produced by the empty sample holder (copper foil alone) is greater than that from the copper-liquid composite sample. This indicates that the liquid acts as a heat sink, or a part of the thermal energy generated at the liquid-copper interface is absorbed by the liquid due to the finite thermal conductivity of the liquid. A comparison of Figs. 3(a) and 3(b) is sufficient to confirm this. The thermal conductivity values of water, glycerol, and air are 0.591, 0.270, and 0.0241 $\mathrm{W\,m^{-1}\,K^{-1}}$, respectively. Water, being a liquid with higher thermal conductivity than glycerol, produces a lesser signal compared to the latter. Figure 4 shows the $\log f^{1/2}$ versus $\log R$ plot, where f is the chopping frequency and R is the ratio of the PA signal produced by the sample holder filled with liquid samples to that of an empty one. From a straight line fit to the ratio of the two signal amplitudes, the thermal effusivities were calculated using Eqs. (3) and (4). The observed values of thermal effusivities of water and glycerol are 0.155 ($\pm$0.002) and 0.094 ($\pm$0.001) $\mathrm{W\,s^{1/2}\,cm^{-2}\,K^{-1}}$. These values agree well with the literature values 0.158 and 0.093 $\mathrm{W\,s^{1/2}\,cm^{-2}\,K^{-1}}$, respectively, for water and glycerol.[20] We have used $l_0 = 75\ \mu\mathrm{m}$, $\rho_0 = 8.96\ \mathrm{g\,cm^{-3}}$, and $C_0 = 0.385\ \mathrm{J\,g^{-1}\,K^{-1}}$ as the thickness, density, and the specific heat capacity, respectively, of the copper foil.[20]

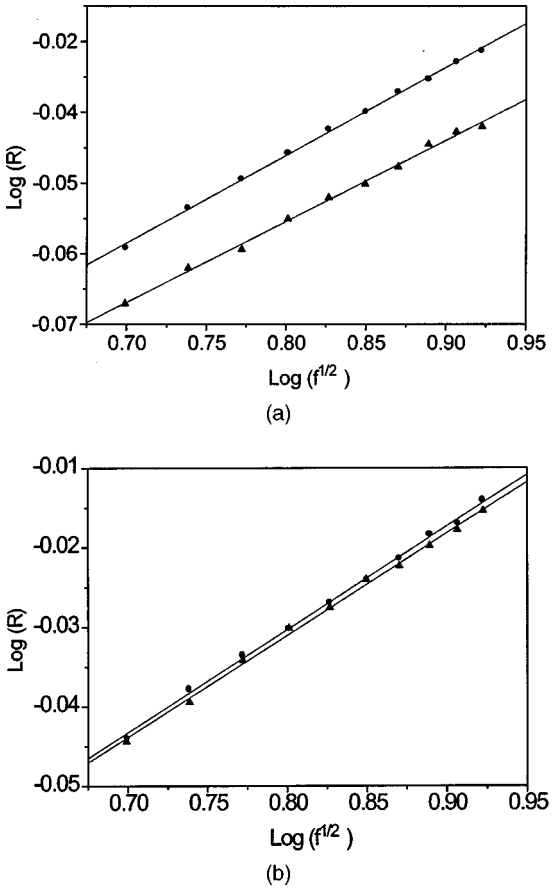

Fig. 5 Logarithmic plot connecting the square root of frequency f and the amplitude ratio R for: (a) BL001 and BL002 with the reference sample (Cu foil), the solid triangle is for BL001 and the solid circle is for BL002, and (b) for BL032 and BL035 with the reference sample (Cu foil), the solid triangle is for BL032 and the solid circle is for BL035.

The nematic liquid crystal mixtures BL001, BL002, BL032, and BL035 were obtained from Merck Inc., UK, and were used without further purification. All these compounds are multicomponent liquid crystal mixtures, which exist in the nematic phase at room temperature. The nematic to isotropic transition temperatures of BL001, BL002, BL032, and BL035 are at +61, +72, +87, and +96°C, respectively, and the nematic to smectic transition temperatures of all the compounds are below −20°C.[21]

Figures 5(a) and 5(b) show the log $f^{1/2}$ versus log R plots of the liquid crystals BL001, BL002, BL032, and BL035. The straight lines represent best linear fit to the experimental data. The estimated values of thermal effusivities are summarized in Table 1. In terms of the liquid crystal molecular orientation, the nematic phase has the translational symmetry of a fluid, but a broken rotational symmetry characterized by long-range orientational order produced by the alignment of their long molecular axes along the director. In the nematic phase, however, the centers of mass of the molecules are still randomly distributed. Therefore, in the absence of any external magnetic or electric fields to align the molecules in any preferred direction, the measured values of thermal effusivity will be the mean value of the

Table 1 Thermal effusivity in the nematic phase (at 27°C) of the liquid crystal mixtures

Liquid crystal mixture	Thermal effusivity in W $s^{1/2}$ cm^{-2} K^{-1}
BL001	0.0625 (±0.0014)
BL002	0.0622 (±0.0013)
BL032	0.0571 (±0.0012)
BL035	0.0569 (±0.0012)

quantity contributed by the average thermal conductivity, given by

$$\langle k \rangle = \tfrac{1}{3}(k_x + 2k_y) \tag{5}$$

where k_x and k_y are the thermal conductivities parallel and perpendicular, respectively, to the director in oriented samples.[22] As the heat capacity or thermal conductivity data of these liquid crystals are not available in the literature, a comparison of the present data is rather difficult. But the measured values of the thermal effusivity fall in the range of several other liquid crystals (calculated from the heat capacity and the thermal conductivity data) in the nematic phase.[2,13,15,16] Also, the experimental calibration using water and glycerol ensures high accuracy for the present method.

Another important observation to be pointed out is that the thermal effusivity of Bl001 and BL002 are almost the same but differ from those of BL032 and BL035. This obviously suggests a different molecular composition for the first two liquid crystal mixtures compared to the other two mixtures. However, being a patented commercial product from Merck, the structural or compositional details of any of these mixtures are not known for an elaborate analysis of the results.

5 Conclusion

In conclusion, we have successfully implemented an open cell PA configuration to study the thermal effusivity of certain liquid crystal mixtures in their nematic phase. Besides the interest in its value, the importance of thermal effusivity as a physical quantity is due to the fact that it is a unique thermal parameter for each material. Knowledge of its absolute value leads us to the evaluation of thermal conductivity or specific heat capacity, if any one of these are known, density being an easily measurable quantity. The present method is very simple and less time consuming, and its high accuracy may render it as a valuable tool for the thermal characterization of liquid crystals. A combination of the present method with the earlier reported conventional PA configurations could be used for a complete thermal characterization of liquid crystals and nonabsorbing liquids.

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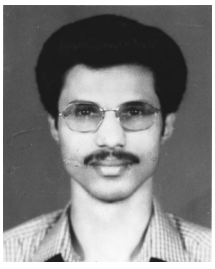

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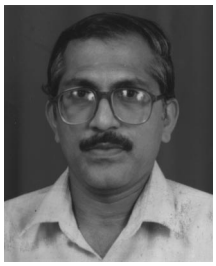

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