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Treball Final de Grau

**Boundary and size effects in chromonic liquid crystal emulsions.
Efectes de contorn i grandària en emulsions de cristalls líquids
cromònics.**

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I have not failed. I've just found 10,000 ways that won't work.

Thomas A. Edison

Gràcies a aquest treball final de grau he pogut trobar una àrea que em sembla fascinant de la química, i que continuaré lligat a ella en els meus estudis post universitaris. Vull agrair a en Francesc Sagués i a en Jordi Ignés per confiar en mi i ensenyar-me una infinitat de coses, a més de fer-me veure que el món de la química física és apassionant.

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Ha estat una època molt complicada i estressant en l'àmbit acadèmic, però donar gràcies a la meva família pel suport incondicional i als meus amics que sempre han estat allà per tot el que he necessitat. Gràcies a tots per acompanyar-me en aquest camí.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

Applying an external stimulus can affect the boundary conditions and optical properties of chromonic lyotropic liquid crystals. To promote the accomplishment of the Sustainable Development Goals (SDG), due to the relatively inert nature of these materials and its sensibility in front of external stimulus, biosensors can be developed to detect certain pathologies only by observing the change of liquid crystal configuration. This development can be associated to SDG goal 3, Good health and people's wellbeing.

Liquid crystal lyotropic compounds can have interesting applications such as biosensors due to their optical properties and ability to respond to specific stimulus. Liquid crystal lyotropic compounds can function as optical sensors by interacting with certain molecules or analysts present in a biological sample. For example, they can be used to detect the presence of biomarkers in blood, urine or saliva that are associated with specific diseases, such as proteins, enzymes, or nucleic acids.

These compounds can be designed to change their structure or optical properties in response to the presence of the target analyte. This can manifest in a change in colour, change in the intensity of transmitted light, or change in the position of spectral bands. These optical changes can be measured and quantified to determine the concentration or presence of the analyte in the biological sample. Biosensors based on lyotropic compounds liquid crystal can offer advantages such as high sensitivity, selectivity, and real-time detection capacity.

In our work we observe this change in optical properties in chromonic liquid crystals before a magnetic field so that we can have a representative idea about the sensitivity of these materials to given stimuli and can extrapolate it to systems such as the aforementioned.

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1. SUMMARY

Liquid crystals (LCs) are unique states of matter that exhibit both liquid and crystal properties. From the 19th century until now, extensive research has been carried out to understand and take advantage of the fascinating properties of liquid crystals.

An intriguing subclass of liquid crystals is the lyotropic chromonic liquid crystal (LCLC). Unlike thermotropic liquid crystals as 5CB, which form through temperature changes, LCLCs are formed when certain organic molecules, known as chromonic dyes, are dissolved in solvents such as water. These LCLCs exhibit a rich variety of phase behavior and unique optical properties, making them of great interest to various applications, including screens, sensors, and biomedical devices. One of the most famous LCLC is Sunset Yellow (SSY). To describe the confinement of 5CB and SSY and observe phenomena such as the boundary effects in emulsified droplets will be one of the aims of our work.

In order to form the emulsions, microfluidic systems will be used. They use small channels and precise control of fluid flows to create well-defined structures and patterns of liquid crystals. This approach offers several advantages, such as high performance, precise control of the size and shape of droplets, and the ability to create complex geometries.

Once the emulsions are generated, we will study the properties of confined LCs in droplets and their behavior in front of an external magnetic field.

Keywords: Liquid crystals, lyotropic chromonic liquid crystals, sunset yellow, 5CB, emulsions, droplets, boundary effects, microfluidic systems, magnetic field.

2. RESUM

Els cristalls líquids (LC) són estats únics de la matèria que presenten propietats tant líquides com cristal·lines. Des del segle XIX fins ara, s'ha dut a terme una àmplia investigació per entendre i aprofitar les propietats fascinants dels cristalls líquids.

Una subclasse intrigant de cristalls líquids és el cristall líquid liotròpic cromònic (LCLC). A diferència dels cristalls líquids termotròpics com el 5CB, que es formen a través de canvis de temperatura, els LCLCs es formen quan certes molècules orgàniques, conegudes com a tints cromònics, es dissolen en dissolvents com l'aigua. Aquests LCLC presenten una rica varietat de comportament de fase i propietats òptiques úniques, fent-los de gran interès per a diverses aplicacions, incloent pantalles, sensors i dispositius biomèdics. Un dels LCLC més famosos és el Sunset Yellow (SSY). Descriure el confinament del 5CB i el SSY, i observar fenòmens com els efectes de contorn en gotes emulsionades serà un dels objectius del nostre treball.

Per formar les emulsions, s'utilitzaran sistemes de microfluidica. Utilitzen canals petits i un control precís dels fluxos de fluids per crear estructures ben definides i patrons de cristalls líquids. Aquest enfocament ofereix diversos avantatges, com ara un alt rendiment, un control precís de la mida i la forma de les gotetes, i la capacitat de crear geometries complexes.

Un cop generades les emulsions, estudiarem les propietats dels LCs confinats en gotes i el seu comportament davant d'un camp magnètic extern.

Paraules clau: Cristalls líquids, cristalls líquids liotròpics cromònics, Sunset Yellow, 5CB, emulsions, gotes, efectes de contorn, sistemes de microfluidica, camp magnètic..

3. INTRODUCTION

3.1. LIQUID CRYSTALS (LCs)

In 1888, the Austrian botanist Friedrich Reinitzer discovered that a substance called cholesterol-benzoate had two intermediate phases between the solid and liquid states. He immediately wrote a letter to the German Otto Lehmann, a physicist known for his work in crystalline polymorphism, and he explained: “At about 145.5 °C it melts, forming a turbid, but completely fluid liquid, that suddenly becomes completely clear at about 178.5 °C.”¹ Otto Lehmann subsequently studied this feature and found that there were other substances showing this behavior classifying them as “liquid crystal” in 1889.

A liquid crystal (LC) is a state of matter that exhibits properties of both liquids and solids. Usually, they can be found as a mesophase within the solid-to-liquid transition. In a liquid crystal, the molecules (or mesogens) have a short-range order like in solids, but they are still able to flow and move like in a liquid (figure 1). They are typically made up of elongated molecules that can be rod-like or disk-like shape. The organization of the liquid crystal molecules is determined by

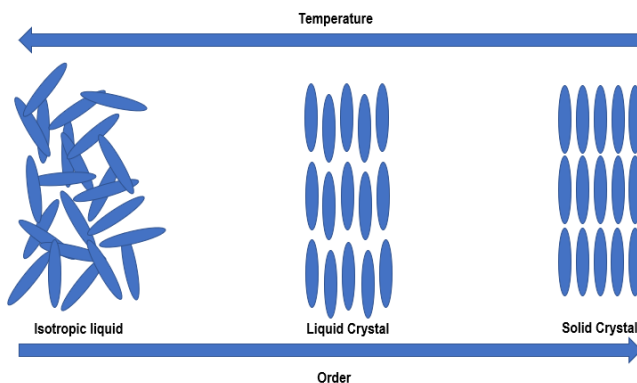


Figure 1. Schematic representation of the ordering of the three phases, isotropic liquid, liquid crystal and crystalline solid, and how the liquid crystal phase is a transition between the liquid and solid phases, classically known.

the different shapes and types of interactions within the mesogens such as Van der Waals interactions, dipole-dipole, hydrogen bonds, among others. These liquid crystal properties are in general temperature dependent, and for some subgroups of liquid crystals they are also concentration-dependent, and thus multiple liquid crystal phases can be found in nature. Moreover, due to the shape of the mesogens, the liquid crystal properties are anisotropic and external fields such as electric fields or magnetic fields allow to control the molecules' orientation within the phases.²

Liquid crystals can be divided into two large groups depending on which factors alter their phase: Lyotropic liquid crystals (LLC), which phases are dependent on concentration and temperature, and thermotropic liquid crystals (TLC), whose phase depends solely on temperature. The reason for this difference in dependence is that, in the first case, lyotropic need a solvent to structure themselves to form the mesogenic unit in the LC phase, whereas thermotropic molecules organize themselves without the need for a solvent.² In this work we studied the interaction of these two large groups, generating emulsions of thermotropic and lyotropic LC phases.³

3.2. LYOTROPIC LCs

The prefix “lyo-“ is derived from the Greek word for “solvent” and it indicates that concentration, as well as temperature, plays a crucial role in the phase behaviour of lyotropic liquid crystals (LLCs). While lyotropic liquid crystal phases can be formed in non-aqueous solvents as well, this work will focus on those formed in water as they are the most important and widely studied.⁴ One of the key properties of Lyotropic LCs is that they are formed by amphiphilic molecules (figure 2). Once they are in a solution, they are capable to self-assemble in different of structures, where its orientation will be modified depending on the polarity of the solvent.⁵

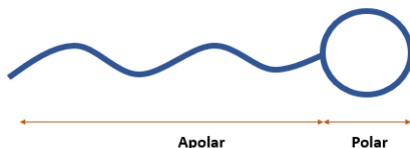


Figure 2. Amphiphilic molecule structure. We can see a head with polar character, while the chain usually has a more nonpolar character.

3.2.1. Lyotropic chromonic LCs

One subgroup of LLCs is the denominated Lyotropic Chromonic Liquid Crystals (LCLCs). These mesogens have the particularity that, due to their discotic, planar or plank-like form, they stack into elongated rods like poker chips (figure 3). The noncovalent intermolecular interactions like a π - π stacking are the responsible of this type of self-assembling. From this different elemental assembling, LCLC also organize in the most common LC phases such as the nematic or columnar.⁶

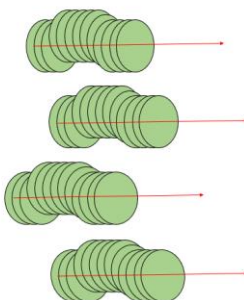


Figure 3. Nematic structure formed by stacks of discotic molecules.

3.3. THERMOTROPIC LCs

The prefix “thermo” comes from the Ancient Greek, meaning “hot” or “heat”, that indicates how the LC behavior is conditioned by the temperature of the phase. Most of the thermotropic liquid crystals phases are composed by rod-like molecules, and the most important three types are the nematic, smectic and cholesteric.⁷

3.4. CLASSIFICATION OF LCs

Liquid crystals display into several phases, or mesophases. The prefix “meso” is translated as “between”, indicating one of the beforementioned features of LCs. Here, we briefly describe the most representative and common phases of LLCs and TLCs. We must make the point that the order and the characteristics of each phase are, in essence, a direct consequence of its director field. The director field (n) is a unit vector that characterizes the alignment of the

mesogens. This vector field represents the average orientation of the molecules and offers insights of the local arrangement and anisotropy of the liquid crystal phase. The director field is important as it is closely linked to the order parameter of our phase. The more aligned the director field is, the more order the LC phase presents. Depending on the type of deformations it may suffer, we obtain the different phases of the LCs.

3.4.1. LCs phases

- Nematic

The nematic phase is the most common organization shown by LCs. Here, the mesogens have their elongated molecular structure parallel to each other's but lack any positional organization such as in solids. Thus, an assembly of mesogens have a preferential orientation, that is characterized by the director field. Nematic phases can be subdivided into calamitic nematic liquid crystals (with elongated and polarized molecules) and discotic nematic liquid crystals (with discoidal and unpolarized molecules). We can add a third category, the ferroelectric liquid crystals, where the nematic structures present a spontaneous electrical polarization (figure 1).

- Smectic

In the smectic phase, an additional degree of ordering is added in contrast to the nematic. In here, the molecules have not only orientational but positional order. As shown in figure 4, the molecules organize in layers like fashion with a common orientation.

- Cholesteric

The cholesteric phase is a nematic structure where the molecules present chirality such as cholesterol derivatives. This phase consists of a stack of layers of the nematic phase, where the director field rotates along the set of nematic layers. A whole rotation of the director field by 360 degrees defines the pitch of the cholesteric phase (figure 4).

- Columnar

Columnar phases are found within discotic liquid crystals. These are a type of mesophase where molecules are arranged in a columnar fashion, forming cylindrical or helical columns that can be organized in two or three dimensions.

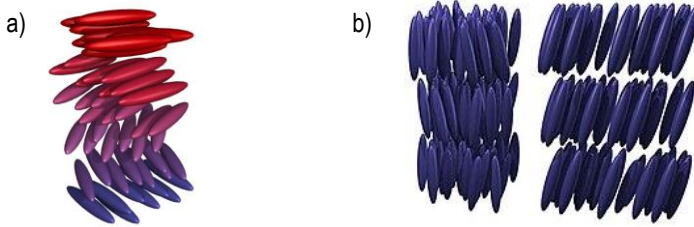


Figure 4. a) Arrangement of mesogens in the cholesteric phase. The rotation of mesogens between neighboring molecules results in a chiral phase. b) Arrangement of mesogens in the smectic liquid crystal phase.

(Kebes, Wikimedia Commons, Creative Commons Attribution)

Other types of LC phases could be:

- Hexagonal

Cylindrical micelles, which in turn create a hexagonal network.

- Lamellar

Organized and layered structure.

- Micellar

Molecules resemble spherical or cylindrical micelles, which can then be grouped to form ordered structures proper to a liquid crystal.

Not all these structures can be found in the two large groups of LCs (lyotropic and thermotropic) at the same time (figure 5).

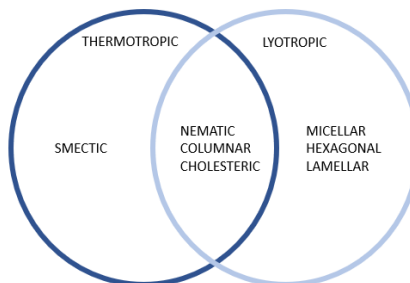


Figure 5. Classification of the different phase types according to their thermotropic-lyotropic character.

3.5. COMMONLY USED LCs

3.5.1. Sunset yellow

In this work, sunset yellow was used as a LCLC. It was mentioned that chromonic LCs are formed by planar mesogens. Since sunset yellow (figure 8b) has sp^2 hybridization in its carbon and nitrogen atoms, the molecule exhibits a significant planar character and can form stacks that result in the LC phase.⁶ In addition to this, the molecule also has non-polar organic groups such as benzene, as well as polar substituents such as hydroxyl or sodium sulfate, which give it an amphiphilic character. The two LC phases the SSY can adopt are the nematic and the columnar (figure 6).

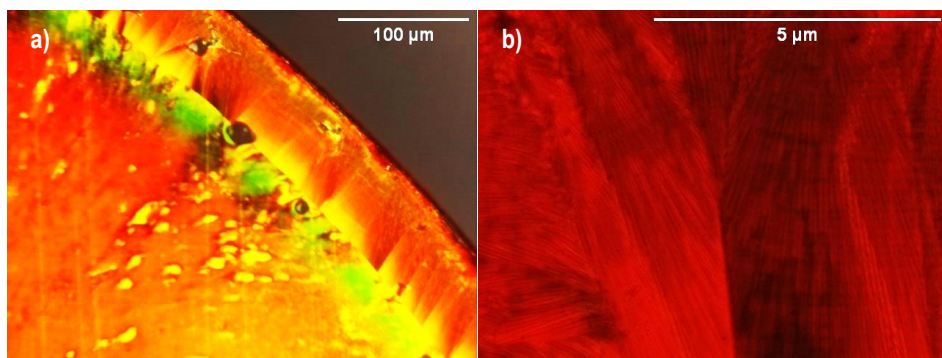


Figure 6. a) Interphase of columnar and nematic phases in SSY and b) Columnar phase in SSY.

In this work, SSY concentration will be adjusted to be in nematic phase, so we will take in account its phase diagram which depends on temperature and concentration (figure 7).⁸

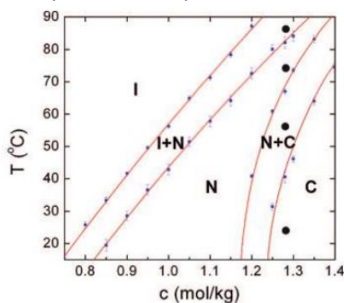


Figure 7. SSY concentration-temperature phase diagram. (Image extracted from Park et. al. (ref 8)).

3.5.2. 4'-Pentyl-4-biphenylcarbonitrile (5CB)

4'-Pentyl-4-biphenylcarbonitrile (5CB) is a commonly used thermotropic liquid crystal compound that exhibits a nematic liquid crystal phase. It is a rod-like molecule composed of two benzene rings connected by a carbon-carbon bond, with a cyano group attached to one of the rings and a pentyl chain attached to the other ring (Figure 8a). The properties of 5CB are directly influenced by its molecular structure. The flexibility and length of the pentyl chain contribute to 5CB's liquid-like behavior, allowing it to flow and adapt to the shape of its container. The benzene ring imparts stability and rigidity, which are essential for its liquid crystalline phase because of the multiple intermolecular interactions (e.g., π - π). The presence of the cyano group enhances the polarity of 5CB, increasing its solubility in polar solvents and affecting its interactions with other molecules. This polarity also plays a role in determining optical properties like refractive index and birefringence.

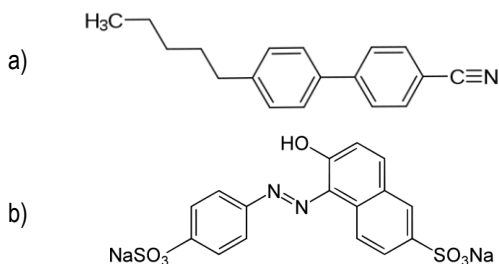


Figure 8. a) 5CB structure. b) Sunset Yellow structure.

3.6. DISTORTIONS IN DIRECTOR FIELD AND LC ANCHORING

The director n in an LC phase is set parallel to the more stable direction of the LC molecules. However, depending on the boundary conditions, one can modify this direction. The ease with which this vector is affected depends on the elastic constants of the several types of deformations that the mesophase can suffer. These deformations can be classified into three types: splay, twist, and bend (figure 9). The constants of the above deformations are a way of quantifying the energy needed to deform mesophase into another type of configuration. The observation of deformations

is accentuated when we have LC phases located like droplets, and not in bulk, as a consequence of the contour the LC has to face.¹

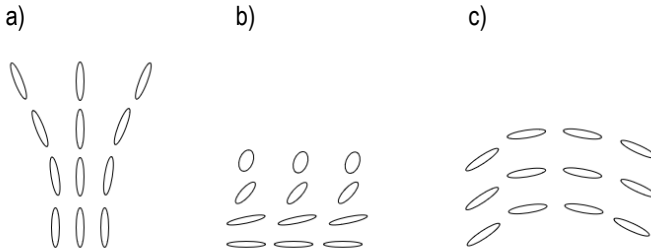


Figure 9. Deformations in director field n . a) Splay. b) Twist. c) Bend.

As a result of these deformations and the boundary conditions, topological heterogeneity is normally observed in LCs in the form of the so-called point defects. In these points of the phase, there are divergences of director field n . Thus, the order in a point defect is zero. These defects can be observed with polarized optical microscopy as dark points/lines within the phase.^{1,9}

In the absence of surfaces or applied forces, the director field is uniform throughout the bulk. However, when mesogens come into contact with a surface, their molecular interaction with the surface causes a new orientation in the LC molecules, this behavior is due to the “anchoring.”¹⁰

The anchoring can induce three different configurations (figure 10). In the planar configuration, the director field is parallel to the surface. In the homeotropic configuration, n is oriented perpendicular to the surface. Between these two extreme cases, the oblique configuration involves orientations between 0 and 90 degrees.

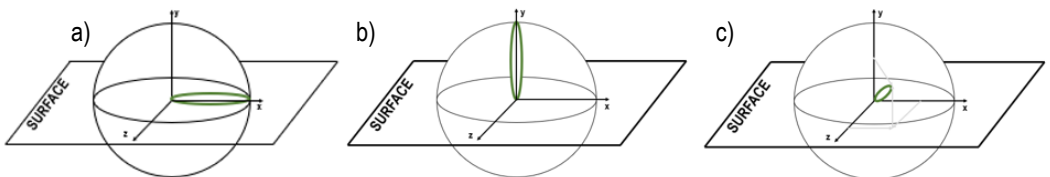


Figure 10. Anchoring of the mesogens in a surface. a) planar. b) Homeotropic. c) Oblique

3.7. ANISOTROPIC PROPERTIES

Anisotropy is a term used to describe systems whose properties depend on the direction of measurement. LCs properties are anisotropic, and those such as viscosity, thermal conductivity, x-ray diffraction, or refractive index show different values that depend on the orientation of the director n .

3.7.1. Birefringence

Birefringence is an optical phenomenon observed in anisotropic materials. These materials have different refractive indices along different axes or directions. When light passes through such materials, it splits into two separate beams (figure 11), each with a different polarization of the electric field and velocity of propagation. The magnitude of birefringence is determined by the difference in refractive indices between the two axes or directions. If the system we are talking about is a LC, the refractive indices depend on the direction of the director field relative to incident light.^{1,3}

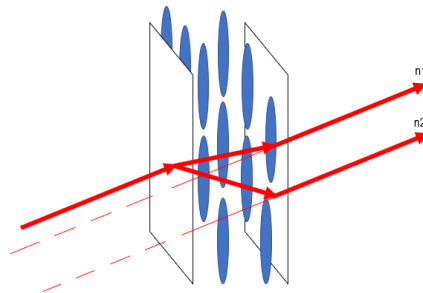


Figure 11. Birefringence in a LC with planar anchoring

It is important to comment that birefringent systems are a direct consequence of a uniaxial symmetry, which means that the material is symmetric around one axis. In this symmetry, the refractive index associated to the parallel direction to the orientation that we will call extraordinary refractive index (n_e). This refractive index depends on the director field of the LC. On the other hand, the index associated with the perpendicular direction to the orientation is called the ordinary refractive index (n_o), which does not depend on the director field of the LC.³

In Liquid crystals, anchoring has important consequences in the birefringence response. As we can see in equation 1, an effective refraction index for the extraordinary beam is expressed. It depends on θ , which denotes the angle between the local director and the light propagation

direction and the parallel and perpendicular refractive indexes. This effective refraction index equals the parallel refractive index when the angle between the light propagation direction and the local director is 90 degrees and equals the perpendicular refractive index when the same angle is 0. We can then understand effective refractive index as a weighted average of the two original indexes, which gives us information about the birefringent character of our material. This deduction is particularly important since, in section 3.11 we will see birefringent character is necessary to visualize anisotropic materials in the microscope.

$$n_{eff} = \frac{n_{\perp} n_{\parallel}}{\sqrt{n_{\perp}^2 \sin^2 \theta + n_{\parallel}^2 \cos^2 \theta}}$$

Equation 1. Relation between the extraordinary refractive index and the angle between the local director and the light beam.

3.7.2. Consequences on applying external fields to LCs

As the material has two refraction indices, it has two dielectric and magnetic permeability constants as well. This condition makes LCs reactive in front an external electric and magnetic fields. The two constants (both magnetic and electric) will be named $\epsilon_{\parallel}/\mu_{\parallel}$ for the extraordinary index or $\epsilon_{\perp}/\mu_{\perp}$ for the ordinary index. The alignment of the mesogens in front of an external field will be determined by which of the two constants is higher. If the extraordinary constant is higher, the mesogen will align its director field parallel to the field. In an opposite way, the director field will be perpendicular.² Anisotropy can be quantified as the difference between the parallel component and the perpendicular one, $\Delta\mu = \mu_{\parallel} - \mu_{\perp}$ and $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$.

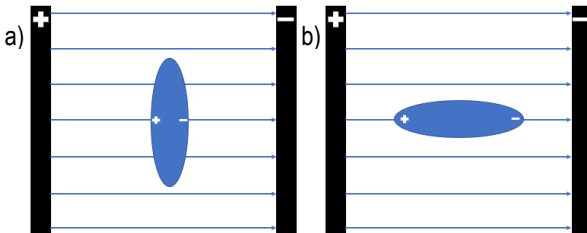


Figure 12. Layout of the mesogen in the presence of an external electric field, in a) the ordinary component is greater than in b) where the extraordinary is the dominant.

3.8. DROPS OF NEMATIC LCs

Nematic LC droplets are spherical or ellipsoidal structures consisting of a self-organized arrangement of LC molecules. Drops are formed when a LC is dispersed into another immiscible liquid, such as water, oil, or another LC, as is this work. When a nematic LC is restricted within orienting boundaries, the interplay between surface ordering and bulk elastic deformation gives rise to a diverse range of atypical director configurations. These configurations, influenced by the ratio of elastic constants and the orientation and strength of the boundary conditions, can also incorporate one or more defects. These defects may manifest either on the surface or within the bulk drop region. Due to their anisotropic nature, liquid crystal droplets can exhibit interesting optical properties.^{11,12}

3.8.1. Nematic LC's droplet configurations

As explained above, the configuration of a droplet of LC depends on several factors such as temperature, concentration (in case of lyotropic) or contour conditions. In this work, working at a constant temperature and concentration, we are interested in the boundary conditions governed by anchoring and the nematoelasticity of LC.

When the anchoring is homeotropic in the surface of the droplet, we obtain a radial drop configuration with a defect in the middle of the drop (hedgehop), while when it is planar, the droplet presents itself as bipolar with two defects (boojums) at either end of the drop. If we have a planar anchoring, but with regions with director fields with opposite directions (heterogeneous planar anchoring), configurations appear because of this distortion such as the twisted bipolar.

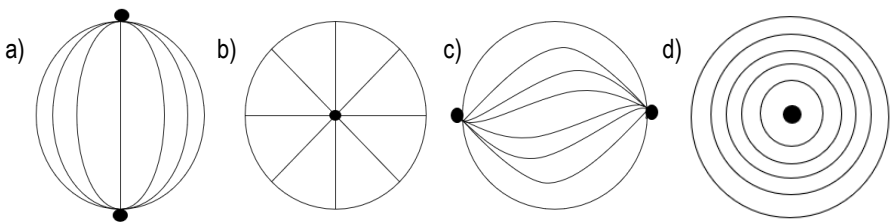


Figure 13. Configurations of LC nematic droplets, a) Bipolar, b) Radial and c) Twisted bipolar and d) concentric. The black points are the defects generated by the confinement within the droplet.

These configurations (figure 13) are preferred because in a nematic framework, the splay deformation is the one that dominates the other two deformations.^{12,13} If the anchoring is planar, but with a bend deformation hegemony, the configuration adopted is called concentric.

3.9. EMULSIONS

Emulsions are a dispersed system where two immiscible components are in contact and mix with each other. As the components of the mixture are immiscible, emulsions are naturally unstable. Within this system, the disperse phase consists of liquid droplets, while the continuous phase refers to the liquid medium in which these droplets are dispersed.¹⁴ Emulsions can be categorized into different classes, including oil-in-water (O/W), water-in-oil (W/O), and oil-in-oil (O/O) emulsions. The first two types of emulsion will be those studied in this work. When dispersing two immiscible liquids, the addition of an emulsifier, acting as a third component, becomes essential. The selection of the emulsifier plays a critical role in the formation of the emulsion and its long-term stability.

3.9.1. Emulsion stability

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, named after the four scientists who contributed to its development, is an invaluable tool for comprehending the stability of colloids. This theory encompasses the balance of forces between electrical double layers, which tend to be repulsive when particles share the same charge, as well as the consideration of long-range van der Waals forces, typically characterized by attractive interactions.

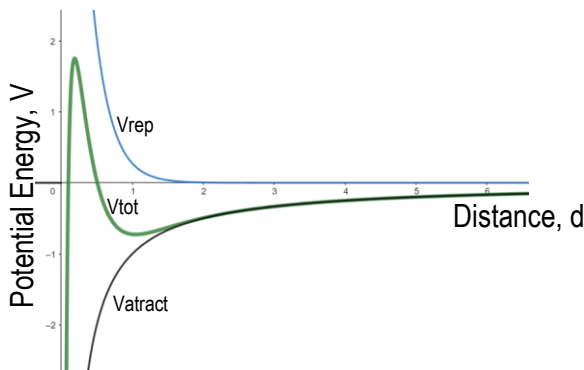


Figure 14. DLVO potential graphic, in blue the repulsion potential, in black the attraction potential, and in green the sum between those abovementioned.

If the repulsion potential is dominant in our emulsion, the maximum of the graph will be higher, so there will not be coagulation in the colloidal system.³ Coagulation refers to the process by which dispersed particles in a colloid come together and form larger aggregates or clumps.

There are many ways to increase the repulsive component of the emulsion, but one of the most used methods is the use of a surfactant. Surfactants are amphiphilic molecules (figure 2). When added to the emulsion, the surfactant molecules are assembled on the interface between immiscible liquids. The hydrophilic part of the surfactant interacts with the water molecules, while the hydrophobic part interacts with the oil molecules. This arrangement forms a protective monolayer around scattered oil or water droplets. Surfactant molecules create a barrier, reducing interfacial tension between oil and water phases. By reducing interfacial tension, surfactants inhibit coalescence and separation of emulsion droplets. The surfactant layer acts as a stabilizing agent, preventing droplets from entering direct contact and merging. This increases the overall stability of the emulsion, making it metastable. It must be said that if we add too much surfactant to the emulsion, it will have the opposite effect and can lead to coalescence and coagulation of the particles.

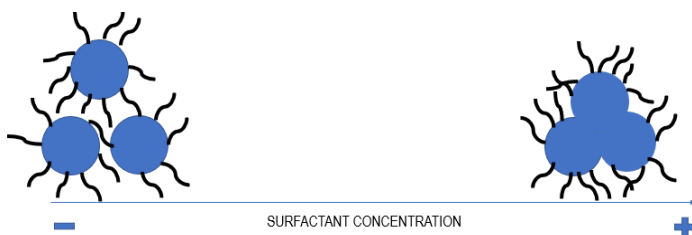


Figure 15. Effect of the concentration of surfactant in the repulsion-attraction equilibrium of an emulsion.

In this work, the use of surfactant will be one of the key points to stabilize droplets of one LC in another.

3.10. MICROFLUIDIC DEVICES

Microfluidics encompasses the scientific and technological study of integrated channels on the microscale, typically ranging from tens to hundreds of micrometres. These channels are designed to enable the controlled and systematic manipulation of small volumes of fluids, typically

ranging from 10^{-9} to 10^{-18} liters. The field of microfluidics originated several decades ago with the need for miniaturization and planarization in biochemical and chemical analyses.

The concept of "lab-on-a-chip" gradually emerged. As fluids are confined to the microscale in microfluidic systems, their specific surface area increases, leading to distinct behaviors compared to macroscopic fluids. These behaviors are characterized by three major phenomena: highly efficient mass transfer, the predominance of viscous forces over inertial forces, and significant surface effects. The high level of integration in microfluidic systems allows for the coexistence and interaction of multiple fluid phases, opening possibilities for precise control and manipulation of individual fluids and fluid interfaces.¹⁵ These systems will be useful in our work to generate size-controlled droplets in emulsions.

3.10.1. PDMS microfluidic system

Initially, microfluidic devices were predominantly manufactured using silicon or glass. However, the demand for disposable chips, presented obstacles in terms of fabrication expenses. Polydimethylsiloxane (PDMS) materials have gained popularity in the field of microfluidics due to their cost-effectiveness and simplicity for prototyping devices using soft lithography with master moulds for replication. The deformable nature of the PDMS, enables the incorporation of microfluidic valves by utilizing the deformation of its micro-channels. This flexibility also facilitates easy and reliable connections for leak-proof fluidic systems. Moreover, the material's deformability enables the detection of extremely low forces, such as those involved in biomechanical interactions with cells. The surface properties of PDMS can be chemically modified, allowing for easy bonding of microfluidic devices with both glass and PDMS itself. These advantages have facilitated rapid prototyping at a lower cost compared to silicon technology.¹⁶ The continuous phase (CP) goes through the exterior channelling of the PDMS microchip and applies a shear stress to the dispersive phase (DP), which has gone through the central channelling (figure 16).

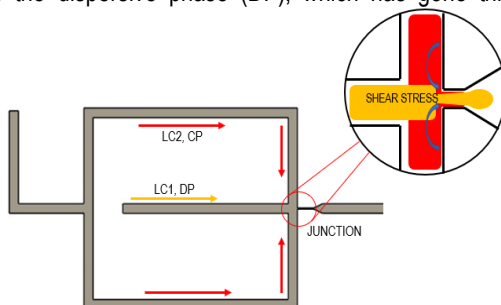


Figure 16. Generation of size-controlled droplets with a PDMS microfluidic

3.10.2. Alternative microfluidic system: Needle-based

Although needle-based microfluid systems have not been used in this work, we believe it is important to mention them, so it is a high-value alternative for microfluidics. These systems emerged as versatile and efficient tools for fluid manipulation in a variety of applications. First, systems offer versatility by allowing handling of a wide range of fluids, including liquids, gases, and suspensions. They provide precise control over the flow of fluids and an adaptation to the injected volume, allowing ease in scaling colloidal systems. In addition, they are deeply compatible as they have an inert character in front of a wide range of materials. Finally, they are relatively easier to build than those of PDMS.

Needle-based microfluidic systems (figure 17) have two inputs (inlets) and one output (outlet). For inlet 1 the dispersive phase (DP) of the emulsion is injected by a needle with an inner diameter d_1 , while for inlet 2 the continuous phase (CP) is injected directly through the T-junction. The outlet is connected to the system via another needle of inner diameter d_2 , bigger than d_1 . The fluid that forms the CP apply a shear stress in the intersection of the two needles, generating droplets of the DP. Inertia makes droplets enter the outlet and then they can be collected.¹⁷

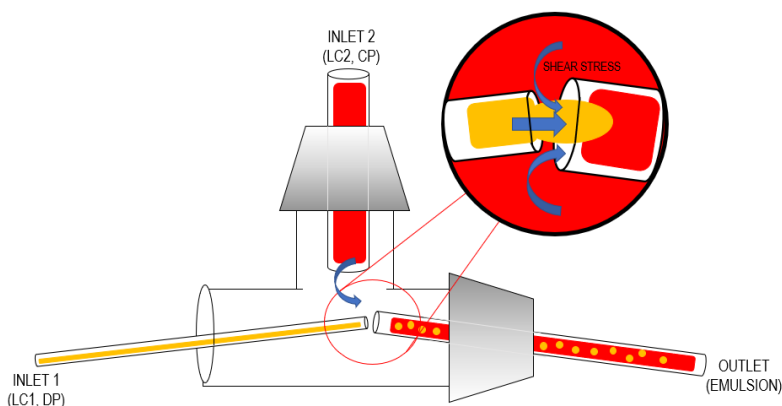


Figure 17. Generation of size-controlled droplets with a needle-based microfluidic device.

3.11. OPTICAL CHARACTERIZATION OF LCS

LCs exhibit birefringence as mentioned earlier that can be detected using polarized optical microscopes (POM). To understand this, we need to consider the characteristics of light and microscopy under these conditions.

Light, in its natural state, is non-polarized, meaning its electric field oscillates along all directions perpendicular to the wave's propagation. However, certain bodies can preferentially transmit specific oscillation directions. To convert non-polarized light to polarized light, engineers have designed polarizers, which restrict the oscillation directions to a single plane. Birefringent materials, like those studied here, act as "natural" polarizers, allowing two perpendicular vibration directions to pass through them, resulting in circular polarization (figure 18).

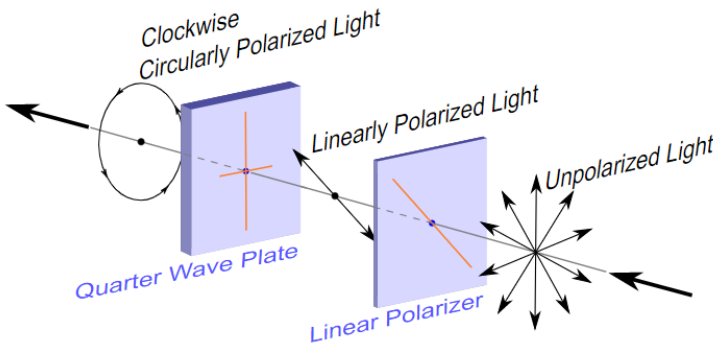


Figure 18. Scheme that represents how non-polarized light polarizes linearly when passing through a polarizer and is circularly polarized again when passing through a birefringent sample.

(Dave3457, Wikimedia Commons, Creative Commons Attribution)

When polarized light encounters a birefringent material, it splits into two perpendicular vibration directions due to the material's two refractive indices, the ordinary one (n_o), with perpendicular orientation to the director field of the mesogen, and the extraordinary one (n_e). These directions move at different speeds, leading to a phase difference between the two waves (figure 19).

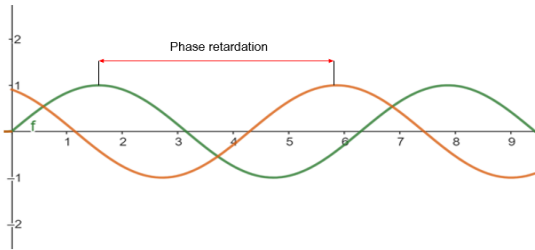


Figure 19. Graphical representation of phase difference between two waves with the same frequency.

3.11.1. Polarized optical microscopy

Polarized optical microscopy (POM) is a technique used to observe birefringent materials such as LCs. POM employs two polarizers: the first is called the polarizer, and the second is the analyzer. A polarized light beam passes through the polarizer and becomes polarized. When it interacts with an anisotropic material, it undergoes a phase shift, causing the beam to split into two rays. These rays recombine using the analyzer, producing interference patterns that form the basis of POM and enable image production. POM is particularly useful for distinguishing between isotropic and anisotropic media. Isotropic materials do not split polarized light, while birefringent materials exhibit changes in light intensity as they rotate when placed between crossed polarizers.

LCs are substances that are observed in polarized optical microscopes (POM) due to their birefringence. We will then explain what characteristics the light that reaches the sample should have and how we have microscopy according to these conditions (figure 20).

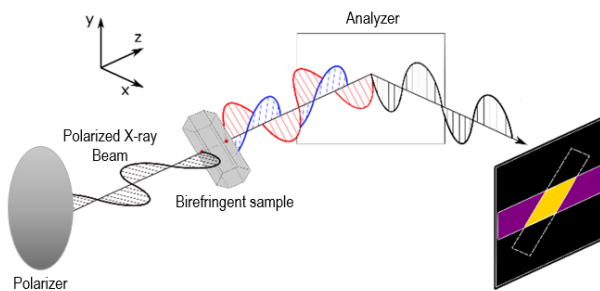


Figure 20. Scheme of the main parts of a POM. The beam gets linearly polarized with the polarizer and circularly polarized with the analyzer.

4. OBJECTIVES

The main objective of this work was to study the interaction between a Lyotropic Chromonic Liquid Crystal and a Thermotropic Liquid Crystal by the formulation of emulsions. For this purpose, microfluidic techniques were used to produce homogenous drops of either the LCLC in TLC or TLC in LCLC. We then highlight the effect of applying magnetic fields over such complex systems.

As complementary objectives that will help us to achieve these main goals we can highlight:

- Understand the main properties of LCs along with the microscopy techniques necessary for their observation.
- Observe the different phases adopted by a concentration-dependent lyotropic LCs.
- To detect the defects and textures corresponding to these LC phases.
- Study the emulsion without the presence of an external magnetic field.
- To have a greater perspective on the microfluidic techniques currently used.

5. EXPERIMENTAL SECTION

5.1. PREPARATION OF SSY SOLUTIONS

5.1.1. SSY purification

The Sunset yellow (SSY, 90%, Sigma Aldrich) underwent purification through recrystallization using ethanol (96% (v/v) for analysis, Panreac). To dissolve the SSY, a minimal amount of deionized water was used, considering its solubility of 190 mg/mL at 25°C. To induce precipitation of the SSY, ice-cooled ethanol was added to the SSY at a ratio of 10:1. The resulting solution was then refrigerated at the fridge for 15 minutes. Subsequently, the solution was filtered under vacuum, and the obtained solid was stored under vacuum conditions at temperatures below 140°C for a minimum of 8 hours. This entire process was repeated twice.

5.1.2. SSY solutions

The solutions we worked with have SSY in water in a concentration of 1–1.1 m in order to display a nematic phase. To dissolve SSY, we deposited the necessary amount of SSY and water in an Eppendorf and combined vortex and ultrasound as agitation methods.

5.2. PREPARATION OF LC CELLS

5.2.1. Glass preparation

The glass slides were initially cleaned using soap and deionized water. Subsequently, they were thoroughly rinsed with deionized water and a detergent is added. This mixture was taken to the ultrasound bath for 15 minutes. Next, the glass slides were immersed in a piranha solution consisting of H₂SO₄ (lab grade, Sigma-Aldrich) and H₂O₂ (30% wt, Sigma-Aldrich) at a ratio of 3:1. This step aimed to completely remove any remaining organic matter and contaminants and lasted for 1 hour. Afterward, the slides were rinsed with Milli-Q water.

Once our glasses were available, they were spin-coated with a polyamide resin (Nissan 825) solution. By applying Nissan 825 coating we get planar anchoring. The spin coating process was performed at a speed of 2000 rpm for 3 minutes in a spin coater (Polos SPIN150i/200i Infinite). To remove the solvent and accelerate the curing of the coating, the coated glass slides were subjected to a temperature of 80°C for 5 minutes and then to 180°C for 1:30 hours. Subsequently, they were left to cool down to room temperature.

After applying the coating, it was necessary to scratch the glass (appendix 1, figure 1) for the covered part of Nissan 825. This scratch was done to promote planar orientation of the LC inside the cell (figure 21).

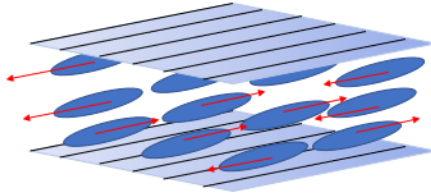


Figure 21. Influence of the coating and scratching in the mesogens orientation and direction.

5.2.2. Cell assembly

Emulsions were placed between the two glass slides we prepared before. To prepare the setup, a fishing line of 60 μm in diameter was used as spacer to control the gap between the two substrates. We placed in an opposite way the scratches of the two glasses to avoid internal tensions between mesogens inside the cell and the formation of twisted defects. The introduction of the sample was done through capillarity. To prevent the solution from drying out, we used UV glue (Norland optical adhesive 81, Norland Products, INC) to seal the cells (figure 22).

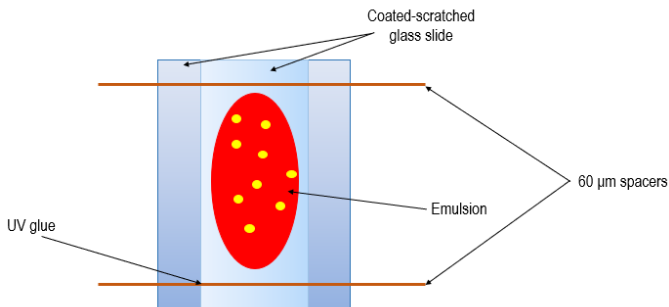


Figure 22. Emulsion cells scheme.

5.3. PDMS CHIPS

5.3.1. PDMS channeling assembly

We applied PDMS mould replication methods in order to manufacture our microfluidic device for the fabrication of the emulsions (appendix 1, figure 2). First, we prepared a mixture of 10:1 (PDMS monomer to catalyser) to have PDMS chips about 2 cm wide. The mixture was vigorously mixed for 5 minutes and moved to the vacuum for 20 minutes to extract the air bubbles. While the mixture was in vacuum, we prepared an aluminium foil envelope to surround the mould. By doing this we generated a vessel to contain the liquid mixture. Once the mixture was free of air bubbles, we removed it from the vacuum and pour it into the container where the mould was located. We made the mixture level and with the minimum bubbles trapped. The polymer was left at 120 °C until it became solid.

Once the mixture was solid, we removed it from the mould and proceed to divide it into the different chips. Secondly, holes were opened in the chips to be able to plug the liquid inlet tubes that will inject the substances under study. After undergoing an O₂ plasma treatment, these devices were bonded onto glass slides. Lastly, the chips were left at 70 °C overnight. After this, the PDMS chips were ready to use (figure 23).

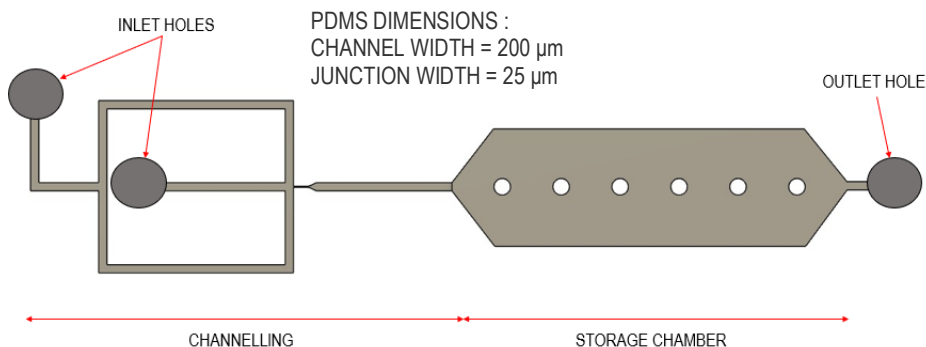


Figure 23. PDMS chip and its dimensions. It is divided in two parts, the channelling part, and the storage chamber.

5.3.2. PVA coating in PDMS

PDMS is a very inert polymer, but it has a slightly hydrophobic character. To counteract this effect, we recovered the channelling of the chip with at 1% (wt.) Polyvinyl alcohol solution (PVA, 88% hydrolysed, M.W.: 88000 g/mol, Acros Organics). PVA gave a hydrophilic character inside the channelling, which allowed the formulation of emulsions with a continuous hydrophilic phase (i.e. 5CB in SSY emulsions).

To do this coating, the initial protocol was to inject through the channelling a 10-time diluted piranha solution for 1 minute, clean it with water, dry and finally inject the coating solution. Due to the risk that the piranha damaged the PDMS, a new coating protocol was tested. We activated the channelling surface with O₂ plasma by generating a flow of oxygen within the apparatus (appendix 1, figure 3), thereby generating a pressure gradient that favours oxygen to enter the inside of the chip. This activation process was performed 3 to 5 times. Once the zone was activated, we introduced the coating product in the device.

5.3.3. Aquapel coating in PDMS

Aquapel is a product that, unlike PVA, accentuates the hydrophobic character of PDMS, allowing us to generate emulsions where the continuous phase is a hydrophobic compound (i.e. SSY in 5CB emulsions). The protocol followed to apply this coating was the same as in the previous section.

5.4. EMULSIONS GENERATION

We shall now describe the various emulsions we prepared. We used the following substances: Sunset Yellow (SSY), 5CB, DSCG and glycerol-water mixture.

5.4.1. Glycerol-water in 5CB

This formulation was done with the purpose to demonstrate the microfluidic device properties and how SSY could behave in the microfluid system. SSY, having a somewhat slow purification process, should not be wasted, and with the aim of adjusting optimal conditions for SSY, we used this "test" emulsion. In order to prepare the mixture of glycerol-water, we used as a reference value the viscosity of SSY in the nematic phase, 45 cp. To obtain this viscosity we mixed glycerol and water in a 3.1-1 ratio. The products that make up the emulsion were filtered before being

introduced into the device. The microfluid system is very sensitive to residual waste and could be easily clogged.

5.4.2. DSCG in 5CB

The DSCG is an LCLC like the sunset yellow, filtered and injected into the microfluid as DP. 5CB acts as CP.

5.4.3. SSY in 5CB and 5CB in SSY

These emulsions were generated using two different methods:

- Agitation based method: We deposited the DP and the CP in 1:20 ratios to an Eppendorf. The mixture were stirred with a vortex monitoring the power, because we could generate droplets so small that they could not be observed with the POM. Products were not filtered in this case, as there was no risk of overloading any system.

- Method based on the microfluid PDMS system: By filtering the solutions before, we injected LCs into the PDMS without coating or with aquapel coating (hydrophobic) in SSY-5CB emulsion or into the PDMS with PVA coating (hydrophilic) in 5CB-SSY emulsion. Two injection methods were used, the first being to inject the LCs into the ducts by two needles into the inlets. In the second, we suctioned the LCs with a syringe in the outlet. This injection/suction process was executed with a programmable syringe pump ALADDIN.

The appropriate arrangement we used to inject LCs into the microfluidic system is the one described in the figure 16.

5.5. MAGNETIC FIELD OBSERVATIONS

Emulsion observations under an external magnetic field was made with two magnets, one of 1 T and one of 400 mT. In the case of the 1 T magnet, the sample was simply placed on top, and the sample was manually rotated. In the second case, a 3D printing mount was used, where the sample was placed below the magnet, and the magnet was rotated (figure 24). Since in both cases the sample was not in the centre of the magnet, the field is slightly modified in value. In the 400 mT magnet, the field where the sample was placed had a module of 30 mT in magnet plane and 230 mT in perpendicular direction. As for the magnet of 1 T we have a value of 500 mT in the magnet plane and a value of 100–200 mT in the perpendicular direction.

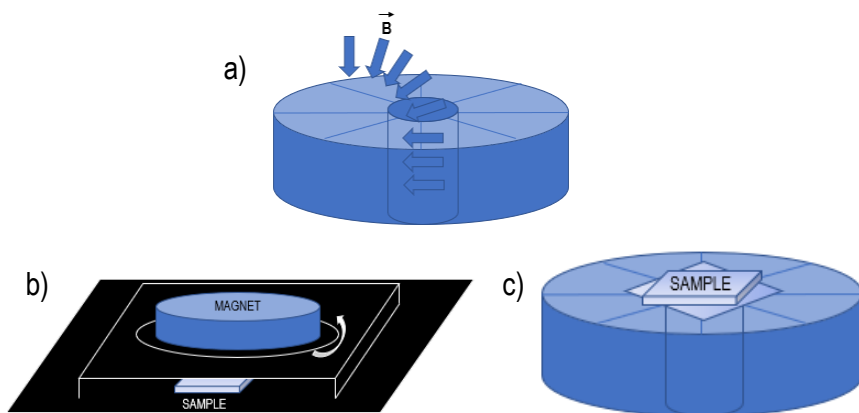


Figure 24. Simple representation of a) the direction of the magnetic field in the magnets used, b) the experimental assembly of the 400 mT magnet and c) the experimental assembly of the 1T magnet.

6. RESULTS AND DISCUSSION

6.1. EMULSIONS IN PDMS MICROFLUIDIC SYSTEM

6.1.1. Effectiveness of coatings in PDMS

In section 5.3.2 and 5.3.3 we have commented that, with the aim of being able to generate O/W or W/O emulsions, the PDMS channelling was covered with PVA or Aquapel. First, with the protocol where piranha solution is used to activate the surface it has not had satisfactory results since the solution, as we had already predicted, destroyed the walls of the channelling.

To address this problem, we decided to implement the plasma oxygen protocol, with satisfactory results. We determined that our protocol was useful due to the shape the LC gets once it is inside the channelling. If the LC has affinity for the coating of the channels, then its profile must be concave with a small contact angle, α , between the channel and itself. Otherwise, if it has no affinity, then it gets a convex profile with a big contact angle between the channel and itself. Due to 5CB is an oil, it has a poor hydrophilic character, so it must get a convex profile in hydrophilic conditions, while it has a concave profile in hydrophobic ones (figure 25).

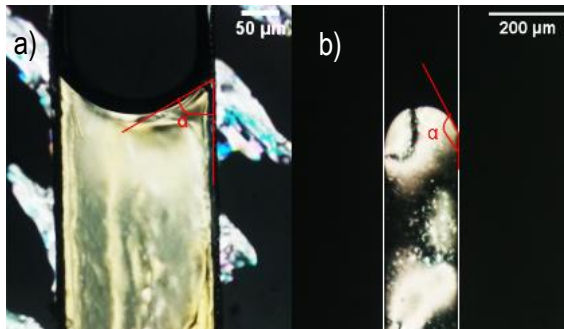


Figure 25. Effect of the coating on 5CB contact angle in PDMS surface. In a) Aquapel coating, hydrophobic conditions and in b) PVA coating, hydrophilic conditions.

6.1.2. Drops of Glycerol-water in 5CB

Since the function of this emulsion was to study the optimal conditions that would be needed in LCs emulsions, here the priority was to observe the best conditions to generate droplets of glycerol-water in 5CB.

By injection we failed to find a regime where droplets were formed, but by suction it was fruitful, at a rate of 21 nL/min (figure 26c). At higher rates, a jetting was formed instead of droplets, and at smaller rates the DP was not able to penetrate the junction to form droplets. Once we had achieved the formation of droplets, we had to study how stable they were, and we saw that droplets coagulated at the beginning of the storage chamber (figure 26a, 26b). This made us try to use a surfactant.

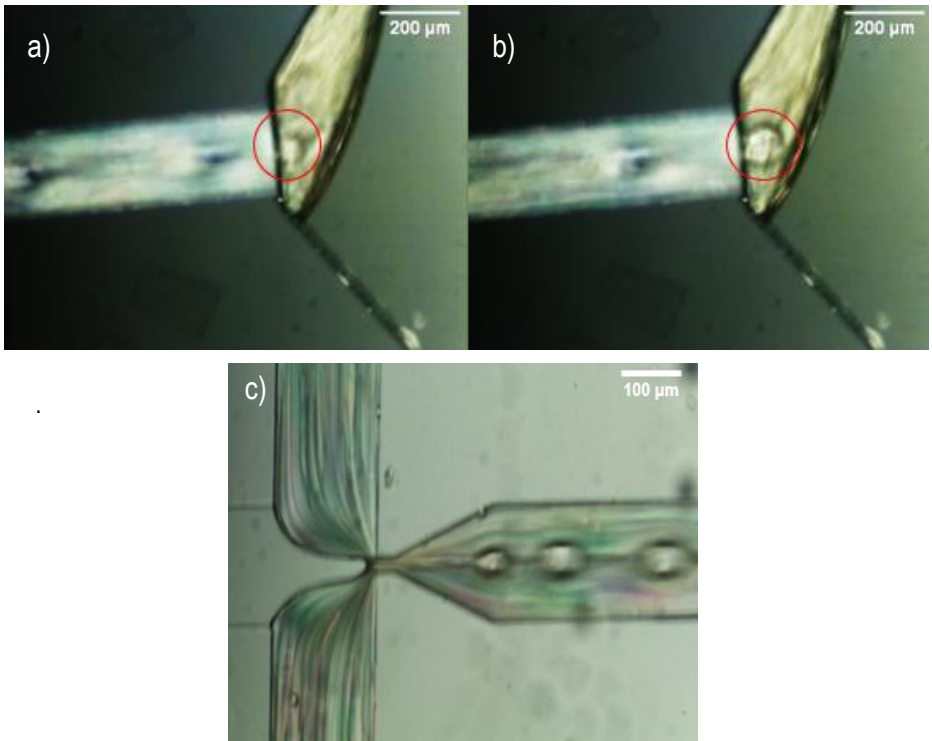


Figure 26. a) and b) Coagulation of the glycerol-water droplets at the beginning of the chamber. In c) droplets formation at 21 nL/min.

6.1.3. Drops of DSCG in 5CB

The injection method failed again to find a regime where droplets were formed. On the other hand, by suction a lower regime than that of glycerol-water, 11 nL/min, was found useful (figure 27).

The fact that we have had a minor flow rate has an explanation. DSCG has a higher viscosity than Glycerol-water mixture (600-700 cp in front of 45 cp).^{18,19} When a liquid flows through a capillary, a velocity gradient is generated, meaning that the speed of the liquid varies along the flow profile. In the centre of the capillary, the velocity is higher, while near the walls of the capillary, the velocity is lower due to this friction effect with the capillary surfaces. This means that the difference in speed between the centre of the capillary and the wall of the capillary is greater in a higher viscosity liquid compared to a lower viscosity liquid, so it suffers a higher shear stress for the same flow rate. From here we can conclude that the flow rate for dropping must be lower in liquids with higher viscosity, in this case DSCG.

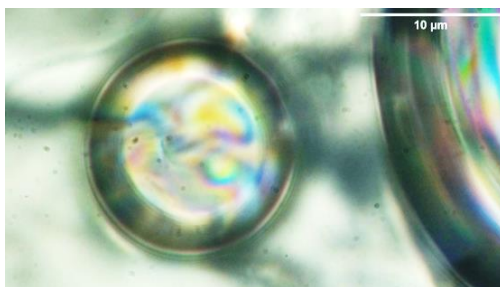


Figure 27. Droplet of DSCG in 5CB.

6.1.4. Drops of 5CB in SSY

Once these "tests" emulsions were made, 5CB drops were dispersed in SSY. A constant flow rate could be found at 1 nL/min. Although the viscosity of 5CB at room temperature is about 25 cP, we cannot compare it to previous cases because the CP is SSY in this case, while in other cases it was 5CB itself. Drops of relatively uniform sizes could be generated (figure 28), but as in section 6.1.2, they coagulate at the end of the camera or even on the channel.

A very small amount of surfactant SDS (less than 0.2% w/w) was added with the aim of stabilizing droplets, but in all cases, coagulation occurred along the channeling (This effect is explained in section 3.9.1).



Figure 28. Monodisperse-size formation of unstable 5CB droplets in SSY which finally have the tendency to coagulate.

6.1.5. Drops of SSY in 5CB

As in the case of 5CB in SSY, this is the reverse phase. A constant flow rate could be found at 21 nL/min, as in glycerol-water emulsions at 5CB, which reaffirms to us that making this test emulsion was a good decision.

As in all cases, we could generate droplets, but they were coagulated not only at the end of the camera but also in the middle of the channelling. By adding surfactant SDS (less than 0.2%), one coagulation jet was generated instead of forming droplets (figure 29).

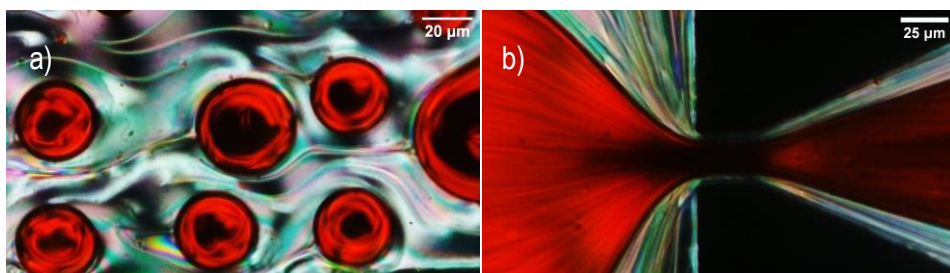


Figure 29. a) Monodisperse formation of SSY droplets in 5CB and b) formation of a coagulation jet in the channelling.

It was not possible to get the drops off, and it was not possible to transfer the drops that could be in a LC cell. Microfluidic has been shown to have the ability to generate droplets of monodisperse size but the method should be improved to be improved so droplets can be collected.

6.2. EMULSIONS IN LC CELLS

Due to the impossibility of isolating the droplets generated with the microfluidic system, the droplets were generated via the vortex emulsion generation protocol (section 5.4) and were transferred in LC cells to be studied (figure 22).

6.2.1. Configuration and defects of SSY in 5CB

In figure 30 we can see the textures of a bipolar drop configuration. The apparition of the boojums it is no appreciable due to the size of the droplet. If the droplets are too small, then the LC inside is able to organize itself in a conventional way, without showing some defects as consequence of the confinement.²⁰

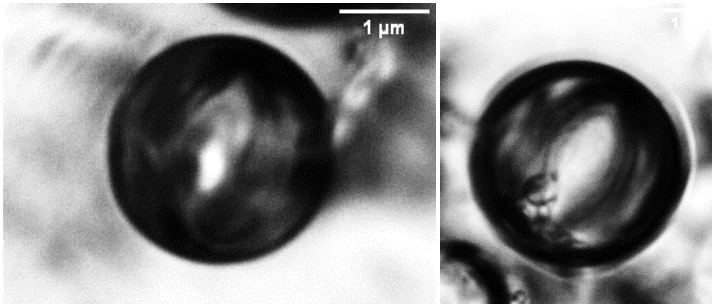


Figure 30. Bipolar configuration of SSY droplets in 5CB.

6.2.2. Configuration and defects of 5CB in SSY

As illustrated in figure 31, the drops exhibited two defects located at the ends of the principal axis, specifically known as boojum defects. Here we are able to observe the boojums since our droplets are at least 5 times bigger than the ones above.

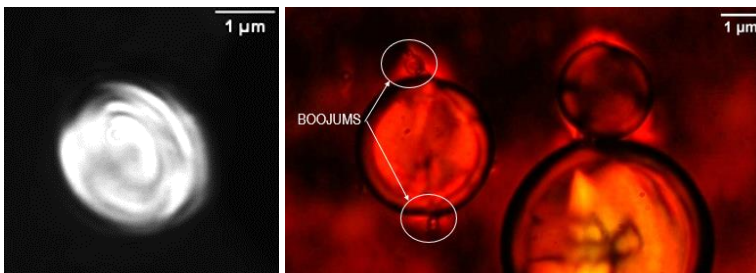


Figure 31. Bipolar configuration of 5CB droplets in SSY.

Now the question we could ask ourselves would be, why is this the configuration chosen by the LC inside the droplet? Well, first, we must be clear that the configuration a drop always takes is to minimize its energy. Section 3.8.1 specifies the type of deformations that an LC may suffer. As we see in table 1, both in SSY and in 5CB, deformations with smaller constants are splay and twist, so it will be the least energetic and the most stable^{21,22}. As described in section 3.8.1, when splay predominates the droplet, it adopts a configuration bipolar or radial. Since the anchoring on the droplet surface is planar, we have bipolar configurations.

Deformation (pN)	SPLAY (K1)	TWIST (K2)	BEND (K3)
SUNSET YELLOW	4.3	0.7	6.1
5CB	6.5	3.5	9.8

Table 1. Deformation constants of SSY and 5CB. (Values extracted from Zhou et. al. (Ref 22) and Iglesias et.al. (Ref 21)).

6.2.3. Configuration under external magnetic field

If we look at the behavior of 5CB droplets with the presence of an external magnetic field of 1T, we see a remarkable phenomenon. The 5CB droplet changes its configuration from bipolar to radial (figure 32).

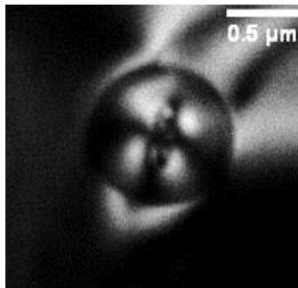


Figure 32. Radial configuration of 5CB droplet in 5CB after applying an external magnetic field, we can observe the Maltese cross in the middle of the droplet.

The change in the configuration of the droplet is due to competition from the applied magnetic field and anchoring that mesogens have at the SSY-Drop interface. When the droplet changes from bipolar to radial, it implies that mesogens change their planar anchoring to homeotropic, as the magnetic field is large enough.

According to the study "Hierarchical organization in liquid crystal-in-liquid crystal emulsions"¹⁸, to change the anchoring of a 5CB drop in DSCG requires 0.3 T, for the observed results, we can determine that under our conditions, the field value for changing the

anchoring is likely to be similar. This value also gives us an explication about why we do not see a change of the configuration with the 400 mT magnet so in the sample zone, the magnetic field is not large enough.

Analysing the behavior of SSY droplets in 5CB in front of a magnetic field observes a very interesting behavior. With the 400 mT magnet, no changes were observed in the sample, but in the 1 T magnet, the droplets tend to align their principal axis parallel to the external magnetic field (Figure 33).

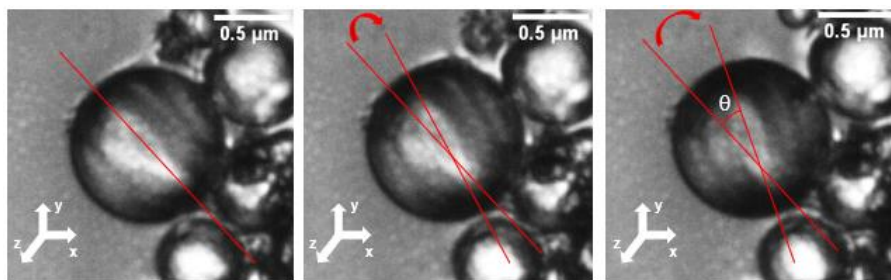


Figure 33. Alignment of the principal axis of the SSY droplet parallel to a magnetic field applied in y direction according to the reference axis. Note a rotation of the principal axis in clockwise direction.

When we apply an external magnetic field to an emulsion of SSY in an isotropic phase like a fluorinated oil, SSY rotates not only, but also changes its configuration from bipolar to concentric.²³ This change in configuration would involve a change in boundary conditions and thus in deformations and anchoring in order to stabilize the droplet structure. In our case, where we do not have an isotropic phase, but another LC as a CP, we do not observe this configuration change. This behavior leads us to believe that, maybe, the anchoring between the two LCs is stronger than the anchoring that SSY can have with the isotropic phase and therefore the droplet only rotates, but without changing its boundary conditions. The rotation effect is a direct cause of the negative magnetic anisotropy of the SSY stacks, which means that the perpendicular permeability constant domains de magnetic behavior of the stacks. As we can see in the figure 3, if the stacks have a perpendicular configuration, the molecules and in consequence, the principal axis of the droplet must have a parallel one. Therefore, although the stacks have a perpendicular tendency, the droplet align itself with the magnetic field.

10. CONCLUSIONS

In this work, we have been able to observe the behaviour of different types of LCs (thermotropic and lyotropic chromonic). SSY molecules are structured into stacks that form the proper nematic and columnar phases of the LCs. 5CB is a thermotropic LC of lower viscosity.

The study of emulsion generation via PDMS microchips has been satisfactory at certain points but has not contributed as much as would have been desired. It has been shown to achieve a monodisperse set of emulsion drop sizes, but they have not been stabilized despite various measures such as adding surfactant or coating on channelling walls. Nor has it been possible to generate droplets in microfluidic via direct injecting LCs, and it has been concluded that, by pushing, the shear stress minimum needed by LCs cannot be reached according to their rheology. However, a new functionalization protocol for PDMS chips has been implemented via O₂ plasma. As an improvement, one might venture to test new microfluidic methodologies such as needle-based chips (section 3.10.2).

Regarding observation of droplets in emulsion, 5CB and SSY droplets have been shown to adopt a bipolar-type configuration without the presence of a magnetic field due to the dominance of splay and twist as less energetic and thus more stabilized deformations. When the field is applied two different phenomena are observed. In the case of 5CB droplets in SSY, a change in the configuration of the droplet, from bipolar to radial, is observed. It results from the change of anchoring on the droplet surface, from planar to homeotropic. In the second case, SSY in 5CB, a rotation of the main axis of symmetry is observed to align with the magnetic field due to the negative magnetic anisotropy of the SSY stacks, but no change in the profile of the droplet is noticeable. It is possible due to the anchoring of the two liquid crystals in this emulsion being too strong to be changed by the applied magnetic field.

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12. ACRONYMS

LC: Liquid crystal

LCLC: Lyotropic chromonic liquid crystal

SSY: Sunset yellow

POM: Polarized optical microscopy

CP: Continuous phase

DP: Dispersive phase

APPENDICES

APPENDIX 1: EXPERIMENTAL MATERIAL USED

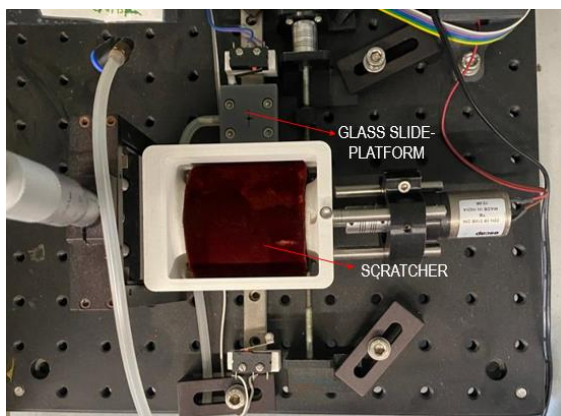


Figure 1. Scratcher machine.

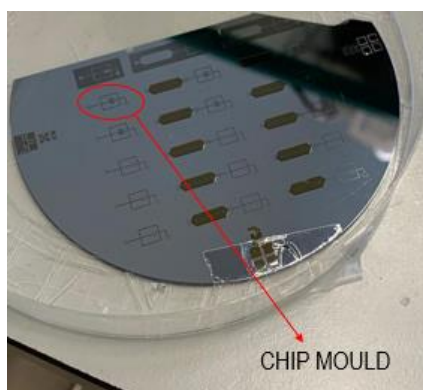


Figure 2. Chip mould design used to do PDMS chips.



Figure 3. Oxygen plasma device.

