Liquid Crystals

ISSN: 0267-8292 (Print) 1366-5855 (Online) Journal homepage: https://www.tandfonline.com/loi/tlct20

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To cite this article: Erol Akpinar, Kemal Otluoglu, Meric Turkmen, Cihan Canioz, Dennys Reis & Antônio Martins Figueiredo Neto (2016) Effect of the presence of strong and weak electrolytes on the existence of uniaxial and biaxial nematic phases in lyotropic mixtures, Liquid Crystals, 43:11, 1693-1708, DOI: 10.1080/02678292.2016.1194491

To link to this article: https://doi.org/10.1080/02678292.2016.1194491

LIQUID CRYSTALS, 2016
VOL. 43, NO. 11, 1693–1708
http://dx.doi.org/10.1080/02678292.2016.1194491

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Effect of the presence of strong and weak electrolytes on the existence of uniaxial and biaxial nematic phases in lyotropic mixtures

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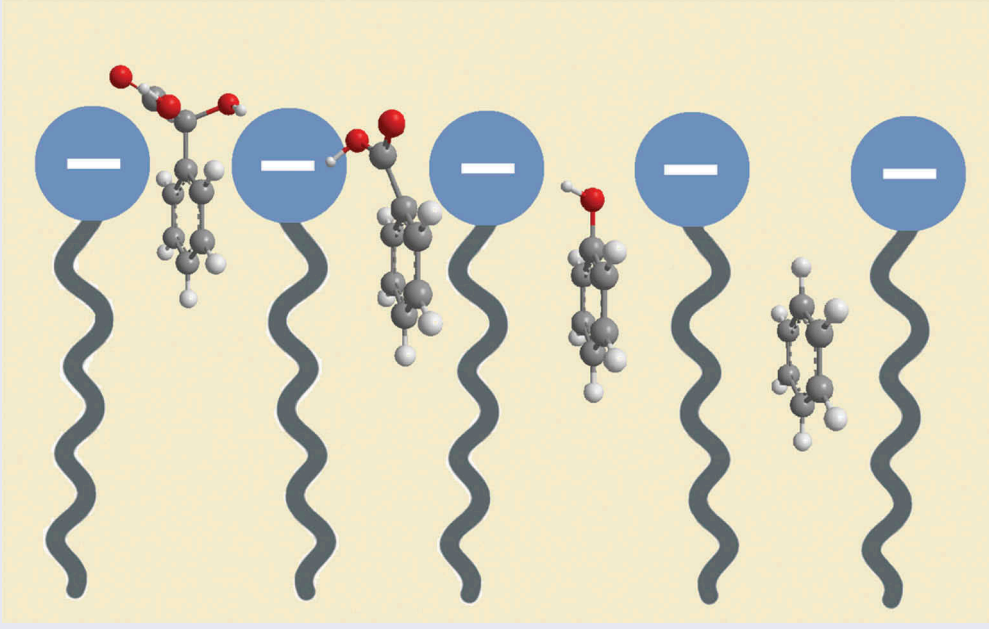
ABSTRACT

The lyotropic mixture of potassium laurate/decanol/water presenting only the uniaxial nematic calamitic phase was doped with one strong (potassium chloride, KCl) and 11 weak electrolytes with phenyl-rings (DL-mandelic acid, benzoic acid, DL-phenyllactic acid, phenylacetic acid, phenol and phenylmethanol) and with cyclohexyl-ring (RS-hexahydromandelic acid, cyclohexanecarboxylic acid, cyclohexaneacetic acid, cyclohexanol and cyclohexylmethanol), separately. We also chose two nonpolar dopant molecules, benzene and cyclohexane, for the comparison of them with weak electrolytes, since they are located in the hydrocarbon core of the micelle. The nematic phase sequences, in particular the presence of the biaxial nematic phase, were investigated as a function of the dopant molar concentration and temperature. The laser conoscopy and small-angle X-ray scattering techniques were used to characterise the different nematic phases. Weak electrolytes having –COOH group as polar part were found to be very effective in stabilising the three nematic phases (two uniaxial and a biaxial). Guest molecules with only the –OH group did not show any effect on the stabilisation of other nematic phases. The experimental results are interpreted considering the screening effect of the hydrophilic parts of the dopants on the repulsion between the polar heads of the main amphiphilic molecules at micelle surfaces. This process favours the increase of the more flat micellar surfaces of micelles, which triggers the orientational fluctuations responsible for the biaxial and discotic nematic phases.



ARTICLE HISTORY
Received 13 November 2015
Accepted 23 May 2016

KEYWORDS
Biaxial nematic phase; uniaxial to biaxial nematic phase transition; weak electrolytes; acid dissociation constant; laser conoscopy; small-angle x-ray scattering

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Introduction

Since the discovery of first lyotropic nematic phases through the end of 1960s [1,2], they have been still attracting the attentions of several research groups. Three nematic phases were identified and reported in the literature. In the case of mixtures made with hydrocarbon chains, two of these nematic phases align with their directors either parallel (calamitic nematic phase, N_C) or perpendicular (discotic nematic phase, N_D) to the magnetic field direction. Both phases were identified as 'optically uniaxial'. The third nematic phase is biaxial, N_B. In contrast to uniaxial ones, biaxial nematic phase has two different optical axes. The N_B is mainly found in lyotropic phase diagrams between the N_D and uniaxial N_C phases.[3,4] It was verified from experimental studies [5] that the uniaxial-to-biaxial phase transitions are of second order, described by a mean-field Landau-type theory.[6,7]

Experimental studies reported in the literature indicated that a co-surfactant might be added into a lyotropic mixture to obtain the biaxial nematic phase.[8] Otherwise, when only one amphiphile, a solvent and eventually an electrolyte are present in the mixture, only uniaxial phases are stabilised.[8–11] This situation requires that the selection of suitable co-surfactants is a key point in order to stabilise biaxial nematic and/or uniaxial phases in a particular lyotropic mixture. In general, long-chain alcohols such as decanol and/or strong inorganic electrolytes (e.g. sodium sulphate) are added into lyotropic mixtures to get nematic phases.[3,12–15] In our recent studies [16], we found that alkyl chain of alcohols affects the formation of different nematic phases: the longer (shorter) the alkyl chain length of alcohol with respect to the alkyl chain length of surfactant molecules existing in lyotropic mixture, mainly gives rise to the formation of N_C (N_D) phases. In addition, we also showed that the interactions at the micelle surface play an important role to obtain different nematic phases.[4]

Now, an interesting question remains without a response: how to control, in terms of sample preparation, the stabilisation of nematic phases by modifying the interactions of the components of the mixture at the micellar surfaces? One of the most common ways is the addition of strong electrolyte in the mixture.[17,18] Experimental studies indicate that increasing the concentration of salts in the mixture favours the stabilisation of the N_D phase. This is due to the decrease of the effective head-group size and screening of the Coulombian interactions at the micelle surfaces. In both cases, the packing in the micelles increases and the micellar growth occurs.[11,19] However, strong electrolytes exist not only at the micelle surfaces to reduce the repulsions between the head groups of the surfactant molecules, but also in the intermicellar (e.g. water) region between the micelles, because of its high solubility in water. In other words, relatively large amount of a strong electrolyte is necessary to manage the nematic phase types of lyotropic liquid crystals.

Alternatively, weak electrolytes, including non-water-soluble (nonpolar) parts in their molecular structure, may be useful to obtain or to manage the phase type in lyotropics instead of strong ones, because their ionisations at the micelle surfaces take place partly. Their polar parts, which are in contact with the free-water molecules, are located at the micelle surfaces, and the nonpolar parts are completely soluble in the micelle hydrocarbon core. As the interactions at the micelle surface play a key role in the stabilisation of different lyotropic liquid crystalline phases, weak electrolytes may be expected to be more effective on the phase transitions from uniaxial to biaxial phase than strong electrolytes.

In the framework of the present study, we investigate the stabilisation of the different nematic phases in lyotropic mixtures doped with weak electrolytes. The classical lyotropic mixture of potassium laurate/1-decanol/water is employed as 'mother mixture' and different electrolytes are added in small concentrations. The chosen weak electrolytes are DL-mandelic acid, RS-hexahydromandelic acid, benzoic acid, DL-phenyllactic acid, phenylacetic acid, cyclohexanecarboxylic acid, cyclohexaneacetic acid, phenol, phenylmethanol, cyclohexanol, and cyclohexylmethanol. The dopants consist of nonpolar phenyl- and cyclohexyl- rings in their molecular structure, and it is expected that they are located at the micelle surfaces differently. It was already reported in the literature that mandelic acid and phenyllactic acid [20] are located at the micelle surfaces, with their nonpolar parts through the micelle core. The nematic phases obtained after the doping with the different electrolytes are characterised mainly by measuring the optical birefringences, using the laser conoscopy, and also by using the small-angle X-ray scattering (SAXS). Parameters of the electrolytes as the solubility and the acidity constant (pK_a) are used in the discussion of the experimental results.

Experimental details

All chemicals were purchased in high purities (>99%) from Sigma, Merck, TCI. Surfactant molecule potassium laurate, KL, was synthesised by the neutralisation of lauric acid with potassium hydroxide, KOH,

in absolute ethanol at room temperature of about 25°C under strong mixing by magnetic stirrer. The neutralisation of lauric acid was controlled with pH-meter (Hanna HI 2221 with electrode HI 1131) and the resulting pH was kept at 10.8 [21] by the addition of excess ethanolic KOH about 2 hours. All ethanol was removed by reducing the pressure with rotatory evaporator. The white powder product KL was precipitated in hot toluene to remove non-neutralised lauric acid from the KL and filtered off under vacuum. Then, it was washed with ether, recrystallised from ethanol two times and dried under vacuum for some days. The disappearance of broad –OH peak of carboxylic acid and appearance of carboxylate ($-COO^-$) peak in the IR spectrum of the final product showed that all lauric acid was completely neutralised to give KL. This is an important point to obtain reproducible results because if KL molecule has large amount of impurities, especially lauric acid, the uniaxial-to-biaxial phase transition temperatures may be shifted with respect to those obtained with pure compounds.

Lyotropic liquid crystalline mixtures were prepared by the weighing of ingredients of the mixture in appropriate amounts into the well-closed test tubes and then well homogenised by applying vortex and centrifuging occasionally. No heat was necessary for homogenisation procedure. In order to align the liquid crystalline sample under magnetic field, a small amount of water-based ferrofluid (from Ferrotec, EMG 605) was added into the samples, typically as 1 μL per 1 g of lyotropic mixture for all measurements, that is, polarising optical microscopy, laser conoscopy and SAXS.

For polarising optical microscope (Nikon Eclipse E200POL, Japan) measurements, small amount of the sample was transferred into a 0.2-mm-thick flat microscope slide, whose both ends were closed with photopolymer. UV-light was applied in the polymerisation process to prevent water loss. Then, the microslides were put in a precise temperature control unit (Linkam Sci., T95-PE) by applying water circulation (Polyscience, with the accuracy of 0.1°C, SD07R model).

Laser conoscopy [8,22] was used to determine the temperature dependence of birefringences of samples. For this measurements, the sample was put between two 2.5 cm of optical glasses (Helma), separated by 2.5 mm of O-ring (Helma). Thus, 2.5-mm-thick samples were obtained for the laser conoscopy measurements. A Lakeshore 335 temperature controller and a Polyscience AD07R water-circulating bath, with accuracies of 0.001°C and 0.01°C, respectively, provided the temperature control.

SAXS experiments were performed in an XEUSS spectrometer from Xenocs (GeniX X-ray beam delivery system; Cu anode microfocus X-ray source; wavelength $\lambda_x = 0.15411$ nm). The collimation system defines a square cross-section beam (0.8×0.8 mm^2) at the sample position. A Pilatus (Dectris) 300 K 20 Hz detector registers the two-dimensional diffraction patterns. Samples were conditioned in cylindrical glass capillaries (1.5 mm diameter), sealed and placed in a temperature-controlled device (precision 0.1°C). A magnetic field of about 1 kG, perpendicular to the X-ray beam, is present in the set up. The nematic phases were aligned according to the same procedure described in the conoscopy experiment. The capillary long axis defines the axis 3 of the laboratory frame; axis 1 is parallel to the magnetic field direction; axis 2 is along the X-ray beam. The typical exposure time was 1200 s, and ultrapure water from Millipore Direct-Q_3 system was used as background.

Results and discussions

To investigate the role of weak electrolytes in lyotropic mixtures, first we will describe the ternary mixture KL/DeOH/water and the role of strong electrolytes (KCl) in the quaternary mixture of KL/DeOH/water/KCl. The results will be discussed in two parts: (a) doping the ternary mixture with strong electrolyte (KCl) and (b) doping the ternary mixture with weak electrolytes.

In the literature, the first lyotropic mixture presenting biaxial nematic phase located between two other uniaxial nematic phases was the KL/DeOH/water.[3] In the present study we investigated this mixture (mixture s0, Table 1) with different compositions than that already reported in the literature. We started with the ternary mixture presenting just the calamitic nematic phase because it is known that the addition of strong electrolytes, such as potassium chloride into a lyotropic mixture, induces the formation of discotic nematic phase. Before adding strong or weak electrolytes as dopant molecules into the ternary mixture, we

Table 1. Composition of the lyotropic mixtures obtained from doping the ternary mixture KL/DeOH/water with KCl.

Mixture	X_{KL}	X_{DeOH}	X_{H_2O}	X_{KCl}	N-phase
s0	3.316	1.212	95.472	–	N_C
s1	3.315	1.211	95.421	0.053	N_C
s2	3.313	1.211	95.371	0.105	N_C
s3	3.309	1.209	95.246	0.236	N_C
s4	3.308	1.209	95.233	0.250	N_D–N_B– N_C
s5	3.306	1.208	95.170	0.316	N_D–N_B
s6	3.303	1.207	95.070	0.420	N_D

X corresponds to the mole fraction. N-phase shows the type of lyotropic nematic phase present in each mixture as a function of the temperature.

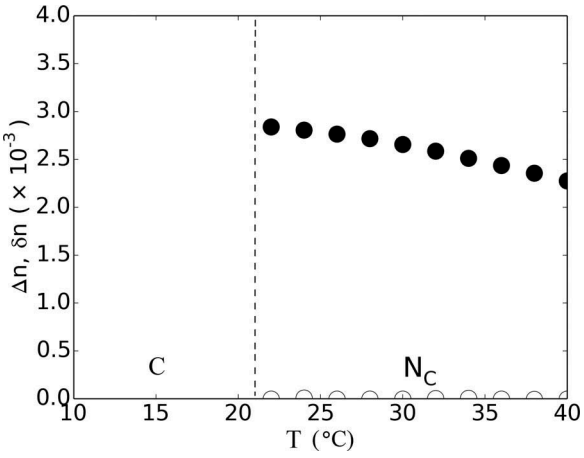

Figure 1. The laser conoscopy result of the ternary mixture KL/DeOH/water (sample s0). Δn (●) and δn (○). Label C means a non-nematic region (not discussed here).

performed the laser conoscopy on it to measure the optical birefringences, Figure 1.

The laser conoscopy technique provides the measurement of the samples' birefringences Δn and δn, which are related to the tensor order parameter ε, the optical dielectric tensor.[5,8] The symmetric nontrivial invariants of ε are σ_2 and σ_3, which are functions of the birefringences. In the case of the N_D (N_C) phase $\sigma_3 = {\sigma_2}^{3/2} (\sigma_3 = -{\sigma_2}^{3/2})$, and in the N_B phase $-{\sigma_2}^{3/2} < \sigma_3 < {\sigma_2}^{3/2}$. At this point, let us associate this macroscopic description of the nematic phases with the symmetry and shape of the micelles, in the framework of the 'intrinsically biaxial micelles model, IBM'. The IBM model was suggested by Neto [23] and Galerne [24] and additional information may be found in our recent studies.[16,25] Summarily, this model assumes that: (a) micelles have orthorhombic symmetry in the three nematic phases and (b) different orientational fluctuations play a key role in the origin of the nematic phases. If the orientational fluctuations are full rotations around the axis perpendicular to the largest micelle surface (perpendicular to the main-surfactant bilayer) of the micelles, the N_D phase is favoured. If those are parallel to the longest micellar dimension in the plane perpendicular to the surfactant bilayer, the fluctuations give rise to the N_C phase. Finally, small amplitude orientational fluctuations around the three symmetry micellar axes, originate the N_B phase. Assuming the IBM, the more anisometric the micelles are, the bigger the optical birefringences in the nematic phases and, consequently, the bigger the invariants σ_2 and σ_3.[8] It is important to stress that a key point for the laser conoscopy measurements is to obtain well-aligned nematic samples. To do so, the lyotropic mixtures were doped with ferrofluid and subjected to a magnetic field. For details about the alignment process in each nematic phase, refer to.[26]

The ternary mixture s0 presents only the N_C phase; however, at low temperature (below ~21.8°C), the conoscopic interference fringes suddenly disappeared. The system transited to a non-nematic region (C). At higher temperature (~44.4°C) the system transited to a biphasic region (N_C + Lamellar phase). The phase sequence is presented below:

$$C \xrightarrow{21.8^\circ C} N_C \xrightarrow{44.4^\circ C} N_C + L \xrightarrow{52.6^\circ C} L + I \xrightarrow{84.3^\circ C} I$$

where the phases L and I are lamellar and isotropic phases, respectively.

Before discussing the doping results, we will summarise some important points about micellar systems, that is, isotropic micellar solutions and lyotropic liquid crystals, to explain the role of electrolytes. When surfactant molecules in concentrations larger than the critical micellar concentration (cmc) are dissolved in water, they form supramolecular structures, named micelle, and then three different regions are present [27]: (a) hydrocarbon core of the micelle, which consists of non-water soluble hydrocarbon chains of the surfactant molecules; (b) the interfacial or palisade region [28], where water-soluble head groups of the surfactants contact with the water molecules, and (c) the intermicellar or water region between the micelles. The interactions in these regions are responsible for the formation of different lyotropic liquid crystalline phases. They are essentially classified as intra- and intermicellar interactions.[29] The former one mainly provides the formation of micelles as a result of van der Waals attractions between the alkyl chains of neighbouring surfactants. Electrostatic, steric and solvation repulsions [30,31] contribute to the intermicellar interactions. Among them, electrostatic repulsions, which are known as 'Coulombic repulsions', are important both in the intermicellar region and at the micelle surfaces. The Coulombic repulsions are strong interactions and effective not only at short distances but also at long ones between the ionic species, that is, micelles of ionic surfactants and the ionic head groups of surfactants.

In the case of low surfactant concentration and/or in the absence of electrolyte, in general, only the isotropic micellar solution is present in the phase diagram. If enough amount of an electrolyte is added to the mixture, new phases may be stabilised. This means that the addition of the electrolytes causes the growth of micelles, which has already been reported in the literature for both isotropic micellar solutions [29,32] and lyotropic liquid crystalline state.

[4,11,19,33] This situation can be explained as follows: when surfactant molecules form the micelle, the repulsions between the surfactant head groups in the absence of any electrolyte or long chain alcohol are at maximum level. If, for example, an electrolyte is added into the mixture, these repulsions are screened or reduced by the entering of the electrolyte ions between the head groups in the palisade layer at the micelle surface. However, it has to be taken into account that strong electrolytes are highly soluble in water, and it should be expected that when a strong electrolyte is added into a micellar solution, first it may prefer to be found in the intermicellar (or water) region with respect to the palisade layer. By increasing the concentration of the strong electrolyte, after the water region is saturated by the electrolyte, it may be located in the vicinity of the palisade layer as well as in the intermicellar region. Let's come back to our experimental results.

First, we studied the effect of strong electrolyte potassium chloride, KCl, on the N_C phase of the ternary mixture of KL/DeOH/water. The compositions of the quaternary mixtures KL/DeOH/water/KCl are given in Table 1. The laser conoscopy results are shown in Figure 2. At low KCl concentrations, the samples s1–s3 gave just N_C phase, like the ternary mixture. This means that the salt ions are most likely to be found in the intermicellar region. If the K-ions from KCl were present at the micelle surface, it would reduce the repulsions between the head groups (acetate, $-COO^-$) of KL molecules, thus N_D phases should be obtained. This last situation was confirmed in our previous study.[4] If we increase the amount of KCl even more, first we obtain three nematic phases (s4),

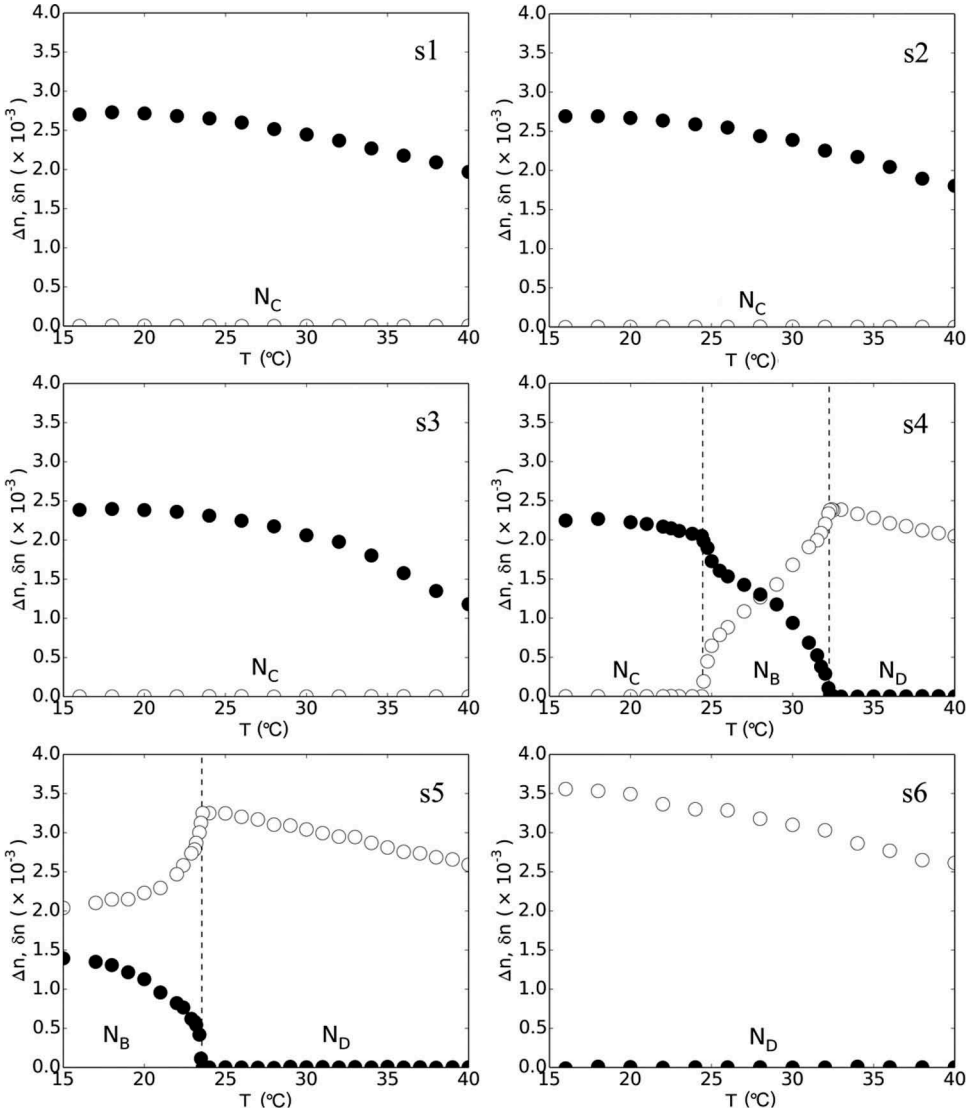

Figure 2. Laser conoscopy results of KL/DeOH/water/KCl samples as a function of the increase in the concentration of KCl. Their compositions are given in Table 1. Δ*n* (●) and δ*n* (○).

then the N_C phase is no more present (s5) with more KCl, and finally, just N_D phase (s6) was observed. In addition, we observed that as the amount of KCl increases, the birefringences of N_D phase also increases. This is in a good agreement with the idea mentioned before, where, at a low KCl concentration, K-ions in the intermicellar region or in the vicinity of palisade layer cannot efficiently screen the repulsions between the head groups at the micelle surfaces. In this case, N_C phase is more favourable. At a high KCl concentration, a larger number of K-ions exists in both regions to give rise to the N_D phase. This is a result of the screening of the Coulombian repulsions between the amphiphilic head groups, favouring the flat micellar surface. Here, we should point out that ion binding in micellar systems follows Manning's theory [34,35], the so-called Manning ion-condensation model.[36] This model essentially explains the counter-ion binding (condensation) onto the poly-ions by reducing the charge density between adjacent monomers in polyelectrolyte systems. [37–40]

Now, we have to find an answer to the question: what is the role of non-water soluble dopant molecules on the formation of different nematic phases? Then, we can make a comprehensive interpretation of the role of weak electrolytes, as it is aimed in the frame of this study. To do so, we chose two nonpolar dopant molecules: benzene (dopant d1) and cyclohexane (dopant d2), Figure 3. These molecules can be considered as 'reference molecules' for the comparison of them with weak electrolytes, since they are located in the hydrocarbon core of the micelle. Especially, some studies about the site of the solubilisation of the benzene in the micellar solutions have been reported in the literature.[41–51] Two structural properties of benzene play a key role in its solubility in the micelles: its high solubility in hydrocarbons and the existence of π-electrons. Since the latter one provides the interaction of benzene with the hydrophilic head groups of the surfactant at the micelle surface [41,50], the former one causes the residing benzene in the interior of the micelle. For instance, in the micellar solution of

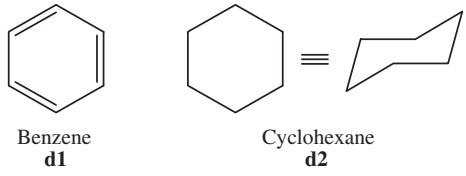

Figure 3. Molecular structures of benzene and cyclohexane. Energetically, the most stable structure of cyclohexane is chair conformation [55]; however, in the frame of this study, this conformation is not a key point and so it is omitted.

octylammonium bromide (OABr), benzene solubilises in the palisade layer by interacting with water.[52] This means that π-electrons of benzene can strongly interact with the positively charged head group of OABr, $-H_3N^+$. However, in another study [53] it was stated that although dodecyltrimethylammonium bromide (DDTMABr) has positively charged head group, $-(CH_3)_3N^+$, it exhibited different behaviour with respect to OABr, but about the same behaviour with sodium dodecylsulphate (NaDDS), which has negatively charged head group. Thus, in the case of DDTMABr or NaDDS, the penetration of benzene towards the interior of the micelle is more favoured. [53,54] This situation may be attributed to the larger head group of DDTMABr with respect to OABr, which reduces the interaction of π-electrons of benzene with the ionic head group, and its longer alkyl chain length, which causes the location of benzene in the hydrocarbon core of the micelle instead of the palisade layer. Furthermore, since cyclohexane does not have any π-electrons in its molecular structure, it may be assumed that it completely solubilises in the micelle. In addition, the phenyl groups (like benzene) show different interaction with the cationic surfactants and with anionic ones: their interactions with the head groups of cationic surfactants are stronger than those of anionic surfactants.[54] Consequently, in our case, KL molecule has a negatively charged head group like NaDDS and same alkyl chain length similar to both NaDDS and DDTMABr, then it may be assumed that benzene can penetrate in the interior of the micelles as it will be supported by our experimental results presented in the following.

Figure 4 shows the laser conoscopy results of the quaternary mixtures KL/DeOH/water/benzene and KL/DeOH/water/cyclohexane. Each mixture has the same dopant concentration in mole fraction when compared with sample s1, doped with KCl. As it can be seen at low concentrations of benzene and cyclohexane, they did not change the partial phase diagram of the ternary mixture, Figure 1, that is, the addition of benzene or cyclohexane did not change the topology of the phase diagram, with only the N_C phase. Further increase in these dopant molecules concentrations did not promote the appearance of the N_B and/or the N_D phases. Increasing the doping concentration, the mixtures lose their homogeneities, the N_C phase region diminishes and a phase-coexistence region increases. This result indicates that, if the dopant molecule is located through the interior of the micelle or away from the micelle surface, there is no change on the nematic phase type, at least when nematic phases are present in the phase diagram. This is another evidence for the

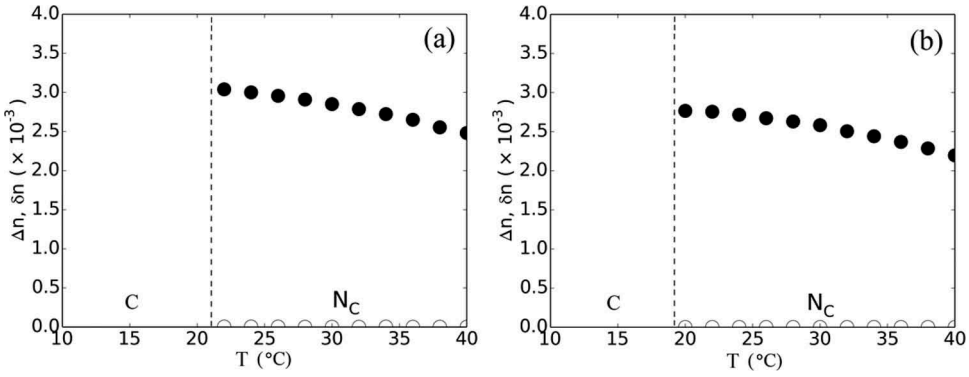

Figure 4. The laser conoscopy results of the quaternary mixtures (a) KL/DeOH/water/benzene and (b) KL/DeOH/water/cyclohexane. Δ*n* (●) and δ*n* (○). C represents non-nematic regions.

importance of the modifications of the interactions at the micelle surfaces to obtain different nematic phases, like we observed for the low strong electrolyte (KCl) concentration.

All experimental results until here showed that the way to obtain different nematic phases, especially the biaxial one, is the selection of dopant molecules located at the micelle surfaces. For this purpose, we chose some weak electrolytes having non-polar phenyl- and cyclohexyl- rings and water soluble polar groups hydroxyl (–OH), carboxyl (–COOH) and both hydroxyl and carboxyl groups. The molecular structures of the selected weak electrolytes are given in Figure 5. In particular, the chiral forms of DL-mandelic acid and DL-3-phenyllactic acid were found to be located at the micellar surfaces of lyotropic mixtures.[20] The phase compositions of the quaternary mixtures obtained with all dopant molecules are given in Table 2.

Figure 6 shows the temperature dependence of birefringences of the quaternary mixtures obtained by doping the ternary mixture with molecules d3–d6. The dopants include just –OH group bounded to the non-polar phenyl- and cyclohexyl-rings. These molecules did not modify the phase sequence of the ternary mixture KL/DeOH/water, Figure 1, and further increase in their concentrations caused the same effect as benzene and cyclohexane. So, we may conclude that the interaction of –OH group with the head group of the surfactant KL at the micelle surface is not as strong as the ions of the strong electrolytes to induce the presence of additional nematic phases. This result suggests that these dopants should be mainly located in the inner part of the micelle.

In the last part of our study, we performed the laser conoscopy measurements on the mixtures prepared with dopants d7–d13. The results are given in Figure 7. As it can be seen in Table 2 and Figure 7, although the concentrations of these dopants are very low in the mixtures (X_{dopant}: 0.053), three nematic phases were obtained. This situation was observed neither for the strong electrolyte KCl (X_{KCl}: 0.053, sample s1) nor for dopants d1–d6 (X_{dopant}: 0.053, samples with benzene and cyclohexane, and samples s7–s10). In addition, when the concentrations of these dopants were doubled (i.e. X_{dopant}: 0.106), all samples with dopants d7–d13 gave just N_D phase. This result indicates that dopants d7–d13 are mainly located at the micelle surfaces (palisade or interfacial region), modifying the micellar shape anisotropy. In addition, the use of these weak electrolytes is relatively more effective to control the obtaining of the biaxial nematic phase with respect to the strong electrolytes. According to the results with the KCl doping, to obtain the N_B and to get only the N_D phase, the concentrations of dopant were X_{KCl} = 0.250 (sample s4) and 0.420 (sample s6), respectively. In the case of weak electrolytes, X_{dopant} = 0.053 and 0.106 for N_B and N_D phases, respectively. Comparing these numbers, the amount of weak electrolytes in the mixtures are about 5 (4) times less than those of KCl to obtain N_B (just N_D) phase.

Figure 8 shows the σ_3 versus σ_2 plots for the mixtures with dopants that gave the three nematic phases (dopants d7-d13).

Among these dopants, d7, d8, d12 and d13 have only –COOH group, while d9–d11 have both –OH and –COOH groups attached to the apolar cyclohexyl- and phenyl- groups. From the results with dopants d3–d6, the interaction of the –OH group with the surfactant head group does not significantly modify the shape anisotropy of micelles, which triggers the characteristic orientational fluctuations to give rise to the different nematic phases. So, it may be concluded that the interactions between the ionic head groups of the surfactants with the –COOH groups of the dopants are more effective than those with the –OH group of the

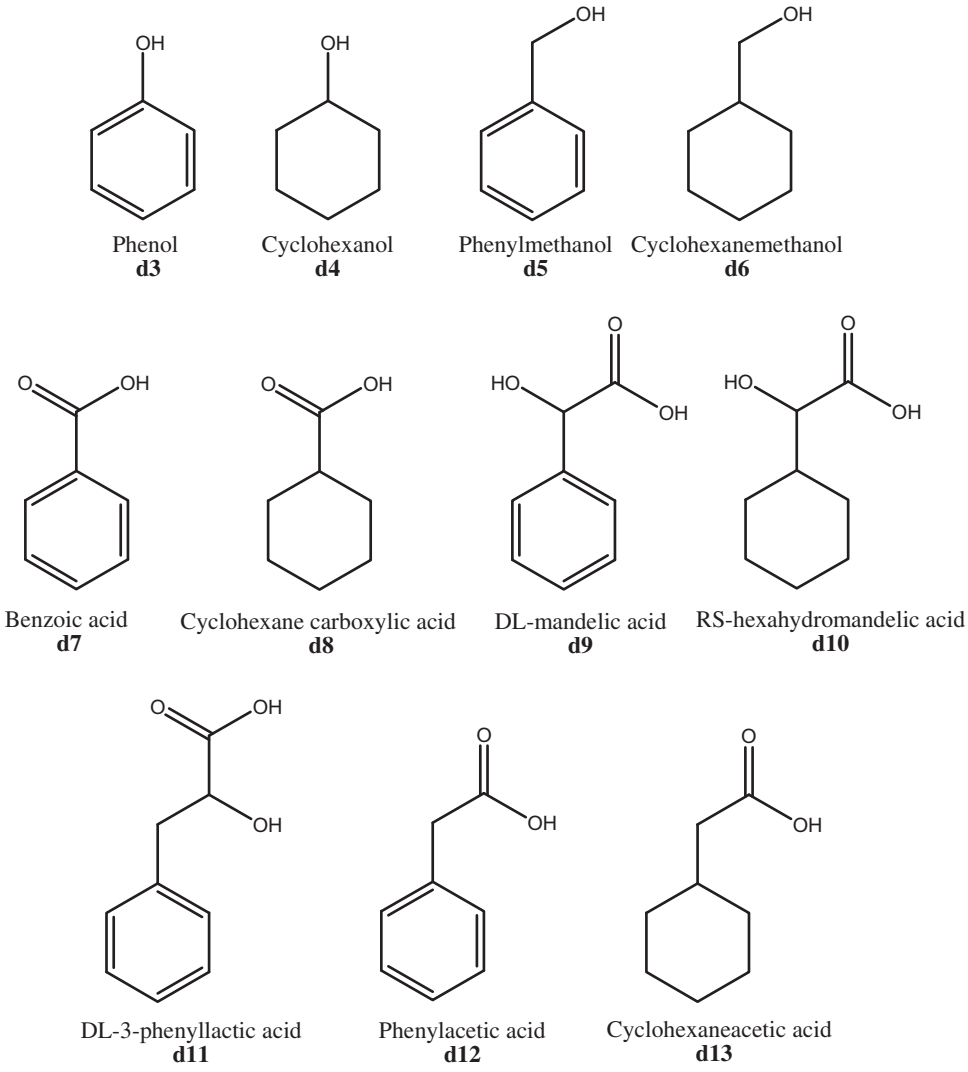

Figure 5. Molecular structures of the molecules employed to dope the ternary mixture of KL/DeOH/water.

Table 2. Compositions (in Mol fraction) of the quaternary mixtures KL/DeOH/water/dopant (or guest) at constant dopant concentrations.

Mixture	Dopant	X_{KL}	X_{DeOH}	X_{H_2O}	X_{dopant}	N-phase
s7	d3	3.315	1.211	95.421	0.053	N_C
s8	d4	3.315	1.211	95.421	0.053	N_C
s9	d5	3.315	1.211	95.421	0.053	N_C
s10	d6	3.315	1.211	95.421	0.053	N_C
s11	d7	3.315	1.211	95.421	0.053	N_D–N_B–N_C
s12	d8	3.315	1.211	95.421	0.053	N_D–N_B– N_C
s13	d9	3.315	1.211	95.421	0.053	N_D–N_B– N_C
s14	d10	3.315	1.211	95.421	0.053	N_D–N_B– N_C
s15	d11	3.315	1.211	95.421	0.053	N_D–N_B– N_C
s16	d12	3.315	1.211	95.421	0.053	N_D–N_B– N_C
s17	d13	3.315	1.211	95.421	0.053	N_D–N_B– N_C

N-phase represents the nematic phases present, as a function of the temperature.

dopants to obtain different nematic phases, especially the N_B phase. This situation may be explained as follows. Although –OH group is soluble in water because of its bond polarity, –OH group in –COOH is more polar with respect to alcoholic –OH group, that is, higher electric dipolar moment. For instance, the dipole moments of propanol and propionic acid are 1.58 D and 1.75 D, respectively.[56] This indicates that the partial positive charge on hydrogen of –COOH group is greater than that of alcoholic –OH, Figure 9. So, the interaction of the dopant including –COOH group with the polar heads of the KL at the micellar surface is stronger than that including only the –OH group. So, we expect that dopants d7–d13 are located between the KL surfactant molecules with their polar groups interacting with the head groups of the KL at the micelle surface (in the palisade layer). However, the polar groups of dopants d3-d6 seem to interact less with the head groups of the KL, which favours the location of these dopants protrudes from the micelle surface to the deeper of the micelles, when comparing with dopants d7–d13. The relative locations of all dopants are sketched in Figure 10, by showing just

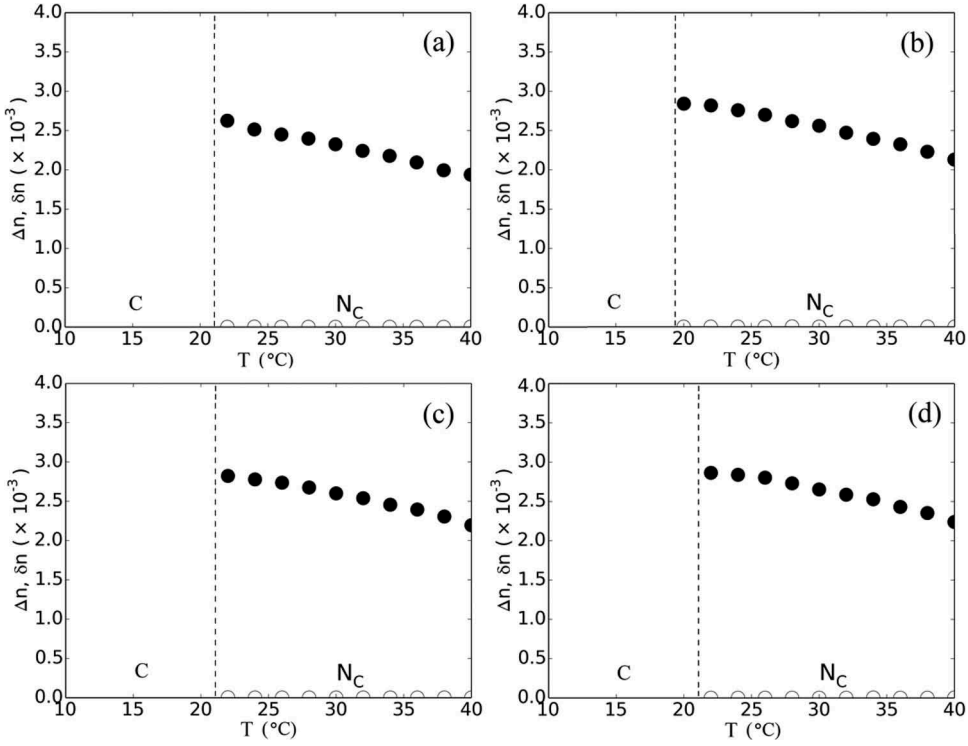

Figure 6. The temperature dependences of the birefringences of KL/DeOH/water/dopant: (a) phenol, (b) cyclohexanol, (c) phenylmethanol and (d) cyclohexanemethanol. C represents a non-nematic region.

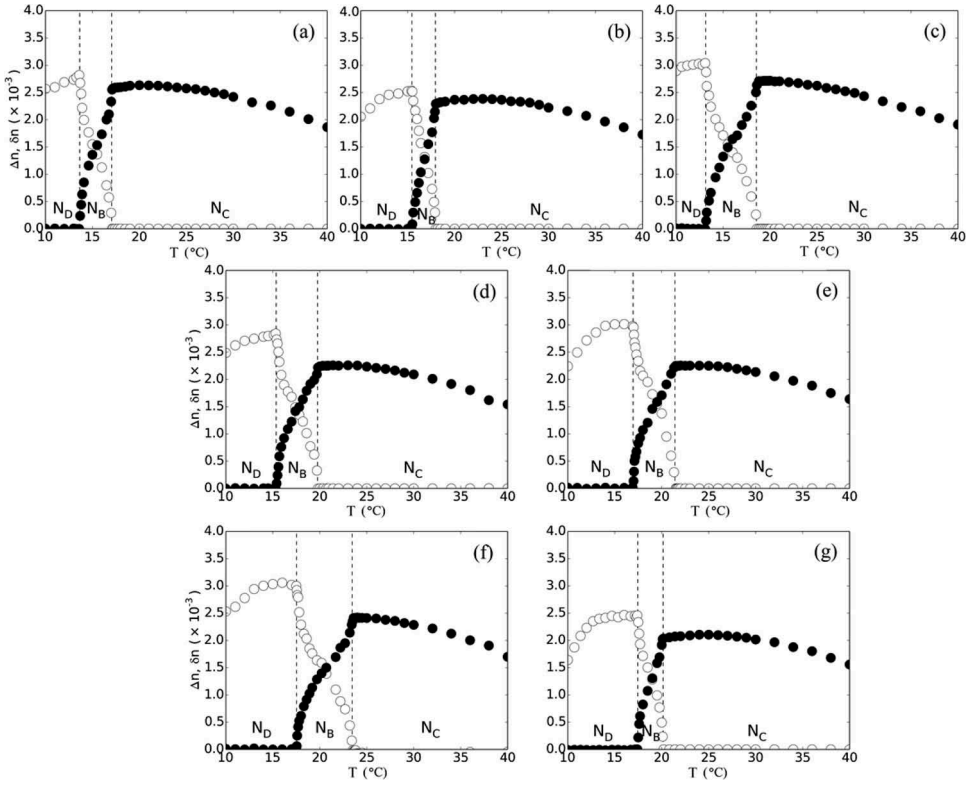

Figure 7. Temperature dependences of the birefringences of samples s11–s17, with the dopants (a) benzoic acid, (b) cyclohexane carboxylic acid, (c) DL-mandelic acid, (d) RS-hexahydromandelic acid, (e) DL-3-phenyllactic acid, (f) phenylacetic acid and (g) cyclohexaneacetic acid.

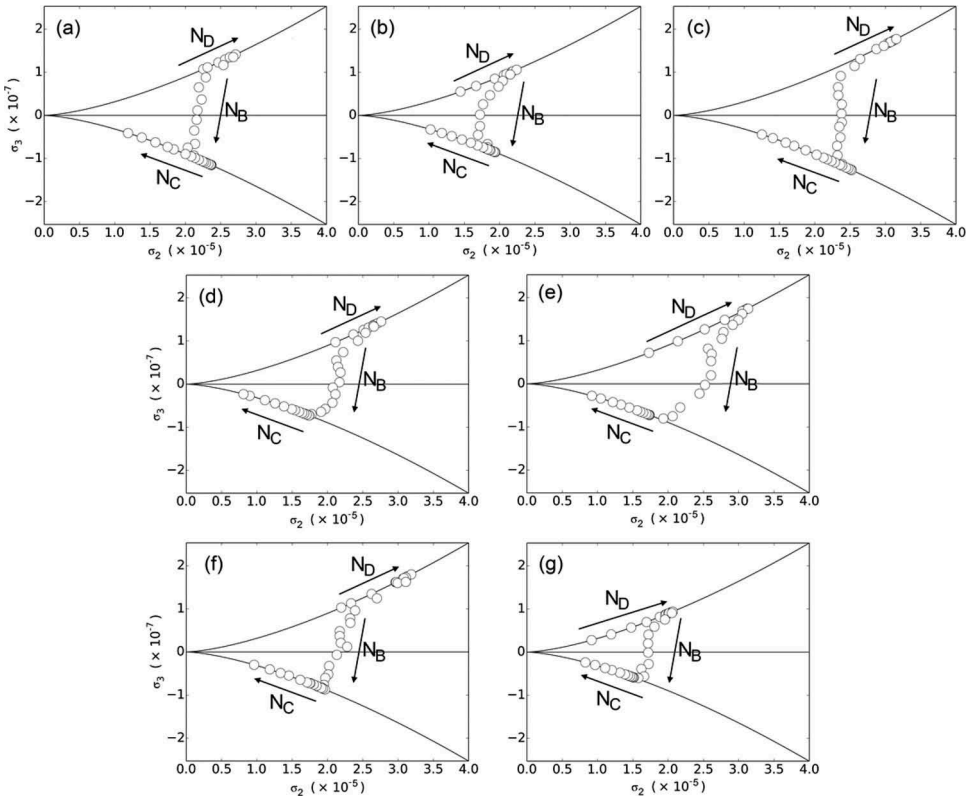

Figure 8. Invariant σ_3 versus σ_2 plots. Lyotropic mixtures doped with (a) benzoic acid, (b) cyclohexane carboxylic acid, (c) DL-mandelic acid, (d) RS-hexahydromandelic acid, (e) DL-3-phenyllactic acid, (f) phenylacetic acid and (g) cyclohexaneacetic acid. The arrows show the direction of the increase in temperature from N_D to N_C, passing through the N_B phase.

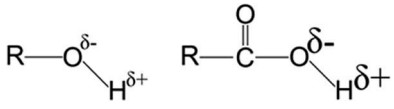

Figure 9. Bond polarities of the hydroxyl group in alcoholic –OH (left) and in –COOH, respectively, arising from the difference in the electronegativities between oxygen and hydrogen atoms. The partial positive charge on the hydrogen in –COOH is bigger than that in alcoholic –OH, because –OH in –COOH is bounded to the electron withdrawn carboxyl- group.

DL-mandelic acid (d9), benzoic acid (d7), phenol (d3) and benzene (d1) for the comparison. As it is expected, the dopants having similar molecular structure would present same locations.

DL-mandelic acid has both –OH and –COOH groups in its polar part, presents relatively higher solubility in water and it prefers to be in the palisade layer with its phenyl- ring entering the palisade layer. Benzoic acid polar part has only –COOH group and its water solubility (2.50 g/L) is much lower than DL-mandelic acid (133 g/L). So, although it interacts with the head group of KL, its location should be deeper in the micelle surface region, but still in the palisade layer. Phenol (or dopants with the similar structure) consists of –OH group bounded to the phenyl- group because its water-soluble part (–OH) prefers to be in contact with water (its solubility is 93 g/L) in the palisade layer. Then, it is expected that phenol is located in the palisade layer. However, it showed the same effect of the nonpolar benzene (its solubility is 1.71 g/L) on the nematic phase sequence. So, its location seems to be towards the micelle core, but still in the vicinity of the palisade layer. This result agrees with the report of Kandori et al.[57], where it was stated that since benzene prefers to be in the micelle core, phenol solubilises in the palisade layer of micelles obtained from the cationic surfactant DDTMABr.

At first sight, it may be thought that there should be a relationship between the solubility of the dopants and their locations in the micelle structure. For instance, the less water-soluble dopant would be located through the micelle core, at the micelle surface. If we compare the solubility of the dopants (Table 3) sketched in Figure 10, the sequence is DL-mandelic acid > Phenol > Benzoic acid > Benzene. According to our results, the dopants having –COOH group exhibited the same effect: the lyotropic mixture presented the three nematic phases. On the other hand, those with only the –OH group, behaves as benzene or cyclohexane in

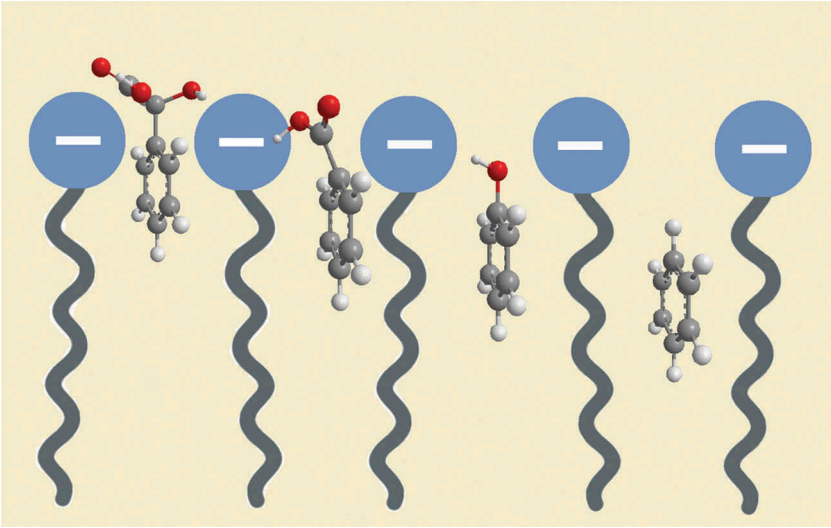

Figure 10. (colour online) Sketch of the relative location of the dopants in the micelle. From left to right: DL-mandelic acid, benzoic acid, phenol and benzene. Red: oxygen; dark grey: carbon; light grey: hydrogen.

Table 3. The solubilities and pK_a values of the dopants given in the literature.

Dopant	Solubility in water (g L^{-1})[a]	pK_a[a]
Benzene	1.71 [59,60]	43 or 37 [61]
Cyclohexane	0.05 (25°C) [62]	45 [61]
Phenol	93.0 (25°C) [63]	9.99 [55]
Cyclohexanol	36.0 [64]	18 [65]
Phenylmethanol	45.1 [66]	16 [67]
Cyclohexylmethanol	9.10 [66]	NA[b]
Benzoic acid	2.50 [68]	4.204 [55]
Cyclohexanecarboxylic acid	2.01 (15°C) [69]	4.90 [55]
DL-mandelic acid	133 (172, 25°C) [70]	3.411 [55,71]
RS-hexahydromandelic acid	NA[b]	NA[b]
DL-3-phenyllactic acid	Very soluble (numerically NA[b])	3.72 [72] (3.46 [73])
Phenylacetic acid	15.8 [74]	4.31 [55]
Cyclohexaneacetic acid	NA	4.51 [55]

[a] The solubility and pK_a values are at 20°C and 25°C, respectively.
[b] NA, Not-available

terms of the nematic phase sequence. This means that, although the solubility is a key parameter, pK_a (acidity constant) of the dopants seems to be a parameter more adequate to be considered in the existence of the three nematic phases in a particular lyotropic mixture doped with weak electrolytes. As it can be seen in Table 3, the dopants with pK_a in the acidic region ($pK_a < 7$) gives rise to the three nematic phases; however, those with pK_a in the alkaline region ($pK_a > 7$) have no strong interaction at the micelle surface to give rise to the different nematic phases. This situation is in a good agreement with the sketch presented in Figure 9, since the polarisability degree of the bond between the oxygen and hydrogen atoms in –OH and –COOH is directly proportional to the partial polar charge on the hydrogen.

At this point, it would be better to discuss the effect of ionisation degree of weak acids (α) and on what happens if the dopants transfer their partly ionised proton to KL surfactant molecule, which results in the formation of lauric acid. Let's start with the α values. As given in Table 3, the most acidic dopant is DL-mandelic acid (pK_a: 3.411; K_a: 3.89×10^{-4}) and the less acidic one is cyclohexanecarboxylic acid (pK_a: 4.90, K_a: $1.26x10^{-5}$). Since, we kept the concentration of each dopant in the mixtures constant (b: ~0.031 mol/kg), then α value of DL-mandelic acid (cyclohexanecarboxylic acid) was calculated as ~0.11 (~0.02), that is, DL-mandelic acid (cyclohexanecarboxylic acid) is approximately ionised 11% (2%). As it is expected, other dopants have ionisation degree between these two values. Thus, part of KL (at most 11% mole fraction of KL) may be transformed into lauric acid as a result of the transfer of proton from weak acid dopants to the head group of KL. Then, we performed the laser conoscopy experiments with two additional mixtures to compare the effect of lauric acid in the ternary mixture with the other dopants, Figure 11. In the first mixture, we added lauric acid into the ternary mixture of KL/DeOH/water with exactly the same concentration of the dopants (X:0.053 in Mol fraction). In the second one, we replaced 0.053 (in Mol fraction) of KL with lauric acid, assuming that dopants completely (α:1 or 100% ionisation) ionises to neutralise KL to give lauric acid. In both cases, we had similar results, Figure 11, with non-acidic dopants such as benzene, phenol etc. within the experimental errors, that is, only N_C phase was observed. This means that the degree of ionisation of weak acids or the formation of lauric acid does not have any effect on the formation

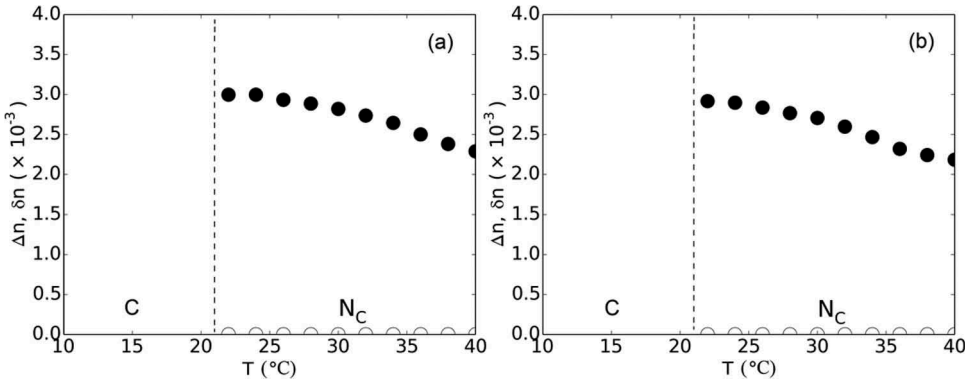

Figure 11. Temperature dependences of the birefringences of KL/DeOH/water/lauric acid: (a) addition of X:0.053 lauric acid into the ternary mixture, (b) replacing X:0.053 KL with lauric acid. C represents a non-nematic region.

of different nematic phases and the degree of ionisation of the dopant can be omitted.

It is interesting to remark that samples d9, d10 and d11 present the higher birefringence values $(3.0 < (10^5 \times \sigma_2) < 3.5$ and $1 < (10^7 \times \sigma_3) < 2)$ of the nematic phases (in this cases N_D). In the framework of the IBM model this implies that the micelles in mixtures doped with d9, d10 and d11 are more anisometric. Since the higher birefringence is observed in the discotic nematic phase, the dimensions in the flat surface of the micelle (perpendicular to the main amphiphilic bilayer) are the largest among all the mixtures investigated. This means that these dopants favour the flat micellar surface reducing the electrostatic repulsive interactions between polar heads of the main amphiphile. Moreover, there is not a preferred direction in this surface. The IBM model stresses that, when the dimensions of the micelles in the flat surfaces are comparable and larger than the bilayer dimension, orientational fluctuations that degenerate the axis perpendicular to the flat surface are favoured, and the discotic phase is stabilised.

At this point let us analyse the X-ray scattering results, in particular those performed with the lyotropic mixture doped with DL-3-phenyllactic acid, which has both –OH and –COOH groups in its polar part, in the N_C, N_D and N_B phase, as a function of the dopant concentration. The analysis of the results was done following the procedure described in [24], and briefly presented in the following. An essential point in these scattering experiments is to obtain a well-oriented nematic sample. From the diffraction-band positions along the three orthogonal axes of the laboratory frame we calculate the mean distances between micelles (according to the nomenclature in [24], A, B and C). To obtain the micellar dimensions A‘ and B’ we assume that the KL bilayer is C‘ = 2.6 nm [58] and that water covers equally all the surfaces of the orthorhombic micelle. The aggregation number (N_{agg}) was evaluated calculating the micellar surface (flattened ellipsoid with axes A″, B″ and C″) and considering that the area per polar head of the KL is 0.50 nm^2.[58] Figure 12 shows the diffraction patterns of the sample in N_C (Figure 12(a)), N_B (Figure 12(b,c) and N_D (Figure 12(d)). The micellar dimensions and the aggregation numbers are presented in Table 4.

In the framework of the IBM model, the effect of the DL-3-phenyllactic acid doping may be described as follows. Initially, the micelles in the ternary lyotropic mixture present a larger shape anisotropy in the plane perpendicular to the main amphiphilic bilayer S_a = (A″–B″)/A″. This micellar shape anisotropy favours the orientational fluctuations that degenerates the axis along the larger micellar dimension, originating the N_C phase. The doping acts to reduce the electrostatic repulsion between the polar heads of the main amphiphile, favouring the increase of the flat micellar surface (in the plane perpendicular to the bilayer), without a preferred direction. This leads to a decrease of S_a, triggering the orientational fluctuations that originate the N_B phase. Further increasing on the amount of DL-3-phenyllactic acid reduces more S_a, triggering the orientational fluctuations that originate the N_D phase. Interestingly, the doping with DL-3-phenyllactic acid initially increases N_{agg} at the N_B phase (from ~140 in the ternary mixture to ~180 in the first concentration doping), and still increasing the doping concentration, N_{agg} decreases in the N_D phase (to ~130). These results indicate that the aggregation number depends not only on the concentration of the dopant, but also on the particular nematic phase. The biaxial phase is that with the bigger aggregation number among the three nematic phases.

Concluding remarks

We investigated the effectiveness of the presence of weak electrolytes in lyotropic mixtures aiming at the

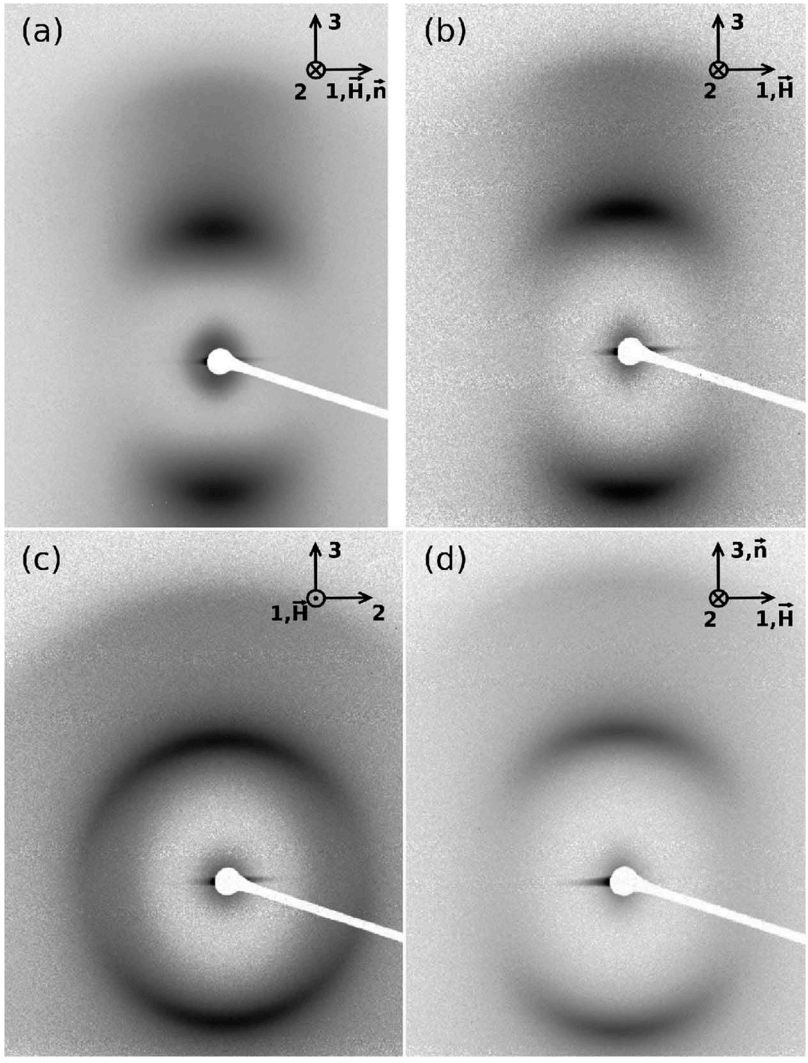

Figure 12. X-ray diffraction patterns: (a) ternary mixture KL/DeOH/water in the N_C phase; (b) and (c) quaternary mixture KL/DeOH/water/DL-3-phenyllactic acid (concentration c_1) in the N_B phase; (d) quaternary mixture KL/DeOH/water/DL-3-phenyllactic acid (concentration $c_2 > c_1$) in the N_D phase. $\vec{n}$ and $\vec{H}$ are optical axis of the nematic phase and magnetic field direction, respectively. 1, 2 and 3 are three orthogonal laboratory frame axes.

Table 4. Micellar average dimensions (A′, B′ and C′), shape anisotropy $S_a = (A' - B')/A'$ and average aggregation number from the X-ray scattering experiments.

	A′ (nm)	B′ (nm)	C′ (nm)	S_a	N_{agg}	Dopant concentration
N_C	5.0 ± 0.4	2.8 ± 0.2	2.6	0.44	136 ± 13	—
N_B	5.3 ± 0.4	3.8 ± 0.2	2.6	0.28	176 ± 11	c_1
N_D	4.0 ± 0.5	3.4 ± 0.2	2.6	0.15	130 ± 13	c_2

Lyotropic mixture undoped and doped with DL-3-phenyllactic acid in two different concentrations $c_1 < c_2$.

stabilisation of the three nematic phases (N_D, N_C and N_B). Among the guest molecules added to the ternary lyotropic mixture of KL/DeOH/water presenting only the N_C phase, weak electrolytes having –COOH group as polar part, exhibited significant effect on the stabilisation of the three nematic phases after the doping. On the other hand, guest molecules with only –OH group as polar part, did not show any effect on the stabilisation of other nematic phases: these mixtures show only the N_C phase. Our results indicated that there is no direct relation between the solubility of the guest molecule in water and its effectiveness to stabilise the different nematic phases. However, we observed that the guest molecule acidity constant K_a or pK_a was an important parameter: dopants with pK_a in the acidic region ($pK_a < 7$) gave rise to the three nematic phases. These dopants were found to be more effective in the stabilisation of the three nematic phases when comparing to strong electrolytes (as inorganic alkali salts) since smaller molar concentrations of them are needed to induce the presence of the three nematic phases. We interpreted the results in terms of the location of dopant molecules at the micelle surfaces and their

effectiveness of screening the polar head (of the main amphiphile) repulsion. This situation favours the relaxing of more curved surfaces in the micelle, increasing the more flat micellar surfaces. These surfaces are perpendicular to the main amphiphilic bilayer. The increase of the micellar dimensions in this plane favours the orientational fluctuations characteristic of the N_D phase, as observed in our experimental results. Finally, the use of weak electrolytes may be accepted as a new control parameter to obtain different nematic phases, especially the biaxial one.

Acknowledgements

The authors thank Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPQ), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Instituto Nacional de Ciência e Tecnologia de Fluidos Complexos (INCT-FCx), Núcleo de Apoio à Pesquisa de Fluidos Complexos (NAP-FCx), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), the Scientific and Technological Research Council of Turkey (TÜBİTAK) [grant number 114Z031]; Abant Izzet Baysal University Directorate of Research Projects Commission (BAP) [grant number 2014.03.03.767] for supporting this work.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Instituto Nacional de Ciência e Tecnologia de Fluidos Complexos (INCT-FCx); Núcleo de Apoio à Pesquisa de Fluidos Complexos (NAP-FCx); Abant Izzet Baysal University Directorate of Research Projects Commission (BAP) [2014.03.03.767]; Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES); The Scientific and Technological Research Council of Turkey (TÜBİTAK) [114Z031]; Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPQ); Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP);

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