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MECHANO-OPTICAL EFFECT IN ISOTROPIC PHASE OF A LYOTROPIC LIQUID CRYSTAL

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In this work we show experimental results reporting the induced order in isotropic phase of a lyotropic liquid crystal (KL/DeOH/water) when it is submitted to a mechanical vibration. We have been found five resonance frequencies for all isotropic domains surrounded by lamellar phases and two principal frequencies in both isotropic regions with nematic phase between them. In order to make a comparison with others isotropic fluids the optical transmittance of the lyotropic has been found of about four thousand when compared with DeOH and, at least three hundred in comparison to water. We are exploring this effect to produce a mechanical vibration sensor able to detect small mechanical perturbations at room temperature. As far we know this appears to be one of the first real technological application of a device based upon lyotropic liquid crystals.

Keywords: isotropic phase; lyotropic liquid crystal; mechanical vibrations; sensors

INTRODUCTION

Lyotropic liquid crystals (LLC's) are mixtures formed by amphiphilic molecules in the presence of a solvent, usually water [1]. Micelles are formed when the amphiphilic molecules achieve a critical micellar concentration. The ordered phases can be described by a macroscopic order parameter called director that vanishes in the isotropic phase [2]. Some efforts have been made to understand the behavior of the complex fluids under flow [3,4] and micellar complex fluids are only beginning to be investigated [5–7]. The combination of fluid mobility with anisotropy of physical

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properties in liquid crystals has made them an interesting object for scientific research and technical applications. In particular, liquid crystal sensors for pressure measurements are recently made using a polarization effect caused by strong rotatory power of chiral nematic liquid crystal [8] and light polarization modulation effect in nematic liquid crystal [9].

The phase diagram of LLC's as a function of temperature and of the relative concentration each compound of the mixture is very rich. The discotic nematic (N_D) region of the phase diagram of the mixture potassium laurate (KL), decanol (DeOH) and water is surrounded by isotropic domains. By changing the relative concentration of each compound of the mixture the isotropic (ISO) phase can be found between two lamellar phases (L_1 and L_2). In the ISO phase of this mixture it is possible to induce birefringence by flow [10] and this effect is also observed in optically isotropic lyotropic sponges phases [11] and thermotropic liquid crystals [12]. The induced order in lyotropic liquid crystals by mechanical vibrations has been interpreted as a resonance effect in reference [13]. Simões *et al.* [14] explained the induced order as a result of two distinct competing causes: the coherent torques caused by the external fields and the Brownian rotation motion that look for the destruction of any uniformity.

Specifically in this work, we show experimental results of the induced order in the isotropic phase of the mixture KL/DeOH/water when it is submitted to an external square mechanical pulse. By using this mixture we observed a great growth in the optical transmittance (about four thousand) in comparison with decanol and, at least three hundred in comparison to water. So, this effect can be used to investigate some macroscopic parameters and can be applied to technological devices such as detectors of small mechanical vibrations [15].

EXPERIMENTAL

The lyotropic liquid crystals used in this work are mixtures of potassium laurate (KL), decanol (DeOH) and water [16]. The relative concentration of each compound (in wt%) are given in Table 1. The phase sequences as a function of temperature, determined by optical and X-ray scattering techniques are given in Table 2, where N_D is discotic nematic phase, N_C is calamitic nematic phase, ISO_1 ISO_2 , L_1 and L_2 are isotropic and lamellar phases at low and high temperatures, respectively.

The set up used to measure the transmittance of the sample as a function of frequency and of the temperature when it undergoes an external vibration is sketched in Figure 1. The lyotropic mixture is encapsulated in a sample holder glass (Hellma) of rectangular section with dimensions: $a = b = 12.56$ mm and $c = 45.0$ mm (a , b , and c are parallel to the x , z ,

TABLE 1 Relative Concentrations of Each Lyotropic Mixtures

Mixture	KL(%wt)	DeOH(%wt)	Water(%wt)
M1	24.79	6.24	68.97
M2	29.40	6.60	64.00
M3	25.70	6.24	68.06
M4	26.99	6.78	66.23
M5	26.89	6.39	66.72
M6	27.39	6.27	66.34

and y axes respectively). The cell is placed in a temperature controlled device ($\pm 0.2^\circ\text{C}$ stability). The y -axis of the laboratory frame is parallel to the c dimension of the cell; the x -axis is the laser beam (He-Ne laser, $\lambda = 633\text{ nm}$) direction. The polarization of the laser beam is parallel to z -axis (see Fig. 1). A function generator (Stanford DS335) is coupled to a loud speaker and an iron wire. The wire touches the cell and promotes the movement of the sample. The external force applied to the cell (always perpendicular to the laser beam direction) is a square wave of $5.0\text{ V}_{\text{RMS}}$ with frequencies between 0 Hz and 200 Hz . Beyond the analyzer, a photodiode detects the light intensity that comes mainly from the induced birefringence. The transmittance of the sample is measured in a rectangular window of the center of the cell and about 3 mm below of the free surface of the mixtures. In order to minimize the signal fluctuations a computer coupled to a lock-in amplifier (Stanford SR830) is used. The software (Delphi) and the card (A-826PG-Industrial Computer Product) allow us to accumulate 10^5 measurements. The time interval between two measured intensities is $39.8\text{ }\mu\text{s}$ and the relaxation time of photodiode is smaller than 1 ns . All the set up is placed on an optical table (TMC) with pneumatic system to isolate spurious vibrations.

TABLE 2 Phase Sequence as a Function of Temperature of Each Mixture

Mixture	Phase	$T_{\text{C}}(^{\circ}\text{C})$	Phase	$T_{\text{C}}(^{\circ}\text{C})$	Phase
M1	ISO ₁	19.1	N _D	28.9	ISO ₂
M2	ISO ₁	14.4	N _C	42.0	ISO ₂
M3	ISO ₁	17.7	N	39.1	ISO ₂
M4	L ₁	10.5	ISO	54.0	L ₂
M5	L ₁	9.5	ISO	50.0	L ₂
M6	L ₁	10.5	ISO	52.0	L ₂

N_D = discotic nematic phase; N_C = calamitic nematic phase; N = nematic range; ISO₁ and ISO₂ are isotropic phases; L₁ and L₂ are lamellar phases.

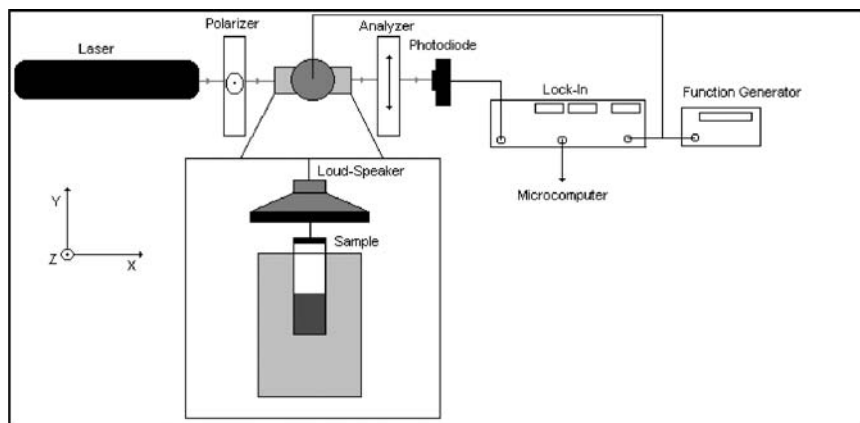


FIGURE 1 Experimental set up to measure the sample transmittance as a function of time and of the temperature.

RESULTS AND DISCUSSIONS

The methodology of the experiment is as follows: by taking a sample of the Table 1 in the isotropic phase, the mechanical oscillation is applied to the cell with a square wave shape of $5.0 V_{\text{RMS}}$ and frequencies changing from 0 Hz to 200 Hz. The acquisition procedure is started after the external frequency is switched on and the photodiode measures the optical transmittance. We have been observed that the optical response of the sample depends on incident polarization. However, in this work, the polarization of the incident light was not changed. Figure 1 shows the best configuration for a maximum optical transmittance. The relative mixture concentration of M4, M5 and M6 has been found in the range: $2.6 \leq C \leq 2.9$, where $C = [\text{KL}]/[\text{DeOH}]$ with [KL] and [DeOH] in %molar. Figure 2 shows the typical optical transmittance (I) as a function of frequency (f) of the lyotropic mixture with ISO phase surrounded by two lamellar phases for M4, M5 and M6 when the temperature is changed. Figure 2 shows sharp peaks in some specific frequencies. We identify such resonance frequencies as possible ones to induce order in the ISO phase of the mixtures displayed on Table 1. The values of the resonance frequencies, f and its deviations, Δf as a function of relative concentration are displayed in Table 3. The deviation Δf is evaluated taking into account the peak value in each temperature of the experiment. The frequencies $f1$, $f4$ and $f5$ have the same values when the temperature or relative concentration of the mixture is changed. For the mixture with $C = 2.90$, $f5$ is more clearly identified. In addition, $f2$ and $f3$ present a small difference when the concentration is

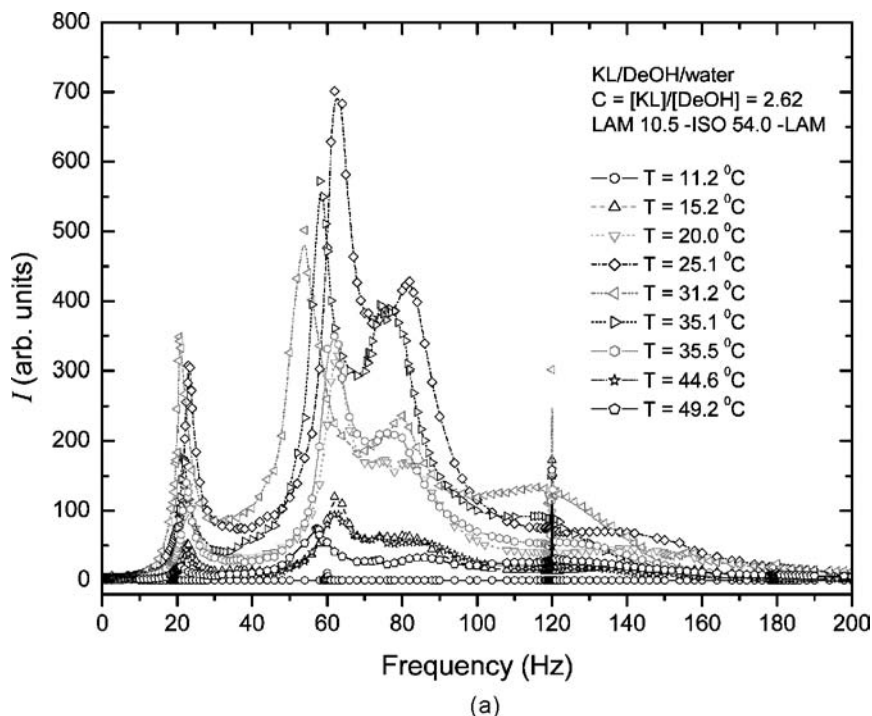


FIGURE 2 Transmittance (I) in arbitrary units as a function of frequency and temperature for three relative concentrations of the mixture KL/DeOH/water: (a) $f_1 = (21.0 \pm 1.0)$ Hz, $f_2 = (58.0 \pm 4.0)$ Hz, $f_3 = (78.0 \pm 4.0)$ Hz, $f_4 = (119.5 \pm 0.5)$ Hz, $f_5 = (179.5 \pm 0.5)$ Hz; (b) $f_1 = (21.0 \pm 2.0)$ Hz, $f_2 = (46.0 \pm 4.0)$ Hz, $f_3 = (60.0 \pm 5.0)$ Hz, $f_4 = (119.5 \pm 0.5)$ Hz, $f_5 = (179.5 \pm 0.5)$ Hz; (c) $f_1 = (19.6 \pm 1.0)$ Hz, $f_2 = (59.0 \pm 1.0)$ Hz, $f_3 = (78.0 \pm 4.0)$ Hz, $f_4 = (119.5 \pm 0.5)$ Hz, $f_5 = (179.5 \pm 0.5)$ Hz.

changed and the reason for this is not yet clear for us. So, the frequencies displayed in Table 3 are expected to be a measurement of the normal modes of vibration proper to rectangular container. The statement is that lyotropic liquid crystal is very sensible to detect the normal modes of vibration. This fact appears to be one real technological application of these systems in devices in order to detect mechanical frequencies.

On observing the usual topology of the phase diagram of the mixture KL/DeOH/water [16], we have notice that for the samples M4, M5 and M6, on increasing the KL concentration (keeping wt% DeOH and water), the nematic domain appears between two isotropic phases (ISO_1 and ISO_2). In both these isotropic phases it is possible to induce birefringence by mechanical vibrations. Furthermore, two principal resonance

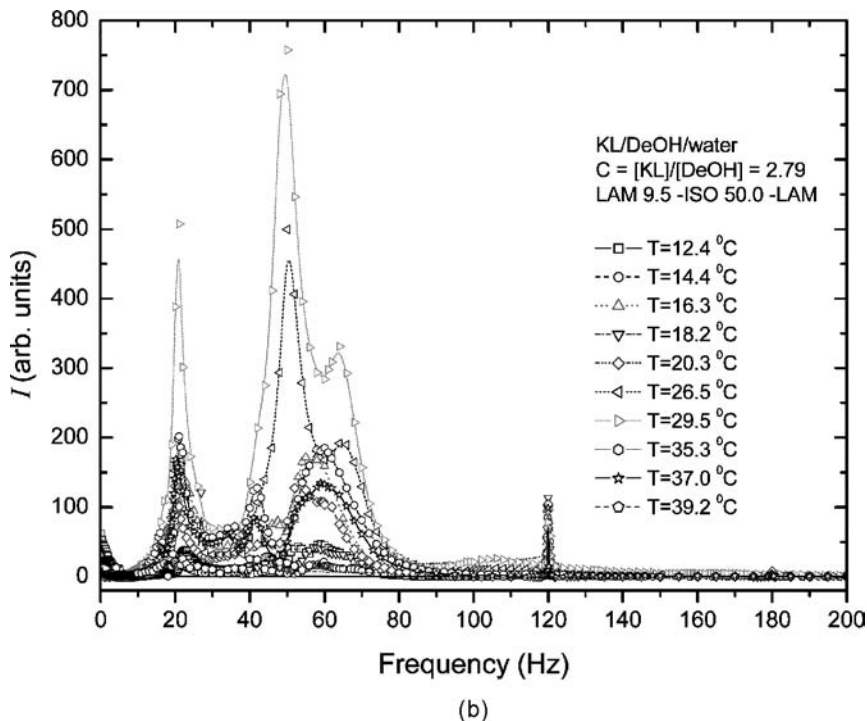


FIGURE 2 Continued.

frequencies (17.0 ± 1.0) Hz and (51.0 ± 6.0) Hz have been found inside of these phases. The existence of the ISO2 for the mixture M1, probably, produces the difference between the minimal normal modes of vibration showed in Figure 1 and Figure 2. In ISO₁ and ISO₂ the maximum values of I have been presented some fluctuations. Such fluctuations in I may be reflecting the instability of the induced order. For this reason, the lock-in technique was applied. In this sense, it was possible to observe that ISO₁ is more stable than ISO₂. Otherwise, in the middle of the nematic region occurs some fluctuations in I , which were not investigated in this work. As pointed out before, taking a mixture with a nematic phase between two isotropic phases, on increasing the water concentration, the nematic domain becomes smaller, always surrounded by an isotropic region. For a given critical water concentration, the nematic domain vanishes and only the isotropic domain remains. The mixtures used in the present work (M4, M5 and M6) are near this critical concentration and the analysis of the resonance frequencies indicates the tendency of these mixtures to present a nematic phase. This behavior, represented by a

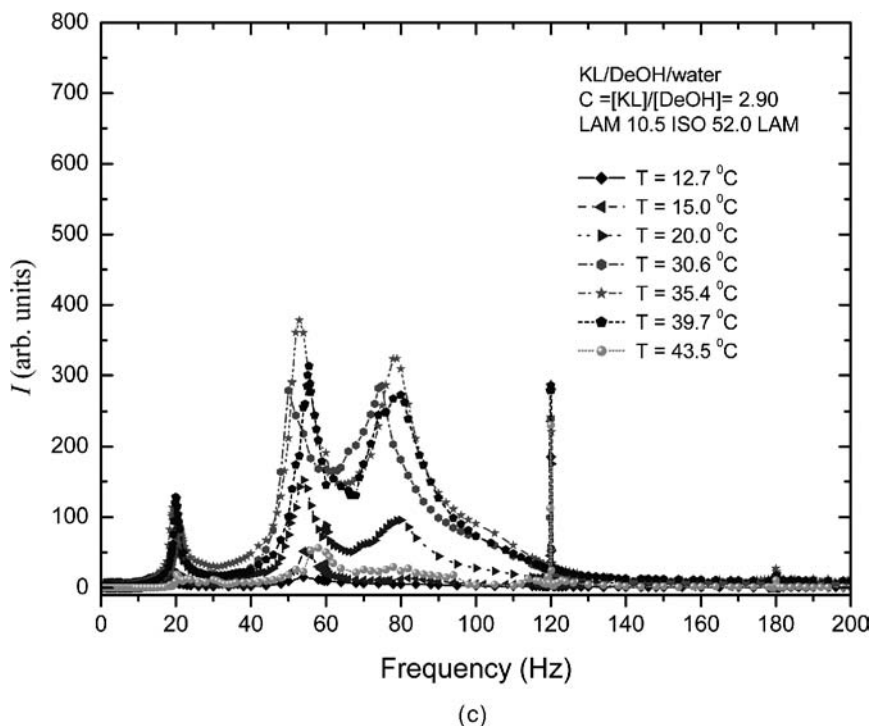


FIGURE 2 Continued.

maximum in the optical transmittance (I) always reaches a local maximum at the middle of isotropic phase and decrease near to lamellar phases. This maximum in I near 30°C for all resonance frequencies of Table 3 indicates that the ISO phase could have different correlation properties between

TABLE 3 Resonance Frequencies as a Function of the Relative Concentration of the System KL/DeOH/Water and of the Temperature; (A) KL/DeOH/Water at Isotropic Phase; (B) Water; (C) Alcohol (DeOH)

Resonance frequencies	Samples		
	M4 C = 2.62	M5 C = 2.79	M6 C = 2.90
f_1	(21.0 ± 1.0)	(21.0 ± 2.0)	(19.6 ± 1.0)
f_2	(58.0 ± 4.0)	(46.0 ± 4.0)	(59.0 ± 1.0)
f_3	(78.0 ± 4.0)	(60.0 ± 5.0)	(78.0 ± 4.0)
f_4	(119.5 ± 0.5)	(119.0 ± 0.5)	(119.5 ± 0.5)
f_5	(179.0 ± 0.2)	(179.0 ± 0.2)	(179.0 ± 0.5)

micelles. In Ref. [17] this maximum in I was interpreted, in terms of relaxation time, as an indication of a virtual nematic phase. A real nematic phase could be produced by a little increase in the amphiphilic concentration in the sample as we experimentally checked.

From a theoretical point of view, the mechano-optical effect in liquid crystal was explained in Ref. [13] by means a resonance approach. This approach is in agreement with order diffusion approach [10] applied to ISO phase of the samples displayed in Table 1 in a transient regime.

In order to make a comparison between ISO phases of the lyotropic liquid crystal with other ordinary fluids the same transmittance experiment as described in experimental section was made using alcohol (DeOH) and water. Figure 3A shows the transmittance (I) as a function of frequency (f) for the mixture M1 (Table 2) at ISO phase. Figure 3B and Figure 3C show I versus f for water and for DeOH at room temperature, respectively. The numbers, above the maximum transmittance, in Figure 3 indicate the resonance frequencies due to the conditions given by the cubic container. The continuum line is only to guide the eyes. The resonance frequencies measured are around 16 Hz and 48 Hz. Note that I grows around 48 Hz

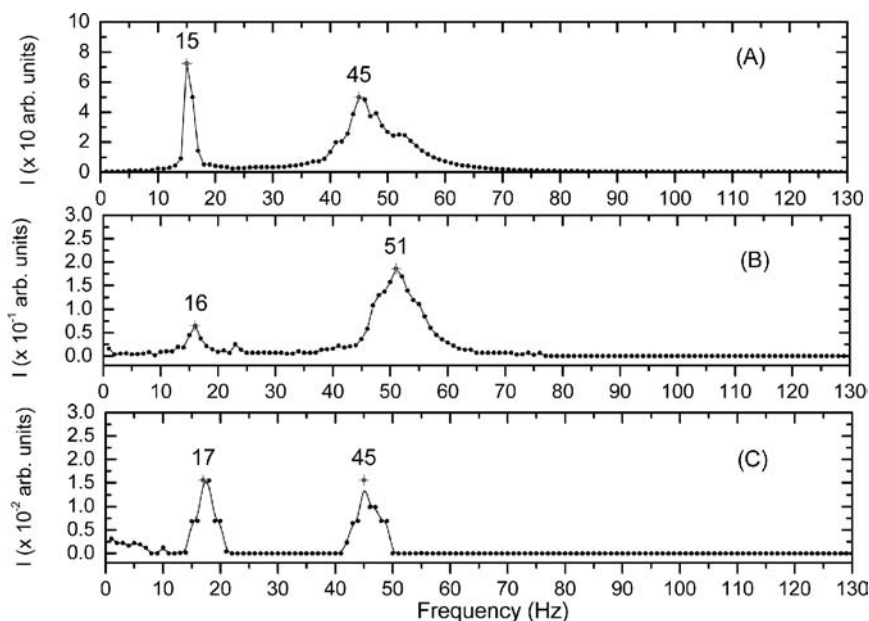


FIGURE 3 Transmittance (I) in arbitrary units as a function of frequency; (A) KL/DeOH/water at isotropic phase; (B) water and (C) Alcohol (DeOH) at room temperature.

for lyotropic mixture by about three hundred in comparison with water and four thousand when compared to decanol. Otherwise, for 16 Hz the transmittance grows, respectively, by about one thousand and four thousand. These measurements show an unexpected great mechano-optical effect exclusively, as far as we know, to systems formed by anisometric basic structures as liquid crystals. This effect can be used to study and to analyze some dynamic macroscopic parameters of complex fluids as liquid crystals and can be applied to technological devices such as detectors of small mechanical vibrations.

CONCLUSIONS

In this work we show experimental results reporting the induced order in isotropic phase of a lyotropic liquid crystal (KL/DeOH/water) when it is submitted to a mechanical vibration. This effect occurs in all isotropic domains of the phase diagram of the mixture KL/DeOH/water. We have been found five resonance frequencies for all isotropic domains surrounded by lamellar phases and two principal frequencies in both isotropic regions with nematic phase between them. These frequencies are expected to be a measurement of the normal modes of vibration proper to rectangular container. This effect has been evaluated of about four thousand in comparison with decanol and, at least three hundred in comparison to water. This one can be used to investigate some macroscopic parameters and can be applied for technology applications. One of them is the prototype (see Ref [15]) specifically to detect small mechanical vibrations. As far we know this appears to be one of the first real technological application of a device based upon lyotropic liquid crystals.

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