Photoacoustic studies on thermal parameters of liquid crystal mixtures

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Abstract
Complete thermal characterization of liquid crystal mixtures in the smectic phase consisting of various relative volume fractions of cholesterol and 1-hexadecanol have been carried out using the photoacoustic technique. Thermal diffusivity values of these liquid crystal mixtures are evaluated using the open cell photoacoustic technique whereas the thermal effusivity value is measured using the conventional photoacoustic technique. From the measured values of these transient thermophysical parameters, the thermal conductivity and heat capacity of the sample under investigation are calculated. Analyses of the results show that all the thermophysical parameters depend strongly on the volume fraction of the constituents. Results are interpreted in terms of enhanced hydrogen bonding and the consequent enhancement in cohesive thermal energy transport with increasing volume fraction of 1-hexadecanol.

1. Introduction

In recent times, considerable efforts have been made into the synthesis and characterization of heterogeneous liquid crystal mixtures due to their wide applications in the photonics industry [1–3]. As these materials are extensive for device fabrication, thermal characterization of these materials demand close scrutiny. The variation in thermal parameters as a function of volume fraction of the constituents have so far not been well investigated experimentally, particularly using nondestructive and nonintrusive techniques. In the present work, focus is paid to the variation in thermophysical parameters, namely, thermal diffusivity, thermal effusivity, thermal conductivity and thermal heat capacity, as a function of relative volume fraction of 1-hexadecanol in a liquid crystal mixture of cholesterol and 1-hexadecanol using the laser-induced nondestructive photoacoustic technique.

All the photothermal methods depend upon the detection of thermal waves generated in the sample after illumination with pulsed or chopped optical radiation [4–6]. Amongst

the variety of techniques available [7–10], the laser-induced photoacoustic (PA) method has gained more popularity due to its simple, elegant experimental technique as well as to its versatility in employing different configurations to measure the required thermophysical parameter with great accuracy [11, 12].

Thermal diffusivity is an important thermophysical parameter, which essentially determines the diffusion of heat through a sample. Physically, the inverse of thermal diffusivity is a measure of the time required to establish thermal equilibrium in a system for which a transient temperature change has occurred [13, 14]. Even though thermal effusivity is a unique thermophysical parameter, it is one of the least explored quantities in physics [15]. Thermal effusivity essentially measures thermal impedance of the material, which in other words, is the sample's ability to exchange heat with the environment. Hence, it is an important parameter for surface heating and cooling processes as well as in quenching processes [16]. By knowing the values of the thermal diffusivity and thermal effusivity, an evaluation of thermal
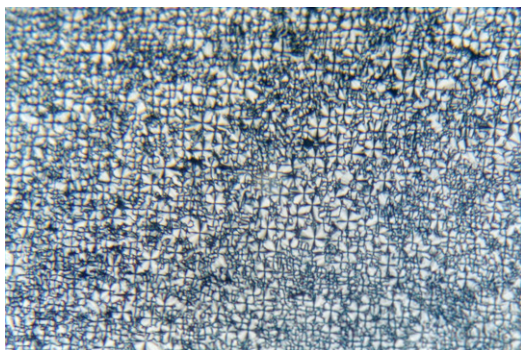
Figure 1. Representative polarized optical micrograph of a mixture containing 70% cholesterol and 30% 1-hexadecanol.

conductivity and thermal capacity of the specimen can be made. The present study is of great physical and practical relevance owing to the immense technological importance of the thermal parameters of liquid crystals.

2. Sample preparation

The samples of the present investigation are prepared by mixing cholesterol and 1-hexadecanol in various relative volume fractions (70%:30%, 60%:40%, 50%:50%, 40%:60%, respectively) and the mixture is heated to a temperature well above the melting point with continuous stirring to ensure thorough and complete mixing. The homogeneous mixture is quickly cooled and solidified by quenching in ice. This procedure is repeated until constant melting and transition temperatures are obtained. The microscopic textural investigations using an Olympus polarizing microscope in conjunction with a heating stage (Linkam—TMS 94) shows that all the mixtures under investigation are in the smectic A phase, which is the most ordered liquid crystalline phase. Smectic is a distinct mesophase of liquid crystals in which molecules exhibit a high degree of translational order. In this state, molecules not only maintain a general orientational order, but also tend to align in layers or planes. Motion is restricted within these planes which gives a more 'solid-like' phase. In the smectic A phase, the director is perpendicular to the smectic plane and there is no particular positional order in the layer. A representative polarized optical micrograph of the specimen containing cholesterol and 1-hexadecanol in the ratio 70:30 is given in figure 1.

3. Experimental set-up and theoretical background

A schematic representation of the open photoacoustic cell (OPC) used here is given in figure 2. Optical radiation from an argon ion laser at 488 nm (Liconix 5000) is used as the excitation source. The laser is intensity-modulated using a mechanical chopper (Stanford Research Systems SR 540) before it reaches the sample surface. Detection of the PA signal in the cavity is made using a sensitive electret microphone (Knowles BT 1754). Details of the PA cell used in the present investigation are explained elsewhere [17]. The cell has a flat response in the frequency range 40–4000 Hz. The phase of the photoacoustic signal is measured using a dual-phase digital
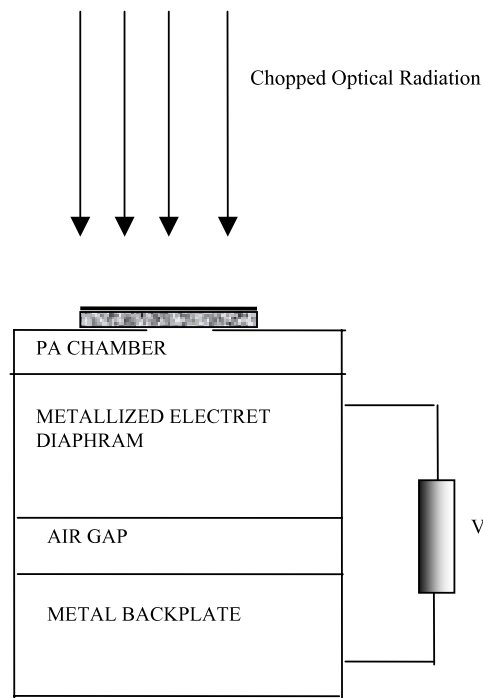

Figure 2. Schematic diagram of the open photoacoustic cell.

lock-in amplifier (Stanford Research Systems SR 830). The laser power used for the present studies is 50 mW with a stability of 0.5%. In this case a thin Al foil (5 μm) is attached to the sample surface to obtain complete opaqueness as well as the same light to heat conversion efficiency. The phase of the PA signal generated by the sample due to its excitation with chopped optical radiation, in the thermally thick region (sample thickness is greater than thermal diffusion length), is given by the expression [18]

$$\Theta_{\mathrm{el}} \cong \Theta_0 + \tan^{-1}\left(\frac{1}{(z-1)}\right), \qquad (1)$$

where Θ_0 is the initial phase and $z = l_{\mathrm{s}}\sqrt{\pi f/\alpha_{\mathrm{s}}}$ for a specimen of thermal diffusivity α_{s}. This has been evaluated by taking into account the thermoelastic bending due to the temperature gradient existing within the sample.

The conventional PA cell employed here for thermal effusivity measurements is given in figure 3. A major difference in this, as compared to OPC, is that the signal is collected from the front side of the sample under investigation. The PA signal is generated by nonradiative de-excitation following the incident chopped optical radiation (488 nm from an argon ion laser—Liconix series). Amplitude of the PA signal is measured using a dual-phase lock-in amplifier (Stanford Research Systems SR 830). In this case, the PA signal amplitude is measured for a sample attached with aluminium foil and aluminium foil alone. The theoretical background for evaluating thermal effusivity has already been explained by Veleva *et al* [19]. According to them, the ratio of PA signal between aluminum foil attached to the sample surface (θ) and Al foil alone (θ_0) in a conventional PA cell
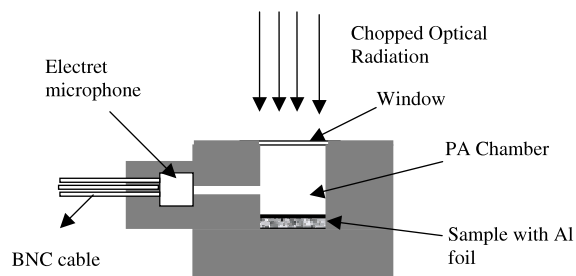
Figure 3. Conventional photoacoustic cell.

Figure 4. Open photoacoustic cell phase spectrum for the liquid crystal mixture containing 70% cholesterol and 30% 1-hexadecanol.

Figure 5. Ratio of amplitude for the liquid crystal mixture containing 70% cholesterol and 30% 1-hexadecanol.

configuration is given by the expression

$$\frac{\theta}{\theta_0} = \frac{1}{1 + (b/l_0\sigma_0)}, \qquad (2)$$

where $b = \frac{\varepsilon_s}{\varepsilon_0}$ in which ε_s is the effusivity of the sample. ε_0 and l_0 is the effusivity and thickness of the Al foil (60 μm) having thermal diffusivity α_0. In this case, $\sigma_0 = (1 + i)a_0$, where $a_0 = \sqrt{\frac{\pi f}{\alpha_0}}$. Thus, by using the known values of thermal parameters of the Al foil, the thermal effusivity value of the sample under investigation can be evaluated. Since the ratio of amplitudes is taken for evaluating thermal effusivity, calculated values are independent of the frequency-dependent transfer function [20]. By knowing these two transient thermophysical parameters, the thermal diffusivity (α_s) and thermal effusivity (ε_s) of the specimen, its thermal conductivity ($k_s = \varepsilon_s\sqrt{\alpha_s}$) and thermal capacity ($\rho C = \frac{k_s}{\alpha_s}$) can be evaluated.

4. Results and discussion

A typical phase spectrum used for thermal diffusivity calculation, measured for the sample with 70% cholesterol and 30% 1-hexadecanol is given in figure 4. The amplitude ratio of the signal used for thermal effusivity calculation is given in figure 5. All other samples showed similar behaviour (not shown here). The evaluated thermal parameters are tabulated in table 1. From the table it is clear that thermal diffusivity increases with increase in volume fraction of 1-hexadecanol in a liquid crystal mixture consisting of cholesterol and 1-hexadecanol while thermal effusivity decreases. In the case of heterogeneous liquid crystal mixtures, as in the present case, measurement of the effective thermal parameters depends on the thermal properties of its constituents. For a heterogeneous mixture, lattice expansion thermal mismatch and interfacial thermal resistance are two key parameters that essentially determine the effective thermal properties of the system. Although cholesterol is non-mesomorphic, it must be considered to be potentially mesomorphic since even cholesteryl chloride gives a monotropic cholesteric phase. It is possible that hydrogen bonding in pure cholesterol increases the intermolecular cohesion and is responsible for its high melting point. Hydrogen bonding is one of the key interactions in the case of liquid crystal mixtures that results in the creation and stabilization of supermolecular liquid crystal materials [21–23]. In the case of a mixture of two different substances, as in the present case, liquid crystal formation will depend on two factors: first,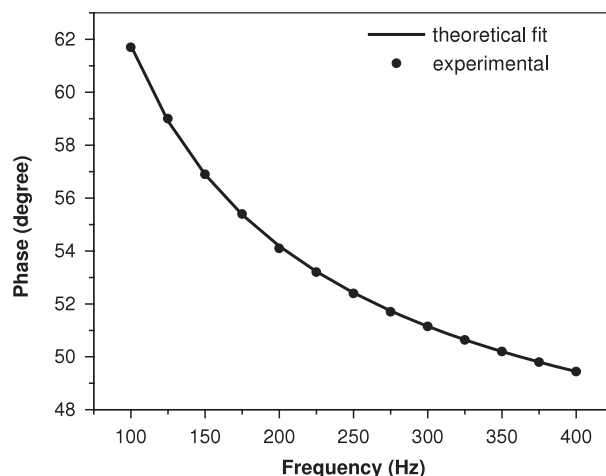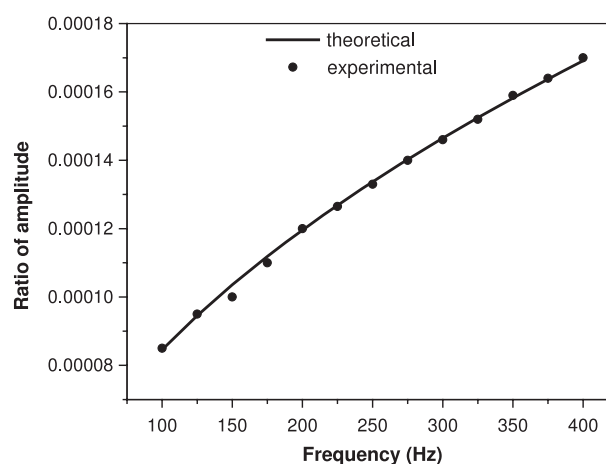 the ability of molecules to pack into a single liquid crystal 'lattice' and, secondly, its mean orientational cohesive energy [24, 25].

Introduction of hexadecanol molecules may create alternate sites to which cholesterol hydroxyl groups can hydrogen bond without providing a high melting crystal lattice, yet giving sufficiently strong intermolecular attractions resulting in an anisotropic melt. The increase in relative volume fraction of 1-hexadecanol increases the number of sites available for H-bonding and consequently more intermolecular attraction. With increasing intermolecular attraction and the consequent cohesive structure, the liquid crystal mixture provides an easier path for heat transport. This results in an enhancement in thermal conductivity with increasing relative fraction of 1-hexadecanol. The unification of components of the mixture through H-bonding causes the reduction in heterogeneity of the liquid crystal mixture. As the heterogeneity of the specimen decreases, factors causing reduction in the thermal parameters, namely interface thermal resistance and lattice expansion mismatch, also decrease [26]. This may also be the cause of increased value for thermal conductivity with increasing relative fraction of 1-hexadecanol,

Table 1. Thermal properties of the material under investigation.

Sample (cholesterol:1-hexadecanol)	Thermal diffusivity (10^{-6} m^2 s^{-1})	Thermal effusivity (W s$^{1/2}$ m^{-2} K^{-1})	Thermal conductivity (W m^{-1} K^{-1})	Heat capacity (10^6 J m^{-3} K^{-1})
70:30	2.304 ± 0.003	17.1 ± 0.2	0.260 ± 0.004	0.113 ± 0.0004
60:40	2.770 ± 0.005	16.5 ± 0.3	0.271 ± 0.005	0.0991 ± 0.005
50:50	3.061 ± 0.003	16.0 ± 0.2	0.281 ± 0.004	0.0915 ± 0.004
40:60	3.602 ± 0.004	15.5 ± 0.1	0.294 ± 0.003	0.0820 ± 0.003

which also explains the observed variation in thermal energy capacity with volume fraction of constituents.

5. Conclusions

In conclusion, results of the dependence of effective thermal parameters on the volume fraction of constituents in a liquid crystal mixture consisting of cholesterol and 1-hexadecanol are presented in this paper. It is seen that the thermal conductivity (thermal diffusivity) of the specimen increases with the increase in volume fraction of 1-hexadecanol whereas thermal effusivity decreases. Analyses of results show that H-bonding plays a key role in determining the effective thermal parameters of a liquid crystal mixture. The present study also suggests that effective thermal parameters can be tunable by varying the volume fraction of the constituents.

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