INTRODUCTION

Unlike common lyotropics, chromonic mesophases are formed through the aggregation of non- amphiphilic molecules which have a plank-like or disk-like polyaromatic central core with polar groups at the periphery [1, 2]. Instead of forming micelles, those molecules stack on top of each other face-to-face to minimize the areas of unfavourable contact with water, leaving the ionic solubilizing groups at the aggregate/water interface. The mesogenic unit of chromonic mesophases are then columns of stacked molecules which lie in a continuum fluid. For certain values of temperature and concentration, the molecular stacks still exist in the Isotropic (I) liquid phase. The most common mesophases in chromonic liquid crystals are the uniaxial Nematic (N) phase and the hexagonal Columnar (C) phase. Between two phases, in a transition from one phase to another, a two-phase state where the initial and final phases coexist is observed. For example, in the process of obtaining the N phase by cooling of an I phase we can observe a N+I state where domains of nematic substance coexist with an isotropic environment. The N phase is characterized by an arrangement of stacked molecules which have a plank-like or disk-like polyaromatic central core with polar groups at the periphery [1, 2]. Instead of forming micelles, those molecules stack on top of each other face-to-face to minimize the areas of unfavourable contact with water, leaving the ionic solubilizing groups at the aggregate/water interface. The mesogenic unit of chromonic mesophases are then columns of stacked molecules which lie in a continuum fluid. For certain values of temperature and concentration, the molecular stacks still exist in the Isotropic (I) liquid phase. The most common mesophases in chromonic liquid crystals are the uniaxial Nematic (N) phase and the hexagonal Columnar (C) phase. Between two phases, in a transition from one phase to another, a two-phase state where the initial and final phases coexist is observed. For example, in the process of obtaining the N phase by cooling of an I phase we can observe a N+I state where domains of nematic substance coexist with an isotropic environment.

The N phase is characterized by an arrangement of the stacks along a certain direction defined by a vector \( \mathbf{n} \) called director, possessing no long-range positional order. This phase has cylindrical symmetry and has no polarity (\( \mathbf{n} = -\mathbf{n} \)). To quantify the orientational order of this phase we use the following quantity [3]

\[
S = \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right).
\] (1)

\( S \) varies between 1 (completely oriented sample) and 0 (isotropic sample) and is known as the nematic order parameter.

In recent years, increasing attention has been given to chromonics in view of their potential technological applications such as the production of biosensors in the detection of antigens and films with semi-conducting properties (see ref. [4] and references therein). Therefore, the study of their physico-chemical properties is a matter of concern and is currently an active topic of research.

Most studies reported in the literature have been focused on disodium cromoglycate (DSCG), a drug used on the treatment of asthma. However in the last years chromonic phases formed by ESY (whose molecular structure is shown in Fig. 1) have been a subject of both theoretical and experimental studies [5, 6]. Chami and Wilson reported results from molecular dynamics simulations that describe the dynamics and structure of aggregates of ESY molecules. Experimental works made use of techniques such as X-ray, optical microscopy and NMR (\(^1\)H, \(^2\)H and \(^23\)Na) spectroscopy [7–9]. Zhou et al. measured the temperature and concentration of the Frank elastic constants splay (\( K_1 \)), twist (\( K_2 \)), and bend (\( K_3 \)) [5] using a magnetic Frederiks transition technique in the nematic phase [6].

Recently, proton NMR relaxometry and pulse gradient NMR techniques were used to study the molecular dynamics in the chromonic nematic and isotropic phases of the binary mixture composed by Edicol Sunset Yellow and heavy water [10]. Here, we extend that work and we investigate the effect of sodium chloride and lithium chloride on the molecular dynamics of the same chromonic compound.

![Figure 1: Molecular structure and atom numbering of ESY.](image_url)
The works reported in the literature are not just focused on the characterisation of chromonic liquid-crystalline systems formed by aqueous solutions but also on the effect of the addition of salts. Investigation using X-Ray, optical, rheological, NMR and dielectric techniques were used to characterise the phase behavior and structure of the mixtures.

Kostko et al. investigated the addition of sodium and potassium salts to the nematic phase of DSCG [11]. Park et al., Jones et al. and Prasad et al. reported the addition of ionic compounds to the aqueous solution of ESY [8, 9, 12].

EXPERIMENTAL DETAILS

Samples Preparation

The objective of this work is to study the effect of salts on the structure and molecular dynamics of ESY’s I and N phases. To this end, we prepared three base solutions of ESY and heavy water (D$_2$O) with concentrations of 30.6 wt%, 27.8 wt% and 26 wt%. In the following, such solutions shall respectively be designated as ESY31, ESY28 and ESY26. The dissolution of ESY in D$_2$O was done in order to distinguish solvent from solute protons in the NMR measurements. Different amounts of NaCl and LiCl were dissolved in the three base solutions to form the samples ESYx+y+z, where x = 31, 28, 26, y designates the salt used in the mixture and z is the amount, in molalities, m (1 m = 1 mol/kg), of salt added (e.g.: ESY28+NaCl0.5 designates ESY+D$_2$O 27.8wt% + LiCl 0.5 m). The samples were placed in standard NMR tubes and flame sealed to avoid water evaporation.

According to the phase diagram present in ref. [7], at room temperature, ESY31 is in the N phase and both ESY28 and ESY26 are in the N+I phase. All the samples were stored at room temperature and no inhomogeneities appeared with time. However, it was detected that heating the ESY28 samples caused them to divide into two coexisting liquid crystalline phases. It must be noted that for the phase separation to take place, it was only necessary to heat the samples 2-5 °C above the room temperature.

Both ESY, NaCl and D$_2$O with a 99.98 percentage of $^2$H atoms were purchased from Sigma-Aldrich (Munich, Germany). LiCl was obtained through Merck Millipore (Darmstadt, Germany). The *chronomic* material was further purified according to the procedure described in [7]. Briefly, the product was dissolved in Milli-Q water with a resistivity higher than 18·MΩ·cm, followed by addition of ethanol. The dye precipitate was recovered and purificated by the spin I of the observed nuclei. The *external interactions* arise due to mutual influence of the nuclei’s electric charges and magnetic moments. A remarkable feature of NMR is that these interactions are usually much weaker than the Zeeman interaction B$_0$ and establishes a set of energy levels completely defined by the spin I of the external field. The *external interactions* are given by the Zeeman Hamiltonian describing the interaction with an external constant magnetic field B$_0$ and establishes a set of energy levels completely defined by the spin I of the observed nuclei. The *external interactions* arise due to mutual influence of the nuclei’s electric charges and magnetic moments. A remarkable feature of NMR is that these interactions are usually much weaker than the Zeeman interaction B$_0$ and establishes a set of energy levels completely defined by the spin I of the observed nuclei.
where $S$ is the order parameter and $\phi$ is the angle between $\mathbf{n}$ and $\mathbf{B}_0$. $r_{ij}$ is the distance between nuclei $i$ and $j$. The quantity $\beta_i$ is the polar angle that defines the position of the inter-nuclear vector in the molecular frame.

The dominant internal interaction for a spin with $I > 1/2$ is the interaction between the nuclei and the involving electronic environment (Quadrupolar Coupling). For an Uniaxial N phase, this interaction causes the following splitting [15]:

$$
\Delta \nu_{ij} = \frac{3}{4} C_{i,Q} \left( \frac{3 \cos^2 \phi - 1}{2} \right) \sqrt{\frac{3}{2} \cos^2 \beta_i - \frac{1}{2}} S. \quad (4)
$$

As before, $S$ is the order parameter and $\phi$ is the angle between $\mathbf{n}$ and the magnetic field. $C_{i,Q}$ is the strength of the electric field gradient felt by the nucleus $i$ and $\beta_i$ is the polar angle that defines the position of such gradient in the molecular frame.

**$^1H$ Spectroscopy**

Inspection of Fig. 2 shows us that each phase possesses a clearly distinct NMR spectrum. In the I phase (Fig. 2(a)) no splitting is observed and the spectrum consists of various peaks corresponding to the chemical shifts of different $^1H$. The spectrum of the N phase (Fig. 2(b)) is characterized by the existence of two, almost symmetric, broad peaks caused by the dipolar splitting. The broad nature of such peaks is attributed to the the inter-proton distance. Because all the $^1H$ nuclei have a similar first-neighbour distance (in the 2.44-2.50 Å range [7]), their spectra overlap, causing the observed broadening. When the sample is in the N+I phase (Fig. 2(c)), the observed spectrum consist in an overlapping of the spectra characteristic to the N and I phases.

![Figure 2: Typical $^1H$ spectra of the I, (a), N, (b), and N+I, (c), phases of ESY.](image)

Due to J-Coupling effects each one of the lateral peaks consists in a combination of two doublets and a triplet. The doublets result from three pairs of protons, one from $H_{24}-H_{25}$ plus $H_{26}-H_{27}$ and another from $H_{19}-H_{20}$; the triplet is due to $H_{21}-H_{22}-H_{23}$. Because they overlap, it is difficult to identify and distinguish the doublets. The two outer peaks of the 1:2:1 triplet can however be identified as the two smaller peaks in the extremes of the spectrum. Following the procedure of Edwards et al. [7], the $\Delta \nu_{ij}$ values were measured as being half of the separation of those two smaller peaks.

The measured $\Delta \nu_{ij}$ values can be related to the ESY mesophases’ orientational order through Eq. (4) with $\phi = 90^\circ$ due to the negative anisotropy of the diamagnetic susceptibility of ESY. Because the measured splitting results from the interaction of $H_{22}$ with both $H_{21}$ and $H_{23}$, $\Delta \nu_{ij}$ is calculated as an average of the splittings caused by $H_{21}-H_{22}$ and $H_{22}-H_{23}$. According to Edwards et al. [7], the distances of those $^1H$ pairs, $r_{21,22}$ and $r_{22,23}$, have constant values of 2.44 Å and 2.48 Å, respectively. In the same ref. [7] it is also considered that $\beta_{21,22} = \beta_{22,23} = 90^\circ$.

**$^{23}Na$ Spectroscopy**

As expected, the $^{23}Na$ spectrum of an ESY sample in the I phase consists in a single Lorentzian distribution. In the N phase, the anisotropy of the electric environment creates a quadrupolar splitting related to the order parameter through Eq. (4). For a sample in a macroscopically aligned state, the N phase spectrum consists of $2I$ equally spaced lines corresponding to the various $m \rightarrow m + 1$ transitions, whose intensities are roughly proportional to $I(I + 1) - m(m - 1)$. In the case of a $^{23}Na$ spectrum we have three lines with a 3 : 4 : 3 ratio.

As before, the N+I phase spectrum is an overlapping of the N and I phases’ spectra. Considering that such spectrum is just a linear combination of a N phase spectrum and an I phase spectrum, we can define the following quantity

$$
Q_{iso} = \frac{1}{3} \left( \frac{5 - 2}{A_{cp}} \right). \quad (5)
$$

where $A_{cp}$ is the central peak area normalized to the total area. The quantity $Q_{iso}$ varies between 1 and 0 and evaluates the quantity of material in the I phase.

To describe the $^{23}Na$ splitting we resort to the ion condensation model. Developed for the study of counterion binding in polyelectrolytes [16], this model distinguishes between weakly bounded ions, termed as “free”, and strongly bound counterions, termed as “bound”. The fraction of “bound” ions is considered to be independent of water content, temperature and addition of simple salts [15, 17]. These ions experience a much more intense electric field gradient, making their contribution to $\Delta \nu_{ij}$ is the dominant one. Since the ion condensation model is normally consistent with the assumption of a single binding site [15, 17], Eq. (4) can be approximated by [15, 17]:

$$
\Delta \nu_{ij} = p_b \Delta \nu_{b,q}, \quad (6)
$$

where $p_b$ is the fraction of “bound” counterions and $\Delta \nu_{b,q}$ is the corresponding splitting. Although the number of “bound” counterions is typically consistent with the neutralization of ~70% of the stacks’ charge, the exact value of $p_b$ is not known. Because the value of $C_{i,Q}$ depends on
the detailed structure of the binding site [15], such quantity is also not known. Thus, Eq. (6) cannot be used to calculate \( S_{zz} \) and only a qualitative or comparative analysis can be done through it.

**Results and Discussion**

**Analysis of the Phase Separation**

As pointed before, by heating a sample of ESY28 one induces a macroscopic phase separation between two phases. This phase separation was visually detected by noting that the heating process caused the sample to divide itself in two regions with distinct colors, as illustrated in Fig. 3(a). The origin of the separation is unclear and, to the author’s knowledge, as of yet there are no reports of its existence in pure solutions of ESY.

![Figure 3: Fig. (a) represents the phase separation of the N+I phase. The darker area corresponds to the more ordered part while the lighter area corresponds to the less ordered part. The difference in colors was exaggerated for clarity. Figs. (b) and (c) illustrate two ways of positioning the phase-separated sample in the NMR coils. In (b) only the ordered part is involved by the coils while in (c) all the material is involved.](image)

To study the phase-separation process, we placed an ESY28 sample in the NMR spectrometer at 25 °C over a period of 140 minutes. During this period the sample was also subjected to a magnetic field of 2.1 T. By measuring a \(^{23}\text{Na} \) NMR spectrum every 5 minutes, it was possible to track the time-evolution of the sample’s phases. The results of this procedure are present in Fig. 4(a) which shows the time variation of \( Q_{iso} \).

![Figure 4: (a), time evolution of the \( Q_{iso} \) values during the phase separation process. The two colors represent two ESY28 samples placed in the spectrometer in two distinct ways. (b), \(^{1}\text{H} \) spectra of the same samples represented in (a) in their phase-separated state. The two colors have the same meaning as in (a). See text for details.](image)

The different colors in Fig. 4(a) identify two distinct samples, placed in the spectrometer in different ways. Both samples were not previously submitted to any measuring or heating event of any kind. Samples with such history shall henceforth be referred to as fresh. The data in blue was obtained for a sample positioned in a way where only its bottom part was involved by the detection coils (see Fig. 3(b)). The points in red describe the totality of the material present in the NMR tube (see Fig. 3(c)). The blue data decreases monotonically until it reaches a point compatible with \( Q_{iso} = 0 \), after which it stays constant within the experimental uncertainty. This evolution shows that the bottom part of the sample condenses into a N phase after, approximately, 1 hour. On the other hand, the red data stays approximately constant for the entire duration of the experiment. Thus, the phase separation process does not alter the total quantity of ordered material. The identification of the two phases as a N+I (all tube) and N (bottom of the tube) was confirmed via \(^{1}\text{H} \) spectroscopy (see Fig. 4(b)).

While performing the aforementioned experiments, we detected no variations of quadrupolar splitting. Both the bottom part and the whole sample kept a constant \( \Delta \nu_q \) during the demixing process. This fact shows that, despite the increase in ordered material at the bottom of the tube, the degree of order is not affected by the phase-separation.

The repetition of the above experience for an ESY31 sample in the N+I phase yielded the same results. In a separate experiment an ESY28 sample was left in a thermal bath at 25 °C for 140 minutes. No magnetic field of any kind was applied to the sample before the NMR measurements. Since the results of this experience were consistent with the ones where the sample was placed in a magnetic field, we see that the field does not influence the phase separation.

The above results indicate that the N+I phase is metastable, being destroyed by a heating process. The destruction of the homogeneous biphasic state is caused by a nucleation process where increasingly larger droplets of ordered material are formed [18]. Because the N material has a higher density, after a certain critical size the droplets suffer a gravity-induced flow to the bottom of the tube, thus explaining the observed phase-separation.

To study the variation of the quadrupolar or dipolar splittings with temperature, the typical procedure is to heat the samples until the I phase is achieved, and to perform the measurements while reducing the temperature. After a temperature cycle where proton spectra were acquired, we noticed that the splitting at room temperature was greater than the value recorded before heating the sample. To study this effect in more detail we submitted a fresh sample of ESY28 to various temperature cycles and measured its \(^{23}\text{Na} \) NMR spectra during such cycles. In Fig. 5 we can see the evolution of \( \Delta \nu_q \) with those cycles.

![Figure 5: Inspection of Fig. 5 shows that the quadrupolar splitting increases with the number of cycles until saturation is achieved at the fourth cycle. A sample whose splitting no longer presents a significant dependence on the temperature cycles is denoted as “saturated”. The phase transitions temperatures were determined from \( Q_{iso} \) within an error of 1.25 °C. It appears that the number of cycles influences the temperature of the I \( \rightarrow \) N+I transition but not the temperature of the N+I \( \rightarrow \) N transition.](image)
Addition of salts

Fig. 6 shows the $^1$H and $^{23}$Na spectra of ESY28, ESY28+NaCl0.5 and ESY28+LiCl0.5. All the spectra correspond to a N phase.

It is seen that the addition of NaCl or LiCl causes a reduction of the dipolar and quadrupolar splittings. According to Eq. (3), the decrease in $\Delta \nu_d$ results from a decrease in orientational order. The decrease in $\Delta \nu_q$ is also consistent with a reduction of the order parameter.

The similar values of $\Delta \nu_d$ of ESY28+NaCl0.5 and ESY28+LiCl0.5 indicate that the two salts have a similar effect on the orientational order of ESY28. Thus, the fact that the quadrupolar splitting of ESY28+LiCl0.5 is smaller than the quadrupolar splitting of ESY28+NaCl0.5 is rather remarkable as both samples appear to have the same value of $S_{zz}$. It is possible that the Li$^+$ ions, smaller than the Na$^+$ counterions, may penetrate through the layer of “bound” Na$^+$. This process could cause a displacement of the sodium ions, with the Li$^+$ ions assuming the old positions of the “bound” Na$^+$ ions. Such behaviour may lower the strength of the quadrupole coupling due to effects of shielding or even reduce the number of “bound” sodium ions, thus explaining the smaller $^{23}$Na splitting of ESY28+LiCl0.5.

We now focus on the variation of orientational order with temperature. In Fig. 7 we can see the effect of temperature on the $^1$H and $^{23}$Na splittings of an ESY28 sample. Those spectra were obtained for a saturated sample which, at ~ 25°C, was positioned according to Fig.

Figs. 7(a) and 7(b) show that both splittings decrease slightly with a temperature increase. The variation of $\Delta \nu_q$ with temperature is similar to the variation of $\Delta \nu_d$, which reinforces the validity of the ion condensation model and suggests that the variation is created by small changes in aggregate ordering. Another noticeable feature of Fig. 7 is the high phase transition temperatures, which are incompatible with the ones reported in ref. 7. The higher transition temperatures are explained by the positioning of the sample, which focus the analysis on the ordered material at the bottom of the phase separated state.

The data showed in Fig. 7 was fitted to the Haller approximation [19]:

$$S_{zz}(T) = S(T) = S_0 \left(1 - \frac{T}{T_c}\right)^\beta,$$ (7)

where $S_0$ is a constant scaling factor and $\beta$ is a material constant. $T_c$ is the temperature, in Kelvins, at which the studied material changes phase. The fits were performed by considering the points belonging to a N phase and the points of the N+I phase with $Q_{iso} \leq 0.5$. The considered phase transition was the I$\rightarrow$N+I one, $T_c = T_{I \rightarrow N+I}$. This procedure simulates the behaviour of a thermotropic nematic and facilitates the comparison with that type of liquid crystals.

The splittings from the $^1$H and $^{23}$Na spectra of ESY28 were simultaneously fitted to Eq. (7) considering a common exponent $\beta$. In such fit, the temperatures $T_c = T_{I \rightarrow N+I}$ were fixed to our measurements. This procedure resulted in $\beta = 0.12 \pm 0.07$, a value slightly smaller than the ones obtained for typical thermotropic liquid crystals, $\beta = 0.16 - 0.19$ [20]. The smaller exponent indicates that the orientational order of chromonics depends less on the temperature.

Fig. 8 simultaneously displays the temperature-evolution of the $^{23}$Na splitting of ESY28, ESY28+NaCl0.5 and ESY28+LiCl0.5. The displayed data corresponds to saturated samples which, at ~ 25°C, were positioned according to Fig. 3(b) All the spectra were measured on cooling.

Inspection of Fig. 8 reveals that the samples with salts present the same qualitative features as ESY28, namely, a small variation with temperature. As before, we fitted the data to Eq. (7) to analyse their temperature. Such fits yielded $\beta = (1.51 \pm 0.08) \times 10^{-1}$ and $\beta = (1.46 \pm 0.09) \times 10^{-1}$ for ESY28+NaCl0.5 and
ESY28+LiCl0.5, respectively. Since the exponents for the salted solutions are higher than the unsalted one, it appears that the presence of additives increases the temperature dependence of the order parameter.

Fig. 8 shows that the addition of NaCl or LiCl increases the phase transition temperatures. The same figure also shows a salt-induced reduction of $\Delta \nu_q$ consistent with our previous discussion. It appears that the NaCl and LiCl have two seemingly inconsistent effects: a stabilization of the ordered phases and a reduction of the degree of order, represented by the order parameter. To better understand this effect we discuss in some detail the effects of the salts in the mesophases structure.

The main effect of ionic additives on polyelectrolyte solutions is the screening of electrostatic repulsive forces. In the case of ESY solutions, there are two types of electrostatic repulsions, those who act between molecules of the same stack and those who act between molecules of different stacks. In ref. [21] it is proposed that the salt-induced screening of electrostatic repulsions increases the aggregates’ length, $L$, and enhances their flexibility. The increase in flexibility is equivalent to a shortening of the persistence length $l$, the characteristic distance between two different parts of the aggregate that are correlated.

The increase of $L$ and the decrease of $l$ induce two competing effects on the orientational order; while the former promotes it, the latter represses it. We then have two opposing trends whose interplay may explain the salt-induced reduction of the order parameter and the salt-induced increase of the phase transition temperatures. The effects of varying the aforementioned lengths on the chromonic’s phase diagram was analysed using the model developed by Khokhlov and Semenov for semiflexible polymers [22]. According to such model, an increase of $L$ coupled with a decrease of $l$ may only cause the experimentally observed effects if the aggregates are rigid ($L/l \ll 1$).

Transposing the previous ideas to the ESY aggregates, it is suggested that the stacks are rigid entities who are elongated and turned more flexible by the addition of salts. The elongation turns the ordered phases more stable due to excluded volume effects while the higher flexibility reduces the order parameter due to a loss of correlation that creates several independent angles $\theta$ along the aggregates, thus affecting the average in Eq. (1).

must be noted that our observations paint a more dynamic picture than the one laid down by Park et al. [20]. In ref. [21] it is proposed that the opposing trends result in two concentration dependent zones: for higher concentrations of ESY the salts suppress the orientational order and for lower concentrations of ESY the salts promote it. However, our measurements show that, even for low concentrations, the orientational order is, to some extent, destroyed as the order parameter is lowered.

**RELAXOMETRY**

**Relaxation Mechanisms and Models**

Based on the assumption that the molecular motions present in a liquid crystal are statically independent or otherwise are characterised by distinct correlation times, the experimental relaxation rate $R_1$ is usually assumed to be described by a linear combination of relaxation contributions, each one associated with a specific type of motion. Cross-terms can be neglected as the characteristic correlation times associated with those motions are usually considerably different. Then, the total relaxation rate can be expressed as

$$R_1 = R_{1,C} + R_{1,IM}$$

where C and IM refer to collective motions and individual molecular motions, respectively.

Here, we summarise the relaxations models used to describe the results. More details can be found in refs. [23, 24].

**Individual Molecular Motions**

Individual molecular motions can be separated into: molecular rotations and translation displacements of molecules by diffusion processes. To describe the rotations we used the Woessner model [24, 25] while for the translation motions we used the model proposed by Torrey [24, 26] for isotropic liquids.

The model proposed by Woessner considers the relaxation induced by reorientations of rigid elongated molecules. This model accounts for the anisotropic nature of a certain molecule by considering rotations along two different axes. The spectral densities are given by:

$$J_k(\nu) = \frac{4}{3} c_k \sum_{m=-2}^{2} \frac{|D^2_{km}(\beta_{ij})|^2}{r_{ij}^6} \langle |D^2_{km}(\theta)| \rangle \frac{\tau_{|m|}}{1 + 4\pi^2 \nu^2 \tau_{|m|}^2},$$

where $r_{ij}$ are the inter-proton distance ($\sim 2.5$Å for the first neighbours of an ESY molecule, according to ref. [2]) and $\beta_{ij}$ denotes the angle between the inter-proton vector and the long molecular axis. $D^2_{km}$ is the second rank Wigner rotation matrix and the averages $\langle |D^2_{km}(\theta)| \rangle$ can be expressed in terms of the second and fourth rank Legendre polynomials of the angle between the long molecular axis and the nematic director [24]. $D^2_{km}(\beta_{ij})$ is the second rank reduced Wigner rotation matrix.

The correlation times, $\tau_{|m|}$, can be expressed as $\tau_0 = \tau_s$, $\tau_1 = (\tau_s^{-1} + \tau_f^{-1})^{-1}$, and $\tau_2 = (\tau_s^{-1} + 4\tau_f^{-1})^{-1}$. $\tau_f$ and
tau are two distinct correlation times that usually correspond to molecular reorientations about an axis parallel and perpendicular to the long molecular axis, respectively. In the present work, the times tau_f and tau_c correspond to reorientations parallel and perpendicular to the packing axis.

According to the Torrey model the relaxation rate can be written as:

\[
\left( \frac{1}{T_1} \right)_{\text{Diff}} = C_D \frac{nT_D}{d^3} \left[ J(\nu) + 4J(2\nu) \right],
\]

where the dimensionless spectral density J(\nu) can be calculated analytically [23]. C_D is the magnitude of the dipolar interaction, tau_D is the average time between diffusion jumps, d is the molecular width, n is the density of \(^1\)H spins. The mean-square jump distance \(\langle r^2 \rangle\) is related with the self-diffusion constant \(D\) and tau_D by the relation \(\langle r^2 \rangle = 6tau_D D\) [23] [24].

Collective Motions

In the nematic phases of thermotropic and lyotropic liquid crystals the collective motions are fluctuations of the director in three orthogonal directions and are known as Order Director Fluctuations (ODF). However, considering that the mesogenic units of a chromonic nematic phase are molecular stacks, it was shown that the collective motions of such phases are described by Elastic Column Deformations (ECD) [10]. The corresponding spectral density is [27]

\[
J_{\text{ECD}}(\nu) = \frac{kT\eta}{2\pi^2} \int_{q_{\perp,1}}^{q_{\perp,h}} \int_{q_{||,h}}^{q_{||,l}} dq_{\perp} dq_{||} \times \frac{q_{\perp} q_{||}^4}{(2\pi \nu^2 \eta^2 q_{||}^4 + (K_3 q_{||}^4 + B q_{\perp}^2)^2}.
\]

\(\eta\) is an average effective viscosity and the quantities \(q_{\perp,1}\) and \(q_{||,h}\) are the components of the largest wave vectors of the deformation parallel and perpendicular to the columns, respectively. The shortest wave vectors are \(q_{\perp,1}\) and \(q_{||,l}\). High and low cut-off frequencies can be defined in terms of the limit wave vectors and the viscoelastic constants.

Close to the temperature of the I\(\rightarrow\)N transition, short-range nematic order can be found in the I phase. Fluctuations of that local order, known as Order Parameter Fluctuations (OPF), can contribute to the spin-lattice relaxation. The resulting spectral density is [23] [24]:

\[
J_{\text{OPF}}(\nu) = A_{\text{OPF}} \int_{\nu_{\text{min}}}^{\nu_{\text{max}}} \frac{\sqrt{x}}{(2\pi\nu^2 + (x + \nu_0^{-1})^2)},
\]

with \(\nu_0 = \nu L^2 / \ell\) where \(\nu\) is an average effective viscosity and \(\ell\) is the coherence length of the fluctuations. The limits in the integral are related to the minimum and the maximum wave vectors and \(A_{\text{OPF}}\) is a constant related with the viscoelastic properties of the liquid crystal in the isotropic phase. In ref. [10], it was shown that OPF contribute significantly to the spin-lattice relaxation of ESY in the I phase.

Results and Discussions

**Nematic phase**

The Nuclear Magnetic Relaxation Dispersion (NMRD) profiles for the samples ESY28, ESY28+NaCl0.5 and ESY28+LiCl0.5 at 15 °C are displayed in Fig. 9. Such temperature corresponds to the N phase for all the samples. The inset of the same figure displays the NMRD profiles of ESY28 and of the ESY+D_2O solution at 30 wt% (ESY30) analysed in [10]. The ESY28 profile was obtained at 15 °C and the ESY30 profile was obtained at 23 °C; both temperatures correspond to a N phase.

Comparison of the two profiles displayed in the inset of Fig. 9 shows that they possess a qualitatively similar behaviour. Despite the similarities between the NMRD profiles of ESY28 and ESY30, they have some differences at intermediate and low frequencies (\(\lesssim 10\) MHz); at high frequencies the two profiles look identical.

The NMRD profiles showed in Fig. 9 present a rather small dependence on the presence of the salts. In fact, at high frequencies the data sets overlap. The minor differences are observed at intermediate frequencies (1-10 MHz) and at low frequencies (below 50 kHz). Despite the small differences in the the NMRD profiles, the \(^1\)H NMRD of the same samples clearly shows a reduction of orientational order induced by the addition of salts.

In order to interpret the \(R_1\), a fit was performed using Eq. [8] and a home written minimization software package [29]. For a detailed analysis the two individual motions contributions in \(R_{1,1M}\) are shown separately. Based on the fact that the profiles of ESY28 and ESY30 coincide at high frequencies, the fit of the former was carried out by fixing the value of \(\nu_{\text{f}}\) to the corresponding one of ESY30 at 23 °C from ref. [10]. Also, the self-diffusion coefficient was extracted from the same work as an extrapolation to 15°C. The fitted experimental data are presented in Fig. [10] together with the separate contributions of the proposed dynamic mechanisms to the total \(R_1\).

The results of the fitting parameters are displayed in Table I, where \(A_{\text{ECD}}\) corresponds to the magnitude of the ECD model and is related to the sample’s viscoelastic
properties, $A_{\text{ECD}} \propto \eta/(B K_3)$. The errors displayed in all the tables of this chapter are not the typical fitting errors. Due to the inter-dependence of the fitting parameters, their errors have a magnitude much higher than it would be physically expected. To estimate the error of a certain fitting parameter, we performed fits where only that one parameter was left as free in order to estimate its fitting error. Such procedure allows us to analyse the impact of a specific fitting parameter to the global fitting quality within a $\sim 68\%$ confidence level [30].

Table I: Details of the fitting parameters according to the proposed models to describe the frequency dependence of $R_1$ for the samples ESY28, ESY28+NaCl0.5 and ESY28+LiCl0.5 in the nematic phase at 15 °C. * Fixed from [10]. The values between parenthesis were obtained when those parameters were included in the fit (see text for details).

<table>
<thead>
<tr>
<th></th>
<th>ESY28</th>
<th>ESY28+NaCl0.5</th>
<th>ESY28+LiCl0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$ [×10⁻⁹ s]</td>
<td>1.2±(1.2 ± 0.2)</td>
<td>1.9 ± 0.4</td>
<td>1.6 ± 0.3</td>
</tr>
<tr>
<td>$\tau_2$ [×10⁻⁹ s]</td>
<td>4.1 ± 0.5</td>
<td>6.2 ± 0.2</td>
<td>4.7 ± 0.5</td>
</tr>
<tr>
<td>$A_{\text{ECD}}$ [×10³ s⁻¹]</td>
<td>13.5 ± 0.6</td>
<td>96 ± 5</td>
<td>338 ± 17</td>
</tr>
<tr>
<td>$D$ [×10⁻¹³ m²/s]</td>
<td>5.5±(5.5 ± 0.7)</td>
<td>4.7 ± 0.6</td>
<td>4.3 ± 0.6</td>
</tr>
<tr>
<td>$\xi$ [×10⁻⁹ m]</td>
<td>1.2 ± 3</td>
<td>0.9 ± 1.3</td>
<td>0.8 ± 0.5</td>
</tr>
<tr>
<td>$S$</td>
<td>0.59</td>
<td>0.56</td>
<td>0.56</td>
</tr>
</tbody>
</table>

From the cut-off frequencies associated to ECD we can estimate the ratio $\sqrt{\omega_{nc}}/\omega_{cl} = \xi/\ell$. $\ell$ and $\xi$ are, respectively, the smallest and largest domains where coherent motions occur. In the case of ESY, $\ell$ is equal to the stacking distance. Using $\xi$ as a fitting parameter we estimate a coherence length compatible with stacks of 5 ± 2, 3 ± 2 and 4 ± 1 molecules for ESY28, ESY28+NaCl0.5 and ESY28+LiCl0.5, respectively. Those values are consistent with the aggregation number of 11 molecules reported by Park et al. [8], and with the values reported by Cachitas et al. [10].

The fact that only a few molecules are involved in the collective motion indicates that this type of movements involves a correlation between molecules of the same mesogenic unit, instead of correlations between mesogenic units. This behaviour is clearly different from the collective motions of a typical thermotropic liquid crystal, which consist of correlations between mesogenic units.

Our fits show the same features as the ones reported in ref. [10]. Namely, collective motions composed of correlated movements within the stacks and individual motions composed of intra-stack translation diffusion processes and anisotropic reorientations. Reorientations along the stacking axis were found to be faster than reorientations perpendicular to it.

The decrease of the self-diffusion coefficient in the samples with salt agrees with the finding of an increase of the viscosity of the ESY solutions with the addition of salts reported by Prasad et al. [12]. A salt-induced increase of the correlation times for the rotations/reorientations is also observed. The fact that ESY28+NaCl0.5 and ESY28+LiCl0.5 have different times $\tau_s$ might be related with the differences between the two ions in the equilibrium and stabilisation of the ESY stacks.

As seen before, the addition of salts decrease the coherence length $\xi$. Another effect of the salts on the ECD is an increase of $A_{\text{ECD}}$. The decrease of both the coherence length and the elastic constants, suggests an increase of the stacks’ flexibility with the addition of salts. A higher flexibility leads to a diminution of the free energy needed to distort the stacks and may reduce the coherent molecular motion to smaller domains, thus explaining our observations. This picture is consistent with the discussion present in ref. [21], where it is argued that the addition of salts may lead to a reduction of the aggregates’ persistence length. In ref. [31], Zhou et al. report a decrease of $K_3$ caused by the addition of NaCl to an ESY solution, a fact that also supports our analysis.

Isotropic phase

Fig. 11 displays the $R_1$ dispersion profiles of ESY26, ESY26+NaCl0.5 and ESY26+LiCl0.5 at 50 °C. The inset of that figure shows the NMRD profiles of the ESY26 sample and the ESY+D₂O solution at 24 wt% (ESY24) analysed in [10]. All the samples represented in the inset are in the I phase. It can be observed that the spin-lattice relaxation profile of ESY26 is very similar to the one of ESY24 at 43 °C. ¹H NMR spectra of ESY26, ESY26+NaCl0.5 and ESY26+LiCl0.5 show that, at 50 °C, the addition of salts causes the sample to undergo a phase transition from an I phase into a N+I phase. The quantity of nematic material is however so low (~1%), that both ESY26+NaCl0.5 and ESY26+LiCl0.5 will be treated as being in an I phase.

Contrary to the N phase, the NMRD profiles of the I phase are clearly affected by the presence of salts. For frequencies below 1 MHz, the solutions with salts have significantly higher values of $R_1$ than ESY26; in the interval 1-10 MHz, we can also observe some differences. Above 10 MHZ, the profiles are identical within the experimental uncertainty of ± 5%.

In Fig. 12 are presented the fits performed using model Eq. [8] and considering the presence of OPF. Since the self-diffusion relaxation mechanism presents a small contribution to the relaxation, the value of the self-diffusion constant was fixed to that measured for ESY24 at 43 °C in ref. [10]. As the $R_1$ profiles in the high frequency regime are similar, it is reasonable to consider that the fast molecular motions in the three samples are characterised by similar correlation times. In fact, very good fits were obtained using the same correlation time $\tau_s$. The fitting parameters are presented in Table [11]. Once again, the errors are not the fitting errors, but estimates made by fitting the data with the other parameters fixed.

Both OPF and molecular rotations provide significant contributions to the fit. The first relaxation mechanism is the most important one at lower frequencies (<800 kHz), the second mechanism dominates the high frequencies domain. These characteristics are consistent with the ones reported in ref. [10].

The effect of the presence of salts in the molecular dynamics are observed at frequencies below 10 MHz. Such region is where order parameter fluctuations and reorientation of the molecules about an axis perpendicular to the stacks’ axis most affect the relaxation dispersion. Accordingly, inspection of Table [11] shows us that the ad-
It is presented a NMR study of a set of ESY solutions with differing concentrations covering the Nematic (N), Isotropic (I) and biphase (N+I) phases. Additional samples were prepared by adding 0.5 mol/kg of NaCl and LiCl salts in order to understand the effects of the presence of the additional Na\(^+\) and Li\(^+\) ions in the system. \(^1\text{H}\) and \(^23\text{Na}\) NMR spectroscopy were used to measure the temperature dependence of the orientational order of the neat and doped with salts ESY samples. Proton NMR relaxometry was used to probe the molecular dynamics of the N and I phases of the samples.

It was observed that a slight temperature variation caused the N+I phase to separate itself into two distinct macroscopic domains. Spectroscopy measurements showed that the phase separation does not affect the order parameter and identified the more ordered domain as being a N phase. This behaviour was found to be an intrinsic property of the biphase state caused by its metastability. It was also found that successive heating-cooling cycles increase the orientational order of the mesophases. \(^1\text{H}\) and \(^23\text{Na}\) spectra showed that the presence of small amounts of NaCl and LiCl induce two effects on the chromonic mesophases of ESY28: stabilization of the ordered phases, evidenced by an increase of the N+I→N and I→N+I transition temperatures, and reduction of the amount of order, evidenced by a decrease in the dipolar and quadrupolar splittings. No major differences were observed between the samples doped with NaCl and the samples doped with LiCl. However, there are evidences that the extra cations introduced by LiCl replace the sodium counterions of the ESY molecules. The effects of the salts were interpreted as being a result of a salt-induced elongation of the aggregates and a salt-induced increase of the aggregates’ flexibility.

The relaxometry results presented here both complement and confirm the ones obtained by Cachitas et al. \[^{10}\]. Once again, the collective motions of the N phase were found to be composed of fluctuations within the mesogenic units instead of fluctuations of the mesogenic units themselves. This distinguishes the dynamics of ESY from the dynamics of typical thermotropic liquid crystals.

In the N phase, the addition of NaCl and LiCl to ESY systems contributed to a modification of the reorientation of the molecules, an increase in the self-diffusion constant and to an increase of the strength of the collective mo-
Figure 12: Fits of the $R_1$ dispersion of ESY26, (a), ESY26+NaCl0.5, (b), and ESY26+LiCl0.5, (c), in the I phase at 50 °C. The solid black curves correspond to the total fitting curves given by Eq. [8] and the dashed coloured curves represent the separate contributions of the proposed dynamic mechanisms. See text for details.

Differences. The first one of these effects was explained by a decrease of orientational order while the second was seen as a consequence of a viscosity increase. Besides increasing in magnitude, the collective motions were also seen to involve fewer molecules upon the addition of salts. In agreement with the spectroscopy results, these two observations seem to indicate a salt-induced increase of the flexibility of the aggregates. The effects of the ionic additives were more visible in the I phase. Here, the salts also affected the molecular rotations/reorientations and increased the strength of the collective motions. Both results were interpreted as being caused by an augment of the local order which was also observed in $^1H$ spectra.

References: