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In this work the quantitative theoretical treatment for two beam mode mismatched thermal lens spectrometry is applied to investigate the thermal diffusivity anisotropy of two lyotropic mixtures: (1) potassium laurate, decanol and water and (2) potassium laurate, potassium chloride and water in the nematic calamitic phase. The ratio between the thermal diffusivities parallel and perpendicular to the director has been shown to be smaller than those reported for thermotropic liquid crystal. This observation is explained by using a simple model where this ratio is correlated to the micellar shape anisotropy. © *1996 American Institute of Physics.* [S0003-6951(96)01624-5]

There has been a growing interest in using photothermal techniques to measure optical and thermal properties of highly transparent materials. These methods are advantageous when compared with conventional thermometry because they allow the experiments to be performed without the difficulties of obtaining the steady state conditions. Thermal lens spectrometry (TLS) is a transient technique which has been increasingly used to investigate the thermal transport properties of transparent materials.[1–4] Thermal lens techniques are also non contacting thus removing the requirement for perfect thermal contact between the measuring device and the sample. The thermal lens (TL) effect is created when the excitation laser beam passes through the sample and the absorbed energy is converted into heat, changing the optical path length, s, and producing a lens-like optical element at the sample. The propagation of a probe beam laser through the TL will result in either a spreading or a focusing of the beam center, depending on the sample properties. The TL signal intensity is mainly controlled by the sample optical absorption coefficient and its thermal conductivity.

The TL in liquid crystals (LC) can produce either laser beam self-focusing or defocusing, depending on the temperature coefficient of the refractive index, dn/dT, and on both laser beam polarization and intensity. The refractive index dependence on laser intensity is associated with Kerr effect, electrostriction, non linear electronic polarization and thermal heating, and each one of these effects can be investigated varying the time scales for the experiments.[5–7] A more complete description of the basic processes and techniques associated with propagation of a laser beam through liquid crystals can be found elsewhere.[8] Earlier TL experiments in thermotropic liquid crystals have been reported for both, pulsed and cw thermal lens.[3–6,9,10] In these experiments the optical nonlinearity of the samples has been investigated. The experimental arrangement used in these investigations was the single beam configuration. However, it has been shown that the two beam mode mismatched TLS, a configuration arranged to have different spot sizes for the two laser beams at the sample, is a much more sensitive arrangement, allowing to measure samples with optical absorption coefficient as small as 10^{-7} cm^{-1}.[11,12] Moreover, in order to make quantitative measurements, the theoretical model for this configuration has been developed.[13] It appears therefore, that the use of this configuration and its theoretical model could be advantageous in the study of liquid crystals.

On the other hand, the thermal transport properties of liquid crystalline materials are not well understood.[14] It has been suggested in a qualitative way that for thermotropics the anisotropy of thermal diffusivity in the nematic phase could be associated with the molecular shape. However, a quantitative description of this association is still lacking. This reinforced our interest in using TLS in this study, since this technique can provide the sample thermal diffusivity anisotropy.

In this work the two beam mode mismatched TL configuration is applied to determine the thermal diffusivity anisotropy of two lyotropic mixtures in their nematic calamitic phase. A simple model considering the sample as an array of thermal resistors is presented, indicating that for lyotropics, the ratio between the thermal diffusivity parallel and perpendicular to the director can be associated to the micellar shape. Furthermore, by using thermal diffusivity data from the literature, we have shown that this model can also be applied for thermotropics.

Lyotropic nematic liquid crystals are mixtures of amphiphilic molecules and a solvent (usually water), under proper temperature and concentration conditions.[15] The basic units of these systems are anisotropic micelles.[16] The mixtures investigated in this work were: (a) potassium laurate (29.4 wt%), decanol (6.6 wt%), water (64 wt%)—mixture 1; (b) potassium laurate (34.5 wt%), potassium chloride (3 wt%), water (62.5 wt%)—mixture 2. The phase sequences were determined by optical microscopic and conoscopic observations which show that: mixture 1 is isotropic up to 15 °C, calamitic nematic from 15 to 50 °C and isotropic above 50 °C; in mixture 2 the nematic calamitic phase upon heating changes to hexagonal phase at about 40 °C.[17] Both

samples were encapsulated in glass cells, with a Teflon separator used to set the thickness at 1 mm. The axes of the directors in the nematic phases were aligned for some hours in a magnetic field (0.8 T) for both orientations, parallel and perpendicular to the sidewalls. The measurements were performed at room temperature.

The higher sensitivity for the mode mismatched configuration is achieved when the sample is positioned at the waist of the excitation beam, where the power density is maximum, and at the confocal position of the probe beam. In previous studies the mode mismatched configuration has been used for quantitative investigations of both solid and liquid samples.[1,2,13,18] Furthermore, considering that the more realistic and more accurate theoretical model to describe the thermal lens effect should consider the aberration of the TL, the aberrant model for mode mismatched configuration has been developed. It treats the thermal lens as an optical path length change to the probe laser beam, which can be expressed as an additional phase shift on the probe beam wave front after its passing through the sample. This model provides a simple analytical expression for absolute determination of both optical and thermal properties of the samples.[13,18] The variation of the probe beam intensity at the detector is expressed as:[2,13,18]

$$I(t) = I(0)\left[1 - \frac{\theta}{2} \times \arctan \left(\frac{2mV}{[(1+2m)^2+V^2]\frac{t_C}{2t}+1+2m+V^2}\right)\right]^2, \quad (1)$$

where

$$t_C = \frac{\omega_e^2}{4\alpha}, \quad \theta = \frac{P_e A_e l_0}{\kappa \lambda_p}\frac{ds}{dT}, \quad V = \frac{Z_1}{Z_c}. \quad (2)$$

In Eqs. (1) and (2), θ is the difference between the thermally induced phase shift of the probe beam at $r=0$ and $r=\sqrt{2}\omega_e$, $m=(\omega_p/\omega_e)^2$, ω_p and ω_e are the probe beam and excitation beam spot sizes at the sample, respectively, α is the sample thermal diffusivity, P_e is the excitation laser beam power (mW), A_e is the optical absorption coefficient at the excitation beam wavelength (cm^{-1}), Z_c is the confocal distance of the probe beam, Z_1 is the distance of the probe beam waist to the sample and $I(0)$ is the value of $I(t)$ when t or θ is zero. Moreover, l_0 is the sample thickness, κ is the thermal conductivity, λ_p is the probe beam wavelength, and ds/dT is the temperature coefficient of the optical path length.

Therefore, in time resolved TL experiments, θ and the thermal diffusivity can be obtained from the curve fitting of Eq. (1) to the experimentally observed time profile of the developing thermal lens.

The above model imposes some experimental conditions to investigate thin samples.[18] In order to avoid heat flow in the laser beam direction it has been shown that experiments with thin samples must be performed only for a short period of time $t < 5\,t_C$, where t_C is the characteristic thermal time constant, and with the ratio between the probe beam spot
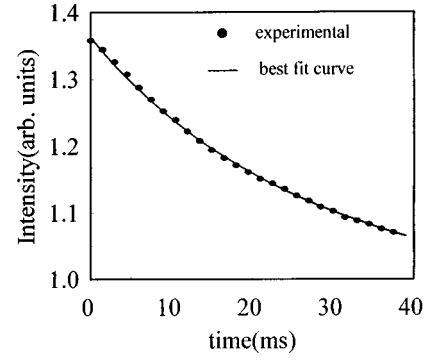

FIG. 1. Thermal lens experimental data of mixture 1 with the director aligned parallel to the sidewalls and their best fit curve.

size, ω_p, and the excitation beam spot size, ω_e, at the sample not larger than 3.[18] Within the employed boundary conditions, a sample with thickness up to 1 mm must be treated as a thin sample. When these conditions are observed, i.e. the small ratio ω_p/ω_e and the short period of time, the analytical expressions for mode mismatched thermal lens, which consider the sample as infinite in both radial and beam direction, can be used to determine quantitatively the optical and thermal properties of thin samples.

The experimental setup used was described elsewhere.[18] An Argon Ion laser was used as the excitation beam (514.5 nm) and a He-Ne laser (632.8 nm) as the probe beam. The exposure of the sample to the excitation beam was controlled by a shutter. The He-Ne probe laser beam was attenuated to 0.1 mW at the sample by neutral density filter. The output of the fast photodiode was coupled to the digital Hewlett Packard 7090A Recorder which was triggered by a second photodiode. Data were transferred from the Recorder to the computer through a GPIB interface, and stored in sequential files for further analysis. Each scan resulted in 1000 measured points. Moreover, the excitation beam spot size at the sample $\omega_e = 6.1 \times 10^{-3}$cm, and the probe beam spot size $\omega_p = 16.8 \times 10^{-3}$cm. The excitation beam power at the sample was 50 mW and 100 mW.

Figure 1 shows the time resolved thermal lens signal for the mixture 1 with the directors aligned parallel to the sidewalls. By using Eq. (1), the curve fitting gave the thermal diffusivity as $\alpha_\parallel = (1.71 \pm 0.01) \times 10^{-3}$cm²/s. Table I shows the thermal diffusivity results for the two mixtures in both, perpendicular and parallel directions of the director. It can be observed that the ratios between the thermal diffusivity parallel and perpendicular are $\alpha_\parallel/\alpha_\perp = 1.20$ for mixture 1, and $\alpha_\parallel/\alpha_\perp = 1.18$ for mixture 2. These ratios are smaller than those measured for thermotropic liquid crystal (6CB, 8CB and MBBA), obtained by several techniques, which are about 2.0.[5,6,14] We would like to stress here that the lyotropic

TABLE I. Thermal diffusivity results of mixtures 1 and 2 and their ratio. The ratio $\alpha_\parallel/\alpha_\perp$ estimated using Eq. (3) is shown in the right column.

Samples	$\alpha_\parallel$ (10^{-3} cm²/s)	$\alpha_\perp$ (10^{-3} cm²/s)	$\alpha_\parallel/\alpha_\perp$ (measured)	$\alpha_\parallel/\alpha_\perp$ (estimated)
Mixture 1	1.71±0.01	1.43±0.01	1.20	1.27
Mixture 2	1.31±0.01	1.11±0.01	1.18	1.27

micellar shape anisotropy (i.e. the ratio between length (L) and diameter (D) of the cylinders) in the calamitic phase is about 1.6.[16] It is smaller than the thermotropic liquid crystal length-to-width ratio which is about 3.[15] These results indicate that the thermal anisotropy in liquid crystals can be correlated to the micellar shape anisotropy, as suggested some years ago by Urbach et al.[14]

The physical behavior of this system can be tentatively understood if we consider the sample as an array of thermal resistors of rod-like shape. The effective thermal resistance[19,20] is obtained by considering both the internal contribution coming from the properties of the micelles themselves and the contribution from their interfaces. If we assume that the interfacial term is proportional to the inverse of the interface area, and that it is much bigger than the internal one, the maximum anisotropy in the thermal conductivity, κ, obeys the relation $\kappa_\parallel / \kappa_\perp = \alpha_\parallel / \alpha_\perp \simeq L/D$. This result is similar to the one obtained from a quasi-lattice model for the ratio between mass diffusion coefficients.[15,21] Following the same procedure of these authors, for imperfect nematic order $S < 1$ the ratio between the thermal diffusivities is expected to be:

$$\frac{\alpha_\parallel}{\alpha_\perp} = \frac{\left(\dfrac{L}{D}\right)(1+2S)+(2-2S)}{\left(\dfrac{L}{D}\right)(1-S)+(2+S)} \ , \tag{3}$$

where S is the scalar order parameter.

Taking $L/D \approx 3$ for thermotropic liquid crystal (from x-ray data)[15] and using $S \approx 0.5$,[22] we will obtain $\alpha_\parallel / \alpha_\perp \simeq 1.9$, which agrees very well with the results reported for thermal diffusivity of thermotropics.[5,6,14] On the other hand, for the lyotropic systems studied here, using the same value for the order parameter, $S \approx 0.5$,[23] and taking the ratio $L/D \simeq 1.6$[16] we found $\alpha_\parallel / \alpha_\perp \simeq 1.3$, again very close to the experimental results for the ratio between the thermal diffusivities presented in Table I. Therefore, our results strongly indicate that the thermal diffusivity anisotropy can be in fact associated with the form of the micelles for lyotropic nematics and the molecular shape for thermotropic liquid crystals, as predicted by Eq. (3).

In conclusion, by using a simple analytical expression for the mode mismatched thermal lens spectrometry, the anisotropic thermal diffusivity of two different mixtures of lyotropic nematic liquid crystals were determined. We have proposed a simple model, which considers the sample composed of a serial thermal resistors. The difference between the thermal diffusivities for the two directions was connected to the geometrical anisotropy of the micelles for lyotropic nematics

in the calamitic phase, or to the molecular shape for thermotropic nematics. This picture explains why the ratio between the components of thermal diffusivity is smaller in lyotropic than in thermotropic liquid crystals. It also provides a more quantitative way to understand why the thermal conductivity has its maximum value along the long micellar or molecular axis, as already pointed out by Urbach et al.[14]

Furthermore, the thermal lens experiment we have presented is very simple to perform. The technique is remote, non-contacting, non-destructive, very sensitive. Moreover, with the thin sample theoretical and experimental conditions established for mode mismatched configuration, this technique can be used to study optical and thermal properties of liquid crystals without addition of dyes. To our knowledge, this is the first application of the thermal lens technique to the investigation of physical properties of lyotropic system. It can be a powerful technique to investigate anisotropic properties of lyotropics and their interfaces with biological systems.

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