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CHOLESTERIC LIQUID CRYSTALS AND THEIR APPLICATIONS IN TEMPERATURE MEASUREMENTS AND IN CONTAMINATION DETECTION

BY

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Abstract. Cholesteric liquid crystals form thin films with special optical properties. Their sensibility to the changes in temperature offers the means for measuring very small variations of local temperature and for evidencing the different mechanic and electromagnetic waves, by their thermal effects. Small amounts of contaminants can be detected in the atmosphere with devices containing cholesteric liquid crystalline layers due to the high sensitivity of their pitch to impurities. An experimental study in which small amounts of tetrahydrofuran vapors of tetrahydrofuran are evidenced by cholesteric layer embedded in polystyrene is realized in this paper.

Keywords: Cholesteric liquid crystals; chiral biphenyl; tetrahydrofuran; temperature determination; contaminant vaporous detection.

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1. Introduction

Liquid crystals are groups of substances named mesogens, with the mobility of fluids and the symmetry of inorganic crystals (Brown *et al*., 1971; De Gennes, 1974; Collings, 1977; Demus *et al*., 1998).

Discovered by Reinitzer (1888) in his study of the cholesterol salts, the new substances were denominated as “liquid crystals” by Liehmann (1889) to underline their double nature.

Liquid crystals can be classified in:

– thermotropic (their degree of order is essentially influenced by temperature);

– lyotropic (they are obtained from mixtures at a given concentration of amphiphilic molecules in a thermodynamically bad solvent for this type of molecules).

After about one hundred years from their discovery, liquid crystals became omnipresent in our life, in technics, in imagistics.

The great importance of both lyotropic and cholesteric liquid crystals in vital processes represent only a part from their large area of applications.

Some applications of cholesteric liquid crystals will be described in this paper, based on their physical and chemical properties.

Cholesteric liquid crystals are included in the group of thermotropic liquid crystals. They have the orientational order of achiral nematics, but the director is constrained in a layer–like structure to precess around the helical axis (HA) perpendicular on the director (Pershan, 1978; Muscutariu, 1981; Collings, 1997). Each layer (Fig. 1) composing Cholesteric contains molecules in a constant thermal agitation having preferential orientation given by the director versor ($\vec{n}$). The director configuration is helical and the repeated length is known as the pitch (p) of the cholesteric liquid crystal.

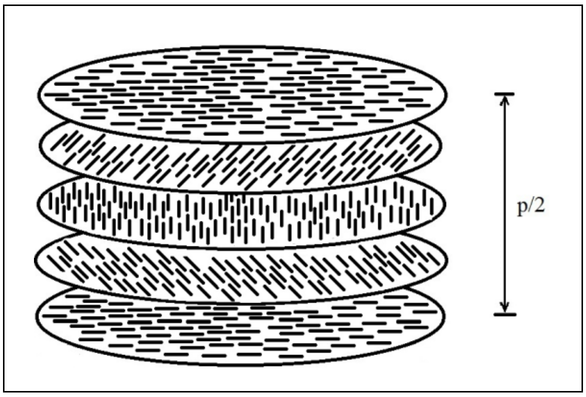


Fig. 1 – Orientation of the mesogenic molecules in a Cholesteric liquid crystal; Pitch (p) of cholesteric.

The mesogenic components of cholesteric liquid crystals (monomers, dimers, polymers) are intrinsically chiral or chiral dopant are added to non-chiral Nematics.

The cholesteric texture possesses a number of properties giving rise to the unique optical effects, such as:

– it is anisotropic uniax with negative birefringence;

– it is optically active with rotatory power many times higher that a normal optically active material;

– it is usually circularly dichroic as it can affect both right and left circularly polarized components of light;

– it scatters the incident white light in a similar manner as the solid crystals.

The ordered state of cholesteric liquid crystal is mainly determined by surface anchoring, cell thickness and also by applied fields (Moțoc and Muscutariu, 1986).

The cholesteric liquid crystals can change their pitch under external factors (changes in temperature or in pressure, variations in external fields). Consequently, they can display the changes in the external factors by changing their color (Meier *et al*., 1975; Kleinert and Maki, 1981; Bunning *et al*., 1996; Shibaev *et al*., 2015).

2. Structural Features of the Cholesteric Liquid Crystals

Observed with a polarizing microscope, cholesteric liquid crystal layers have different visual aspects (named textures) depending on their molecular chemical structure, on the orientation of the mesogen molecules related to the internal walls of the cell (in which liquid crystals are kept), or on the type of interactions between the mesogens and the anchoring molecules.

The molecules of cholesteric liquid crystals can adopt different orientations (Fig. 2) in the cells where they are kept (Muscutariu, 1981):

– Planar (homeotropic) orientation

– Homeotropic orientation

– Inclined orientation

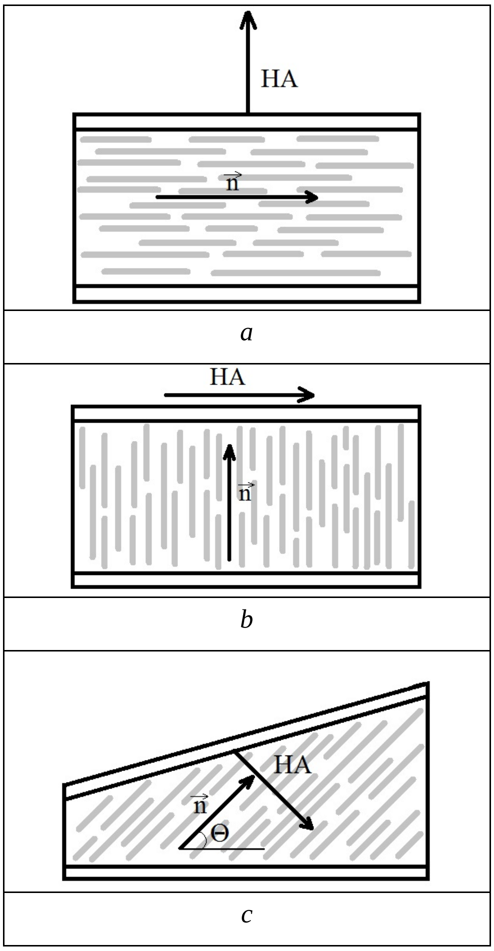
The cells can have parallel or inclined walls (Fig. 2).

The relative orientation of the director versor ($\vec{n}$) and of the helical axis (HA) is suggested and also the angle θ between the director versor ($\vec{n}$) and the contact surface is plotted for the inclined walls of the cell, in Fig. 2.

In order to orient the mesogenic molecules in the vicinity of the cell surface, an adequate treatment of the contact surfaces (internal walls of the cell) is necessary. The known procedures (Dumitrașcu and Dorohoi, 2015) for this treatment can be classified in two main groups:

– mechanical treatment;

– chemical treatment.



a

b

c

Fig. 2 – Orientation of the director versor ($\vec{n}$) and of the helical axis (HA) relative to the contact surface; *a* – Planar (homotropic) orientation ($\theta = 0$); *b* – Homeotropic orientation ($\theta = 90^{\circ}$); *c* – Inclined orientation ($0^{\circ} < 0 < 90^{\circ}$).

The orienting action of the internal surfaces of the cell in which cholesteric liquid crystal will be kept can be realized by chemical cleaning and treatment, by deposing of thin films of organic or inorganic materials on the internal surfaces, or by scratching or deformation of the surfaces.

In the case of non- scratched plane surfaces of the cells, the orientation procedure is based on intermolecular interactions or on the mechanical interactions with surface resulting from the anisotropy of the mesogen molecules.

In order to understand the functioning of the devices based on cholesteric liquid crystals one can have in mind that the mesogens are dipolar molecules or can become dipolar in interactions with external fields.

In the case of a planar homotropic anchoring, the director versor ($\vec{n}$) of the cholesteric is parallel to the surface of cell walls and the helical axis is perpendicular on the cell walls (Fig. 2*a*). The homeotropic cholesteric structure corresponds to a director versor perpendicular to the cell walls and the helical axis parallel to the cell walls (Fig. 2*b*).

The cells with plane but non- parallel opposite walls are used to visualize the irregularities in the homogeneous structures of cholesteric liquid crystal formed parallel to the edge of the cell, by the modifications in interference fringes obtained in monochromatic radiation, due to the periodic structure of the layer (Muscutariu, 1981).

The homogenous planar structure of a cholesteric is characterized by uniform texture, having a color that depends on the pitch of the helix and/or on the phase delay during the propagation through the liquid crystal. Various irregularities in the homogenous planar structures of cholesteric liquid crystals (defects in the networks) can be visualized at the polarizing microscope illuminated by white light, or by using a confocal microscope equipped for fluorescence (Dumitrașcu and Dorohoi, 2015).

3. Action of the Low Intensity Electric Fields on the Cholesteric Liquid Crystalline Layers

In the presence of low intensity electric fields, cholesteric liquid crystals can modify their structure.

Let us suppose that an external electric field of low intensity is applied perpendicularly on the walls of the special cell keeping the cholesteric liquid crystal in a planar orientation.

As a result of interaction between mesogen molecules and electric field rotational moments act on the mesogen molecules, tending to reorient them along the field lines, but the process is limited near the separation surfaces (Demus and Lothar, 1978).

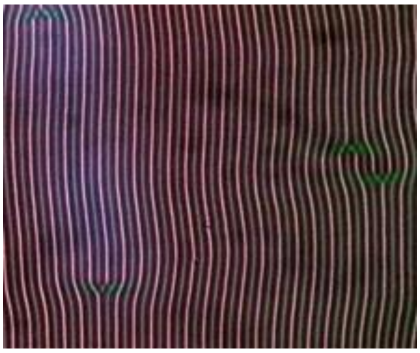


Fig. 3 – One dimensional undulations in p-azolyanisole for d/p ≤ 3.

So, under the electric field action, the planar orientation of cholesteric liquid crystals can be modified by periodical sinusoidal distortions called undulations (Dumitrașcu and Dorohoi, 2015). The dependence of the undulation aspects on the ratio d/p (thickness of the cholesteric liquid crystals layer/ pitch) is illustrated in Figs. 3 and 4.

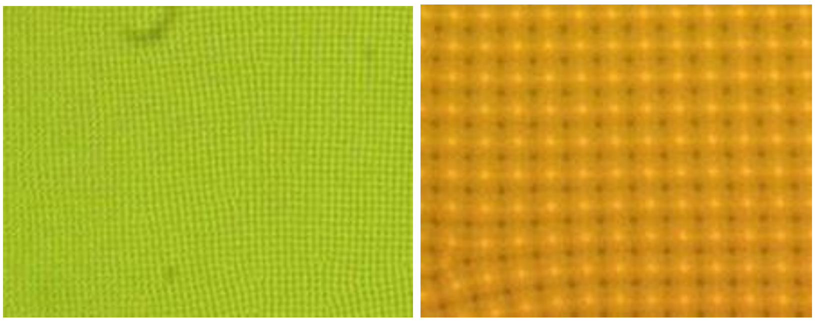


Fig. 4 – Bidimensional undulations in Cholesteric liquid crystals for d/p > 10 (The size of the pitch increases from left to right).

Weak electric fields applied to cholesteric liquid crystals produce undulations significantly depending on the ratio between the layer thickness and the pitch of helical structure. Using a polarizing microscope unidirectional undulations were observed (Fig. 3) for $d/p \leq 3$ and bidirectional undulations for $d/p > 10$ (Fig. 4).

The spatial period of the undulations depends on the thickness of the cell and the cholesteric pitch.

The bidimensional undulations in cholesteric liquid crystals produce diffraction of the laser beams. So, the undulation phenomenon can be used in determining the spatial period of undulations and the pitch, when the cell thickness is known.

The homeotropic cholesteric liquid crystals have the director versor oriented perpendicularly on the cell walls and the helix axis parallel to the walls surface. The structures obtained in very weak electric fields are named “digital print” textures. The aspects of such textures depends on the ratio d/p (thickness of the cell/ pitch of cholesteric) and on the strength of the anchoring to the cell surfaces. For strong anchoring of the mesogene molecules to the cell surfaces, the rotation of the director versor around the helix axis is totally lost. The effect has been evidenced for very thin liquid crystal layers.

Based on the important property of cholesteric liquid crystals to change their pitch under external influence (changes in temperature, pressure, in the presence of some mechanical waves (ultrasounds) or electromagnetic waves (infrared, microwave), a great number of their applications were developed.

4. Contaminant Vapors Action on the Cholesteric Liquid Crystalline Layers

Based on the sensing approach for the polar solvent vaporous, some applications of cholesteric liquid crystals were developed for monitoring the solvent vapor concentrations (Mujahid *et al*., 2010; Shibaev *et al.*, 2015).

A special cell with lateral transparent windows contains in vertical position one Cholesteric liquid crystal (a mixture of chiral biphenyls achieved from Merck Company) embedded in a thin polyurethane layer. A jet of air (pure or containing variable contaminant vapors) can be introduced in this cell by the filling aperture and also can be eliminated by other aperture (Fig. 5).

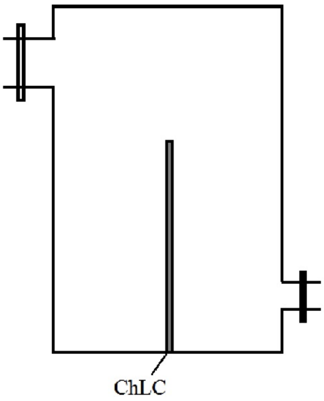


Fig. 5 – Cell containing Cholesteric liquid crystal embedded in polyurethane film.

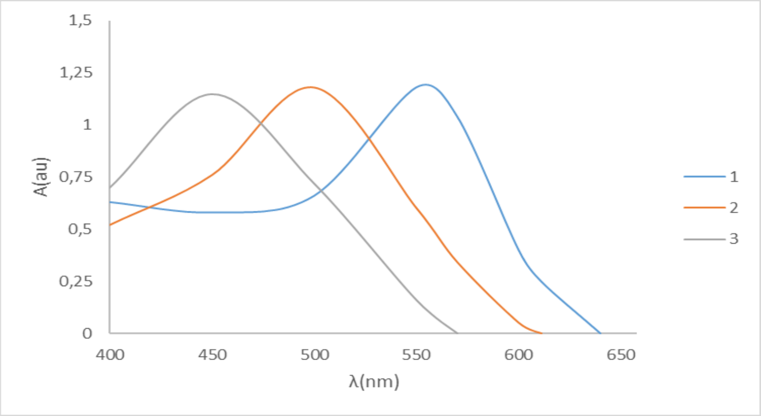


Fig. 6 – Electronic absorption spectra of Cholesteric liquid crystal in the presence of tetrahydrofuran vapors (1 – C=0; 2 – C=0.1%; 3 – C=0.2%).

The electronic absorption spectra of the cell were recorded at a Specord UV Vis spectrophotometer with data acquisition system. The absorption band of cholesteric liquid crystal was shifted to small wavelengths when the pollutant concentration increased (Fig. 6).

Our experimental data refer to tetrahydrofuran (THF) vapors introduced in increasing quantities in the air jet. The concentration of the THF vapors was under 0.2%. A gradual decreasing in the wavelength was observed when the THF vapor concentration was increased, as one can see in Fig. 7.

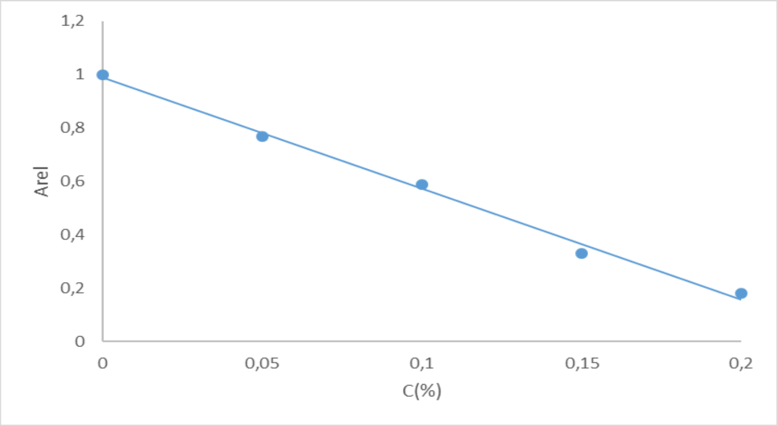


Fig. 7 – Dependence of the absorption band position in the wavelength scale on the THF vapor concentration.

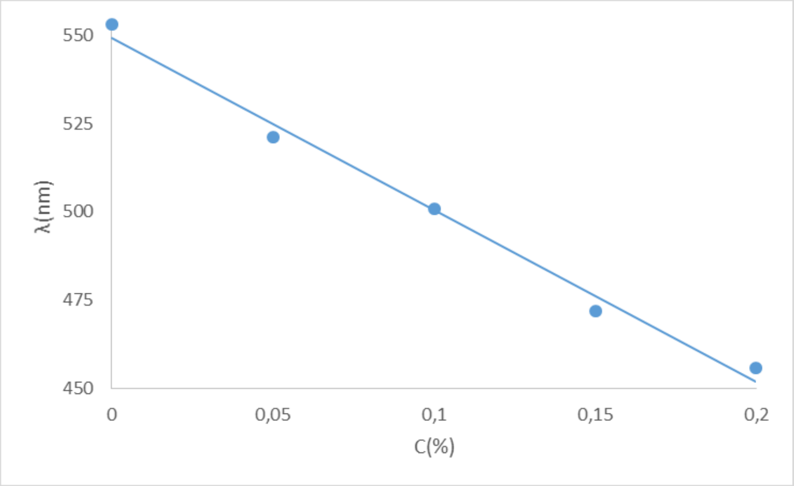


Fig. 8 – Dependence of the relative absorption measured at a fixed wavelength on the vapor concentration.

If one measure the absorbance at a fixed wavelength, for example at 553 nm corresponding to the cell spectrum in the absence of the contaminant vapor, the increase in the relative absorbance is monitored (Fig. 8). The relative absorbance is defined as the ratio between the absorbance measured in the contaminant vapors presence and the absorbance (measured at the same wavelength) in the absence of the contaminant vaporous.

As it results from Figs. 7 and 8, using a thin Cholesteric layer embedded in a polymer, very small amounts of contaminant vapors can be detected using the spectral information.

5. Applications of Cholesteric Liquid Crystals. Technical Devices

Due to their marked photo stability, reversibility and high sensitivity, cholesteric liquid crystals offer widespread applications as sensor materials, for detection of solvent polar molecules without pronounced reactivity.

As it was demonstrated (Mujahid *et al.*, 2010), cholesteric materials are able to discriminate between different polar solvents. A nearly linear dependence between the absorbance A and the molar mass of the polar solvent at passing its vaporous through a cholesteric liquid crystals layer is established by Mujahid and his co- workers. The measurements were made with cholesteric liquid crystals encapsulated in a polystyrene matrix. The cholesteric liquid crystals in the imprinted polymer matrix provide selectivity for solvent vaporous detection. The weight and the chemical structure of the solvent influence the pitch of the cholesteric liquid crystals, and so, one can change the absorbed light spectral composition. Small amounts of contaminants are detected in the atmosphere with devices containing cholesteric liquid crystalline layers described by Shibaev and his co-workers (Shibaev *et al.*, 2015).

Cholesteric liquid crystals are thermochromic materials that change their color over a wide range of temperatures from as low as -30^{o}C to far above 100^{o}C. These limits are delimited by crystallization at low temperatures and by the stability of liquid crystal and also by the stability and lifetime of the device itself.

Thermochromic devices have considerable advantages over other thermometers in that they are cheap, flexible, virtually unbreakable and easy to read.

The ability to monitor and to map the temperature of a surface area recommends the thermochromic liquid crystals for engineering applications. For example, in electronics, cholesteric liquid crystals can be used to detect short circuits, open circuits, inoperative devices, or to map operational in integrated circuits. The defects of materials, causing an interruption in thermal conductivity can be also evidenced using cholesteric liquid crystals.

Thermography based on liquid crystals was used in evaluation of thermal transfer between fluids and solid surfaces (Ireland and Jones, 1985) and also in mapping local temperature variations in a flowing fluid (Wozniak and Wozniak, 1991; Stasiek and Kowalewski, 2002).

4. Conclusions

Firstly recognized mesophases**,** cholesterics form the basis of widespread liquid crystals devices and they continue to find new applications in high- technology.

The change in pitch under small variations of pressure, temperature, or in presence of contaminants recommends cholesteric liquid crystals as rapid and regular products for thermometers and very sensitive materials for detection of noxious vapor detection.

REFERENCES

Brown G.H., Doane W.J., Neff V.D., *A Review of Structure and Physical Properties of Liquid Crystals*, CRC Press, Cleveland Ohio, 1971.

Bunning T., Chen S., Harthorne N., Kajiyama T., Koide N., *Liquid Crystals for Advances Technologies*, Materials Research Society, Pitsburg, 1996.

Collings P., Hird M., *Introduction to Liquid Crystals – Chemistry and Physics*, Taylor and Francis, 1997.

De Gennes P.G., *The Physics of Liquid Crystals*, Claredon, Oxford, 1974.

Demus D., Lothar R., *Textures of Liquid Crystals*, Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1978.

Demus D., Goodby J.W., Gray G.W., Spices H.W., Vill V. (Eds.), *Handbook of Liquid Crystals Fundamentals,* Wiley VCH, Weinheim, 1998.

Dumitrașcu I., Dorohoi D.O., *Optical Anisotropy*. Applications, Ed. Tehnopress, Iași, 2015.

Kleinert H., Maki K., *Lattice Textures in Cholesteric Liquid Crystals*, Fortschritte der Physics, **29**, 219-259 (1981).

Ireland P., Jones T., *Heat Transfer and Cooling in Gas Turbines*, AGARDCD – 390, Bergen, Norway, 1985.

Meier G., Seckmann E., Grabmaier J.G., *Applications of Liquid Crystals*, Springer, Verlag, Berlin, 1975.

Moțoc I., Muscutariu I., *Introducere în Fizica Cristalelor Lichide*, Edit. Facla, Timișoara, 1986.

Mujahid A., Stathopulos H., Lieberzeit P.A., Dickert F.L., *Solvent Vapour Detection with Cholesteric Liquid Crystals* - Optical and Mass – Sensitive Evaluation of Sensors Mechanism, Sensors, **10**, 4887-4897 (2010).

Muscutariu I., *Cristale Lichide și Aplicații*, Edit. Tehnică, București, 1981.

Pershan P.S., *Structure of Liquid Crystals Phases, Word Scientific*, Singapore, 1978.

Shibaev P.V., Wenzlick M., Murray J., Tantillo A., Howard – Jennings J., *Rebirth of Liquid Crystals for Sensoric Applications: Environmethal and Gas Sensors*, Advanced in Condensed Matter Physics, Vol. 2015, http://dx.doiorg/10.1155/2015/729186.

Stasiek J.A., Kowalewscki T.A., *Thermotropic Liquid Crystals Applied for Heat Transfer Research*, Opto-Electronics Review, **10**, *1*, 1-10 (2002).

Wozniak G., Wozniak K., *Simultaneous Measurements of Temperature and Velocity Fields in Thermo-Conductive Liquid Flows – Development of New Measuring Technique*, Monography Research; Material and Fluid Science, Adv. Space Res., **11**, 33-38 (1991).

CRISTALE LICHIDE COLESTERICE ȘI APLICAȚIILE LOR ÎN MĂSURAREA TEMPERATURILOR ȘI ÎN DETECȚIA CONTAMINĂRII CU VAPORI

(Rezumat)

Cristalele lichide colesterice formează filme subțiri cu proprietăți optice speciale. Sensibilitatea lor la schimbări de temperatură oferă posibilitatea măsurării unor variații mici de temperatură sau a evidențierii diferitelor unde mecanice sau electromagnetice datorită efectelor lor calorice.

Cantități mici de vapori contaminanți din atmosferă pot fi detectate cu dispozitive conținând cristale lichide colesterice datorită sensibilității ridicate a pasului colestericului la impurități. Un studiu experimental pentru evidențierea vaporilor de tetrahidrofuran a fost realizat cu un cristal lichid colesteric încapsulat în matrice poliuretanică.