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Review

Experimental Conditions for the Stabilization of the Lyotropic Biaxial Nematic Mesophase

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Abstract: Nematic phases are some of the most common phases among the lyotropic liquid crystalline structures. They have been widely investigated during last decades. In early studies, two uniaxial nematic phases (discotic, N_D, and calamitic, N_C) were identified. After the discovery of the third one, named biaxial nematic phase (N_B) in 1980, however, some controversies in the stability of biaxial nematic phases began and still continue in the literature. From the theoretical point of view, the existence of a biaxial nematic phase is well established. This review aims to bring information about the historical development of those phases considering the early studies and then summarize the recent studies on how to stabilize different nematic phases from the experimental conditions, especially, choosing the suitable constituents of lyotropic mixtures.

Keywords: Lyotropic liquid crystals; uniaxial nematic phase; biaxial nematic phase; stabilization of nematic phases; micelle; surfactants

1. Introduction

Lyotropic liquid crystalline phases may be encountered in mixtures of amphiphilic molecules and a solvent, with or without a salt, in particular regions of the multidimensional phase diagram (relative concentrations and temperature) of these mixtures [1,2]. From the symmetry point of view, two types of lyotropic nematic phases exist: uniaxial (two of them were identified, the discotic, N_D, and the calamitic, N_C, phases, $D_{\infty h}$ symmetry), and one biaxial (N_B, D_{2h} symmetry). In the uniaxial phases we define a director represented by a vector $\vec{n}$ that corresponds to the optical axis of the phase. The $\vec{n}$ and $-\vec{n}$ states are indistinguishable. In the case of the N_B phase, there are three orthogonal two-fold symmetry axes ($\vec{l}$, $\vec{m}$ and $\vec{n}$, where $\vec{n} = \vec{l} \times \vec{m}$) and two optical axes [3–5]. These phases are diamagnetic and high-intensity magnetic fields ($H \sim 10kG$) are used to orient them in actual experiments.

After the discovery of the first lyotropic mixture showing the biaxial nematic phase [1], intensive studies have begun to characterize its properties and structure [6]. These studies were mostly conducted to understand whether the biaxial phases are thermodynamically stable or whether a mixture of the two uniaxial phases. Many experimental and theoretical studies have confirmed the first hypothesis.

In the phase diagrams of lyotropic mixtures presenting the three nematic phases, the N_B phase is mainly located between the other two uniaxial phases [1,2,7–15]. The transition from the uniaxial (N_D or N_C) to the biaxial phase is of second order, as predicted by the Landau-type mean-field theory [16,17]. Since the N_B phase domain (at least in some phase diagrams) is located in between those from the N_D and N_C phases, some researchers claimed that the N_B phase was thermodynamically unstable and even constituted by a mixture of both uniaxial phases [18–22]. Assuming that the N_D and N_C phases consist of disc-like and cylindrical-like micelles, respectively, the N_B phase should be composed by a mixture of these types of micelles. However, it was theoretically proved that disc-like and cylindrical-like objects could not coexist, i.e., a mixture of both objects (in the case of nematic phases, micelles) is not stable and phase separation occurs [23].

This review article deals with the recent studies related to the stabilization of different lyotropic nematic phases from the experimental point of view. Mainly, we will review some important studies obtained in our research laboratories, giving to experimentalists hints of mixture compositions that favor the presence of the N_B phase in the phase diagram.

2. Background

The first lyotropic nematic phase was reported towards the end of the 1960s [24]. In the following years, many studies were conducted to understand the properties of this phase. In these early studies, the existence of two types of nematic phases was determined and these phases were classified as Type I and Type II, according to the orientation of the phase director with respect to an external applied magnetic field [25–27]. Since the lyotropic mixture investigated was composed by amphiphilic molecules with carbonic chains, it was verified that the director of the Type I (Type II) phase aligns parallel (perpendicular) to the magnetic field direction. In the following years, Type I (Type II) phase was named N_C (N_D) [28]. At that time, it seemed natural to assume that Type I and Type II phases were composed of cylindrical-like and disc-like micelles [28–32], respectively, as shown in Figure 1.

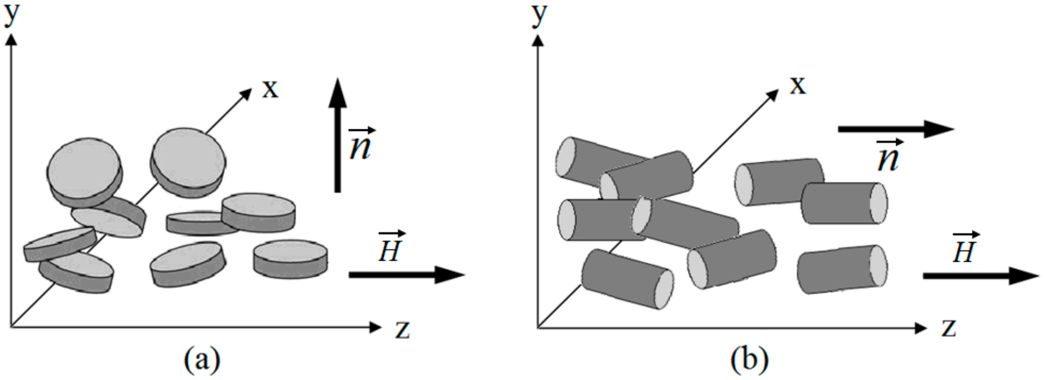


Figure 1. Orientations of (**a**) disc-like and (**b**) cylindrical-like micelles perpendicular and parallel, respectively, to magnetic field direction, $\vec{H}$, along z. $\vec{n}$ (phase director) represents the preferred alignment of the individual micelles with their local directors.

Freiser [16,33] theoretically predicted the existence of the N_B phase for the first time [5,34–38] after Taylor et al. [39] reported a biaxial smectic C phase in thermotropic liquid crystals. However, at that time, there were no experimental results to support this theoretical prediction. In 1980, Yu and Saupe [1] experimentally showed the existence of the N_B phase for the first time in the ternary mixture of potassium laurate (KL)/decanol (DeOH)/D_2O via Nuclear Magnetic Resonance (NMR) and microscopic conoscopy studies, as shown in Figure 2. They constructed the partial phase diagram of this ternary mixture where the N_B phase was an intermediate phase between the two uniaxial N_D and N_C phases. In 1985, Neto et al. [40] investigated the same ternary mixture in more details. They used the optical microscopy, laser conoscopy and X-ray diffraction techniques and found that the biaxial phase domain was relatively large (~15 °C) for appropriate relative concentrations of the mixture compounds.

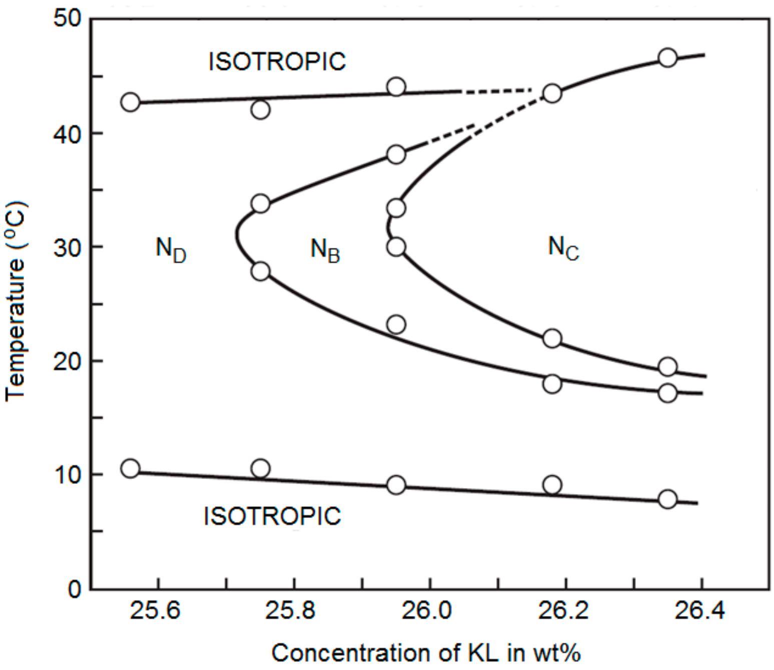


Figure 2. Phase diagram of KL/DeOH/water mixture which was established for the first time in the Reference [1].

In 1982, Bartolino et al. [7] reported a partial phase diagram of the ternary mixture of sodium decylsulfate (SdS)/DeOH/H_2O to contribute to the understanding of the biaxial nematic phases, as shown in Figure 3a. They showed that the uniaxial N_D (N_C) phase had positive (negative) birefringence, as shown in Figure 3b. Their results seem to show a discontinuity of the birefringence in the biaxial domain, however, to prove this claim it should be necessary measurements of the birefringences with more precision in temperature.

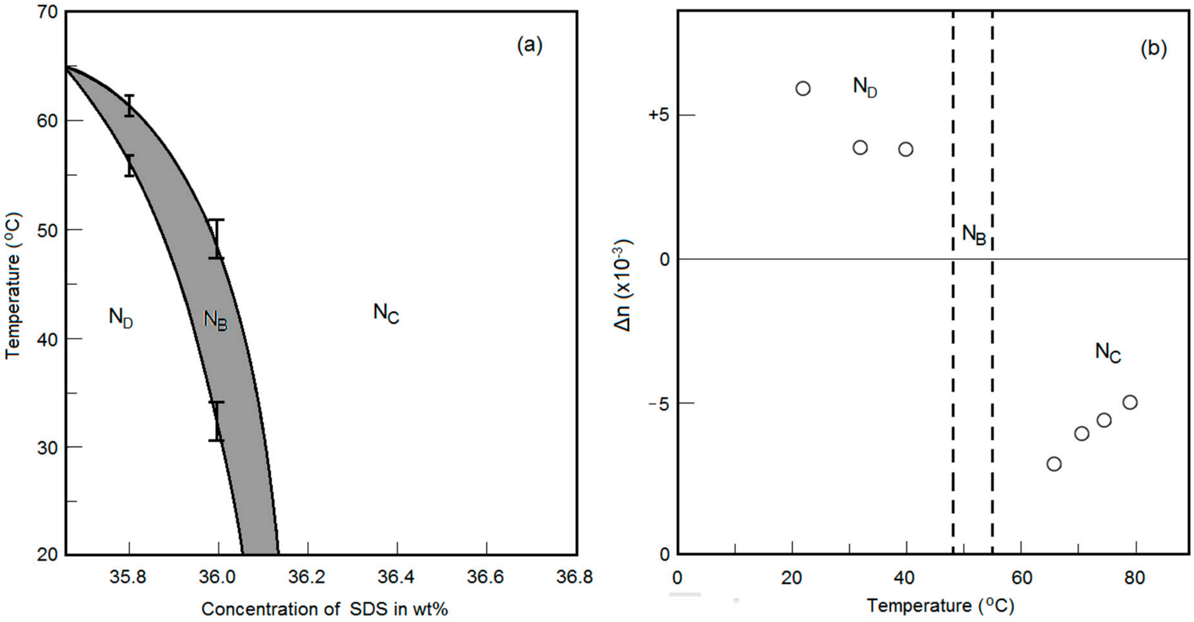


Figure 3. (**a**) Partial phase diagram of SDS/DeOH/water mixture given in the Reference [7]. (**b**) The birefringences of the uniaxial nematic phases for the sample of 35.8% SDS.

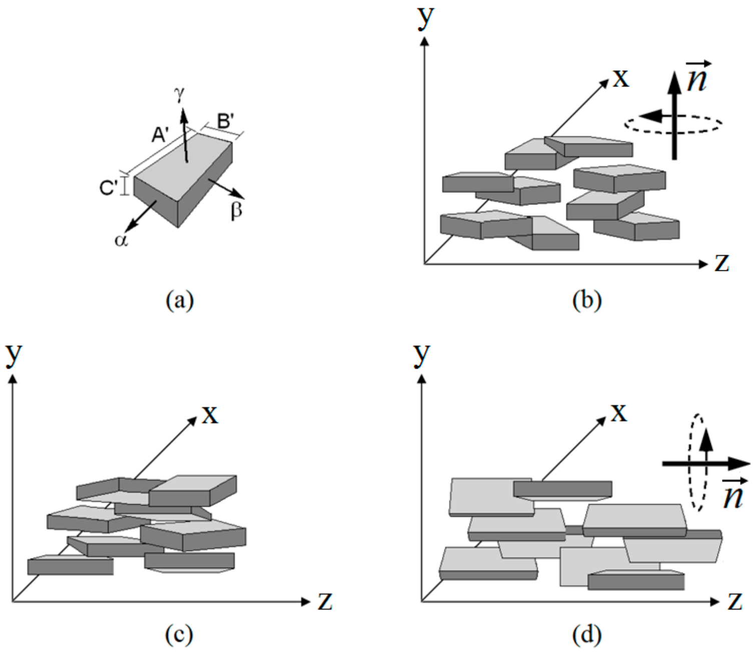
Finding the first biaxial nematic phase Yu and Saupe not only verified Freiser's prediction on the existing that phase, but also started interesting discussions about the nature and structure of the N_B

phase [1,36,41–47]. Theoretical and computer simulation studies of binary mixtures of rod-like and disk-like rigid particles were reported [19–21,48–57]. In 1984 Stroobants and Lekkerkerker proposed a model, based on the Onsager's theory, where rod-like and disc-like particles coexist (mixture of disc-like and cylindrical-like micelles, MCD model), giving rise to a biaxial nematic phase [21]. However, some theoretical and experimental studies showed that MCD-type models presented problems to describe the N_B phase [58]. For instance, in 2000, Kooij and Lekkerkerker reported an interesting experimental study about the liquid crystal phase behavior of suspensions with mixtures of rod- and plate-like units. They verified that this type of mixture separates, i.e., the coexistence of rod- and plate-like particles is not stable [23]. In another study, Palffy-Muhoray et al. [22] investigated the phase behavior of a binary mixture of uniaxial nematic liquid crystals (rods and disks), in the absence of the external field, employing the Maier-Saupe mean-field theory. They concluded that the N_B phase was not thermodynamically stable. In a recent study Martinez-Raton et al. showed that phase-separation of rod-plate mixtures and the stability of the biaxial phase depend on the aspect ratio and molar fraction of the rods [59]. Sharma et al. [60] showed that there could be a possibility to stabilize the biaxial phase in mixtures by increasing either the isotropic or the anisotropic parts of the interspecies interaction strength. The latter situation was also supported by other theoretical studies, i.e., biaxial phase may be favored in multi-component (polydisperse) mixtures [61] by the specific interactions (indeed, hydrogen bonding) between the unlike basic units [62,63]. However, for the symmetric [64–67] or asymmetric [23,68–73] binary rod-plate mixtures, considering the stability of the biaxial phase with respect to phase separation, the coexistence of rod-plate particles is not possible and the phase separation is favored. In summary, the separation of the rod and plate-like objects (in the case of the lyotropic systems, prolate or cylindrical-like and oblate or disc-like micelles) requires the rejection of the MCD-type model, as experimentally showed by Kooij and Lekkerkerker [23].

Although the discussions about the stability of the N_B phase were going on, experimentalists tried to find new lyotropic mixtures presenting the N_B phases. In 1985, Galerne et al. [8] introduced a new ternary mixture of rubidium laurate (RbL)/DeOH/H_2O. They investigated the defect lines (disclinations) in both uniaxial and biaxial nematic phases and observed that the disclination lines in the biaxial region made "zig-zags" while the uniaxial counterparts exhibited a "flexible" behavior, i.e., the disclinations observed in the biaxial phase seem to be different from those in the uniaxial phases. However, some time later the same authors show that the same zig-zag disclinations were observed in uniaxial phases with different mechanism than in the biaxial [74–76]. Santos and Galerne investigated the uniaxial discotic nematic phase of KL/DeOH/D_2O by Rayleigh-scattering technique [77] in the vicinity of the uniaxial to biaxial phase transition. They observed the dynamic of fluctuations of the biaxial order parameter close to the uniaxial to biaxial phase transition, at the uniaxial phase domain, and showed that the micelles in the uniaxial discotic nematic phase exhibit biaxial ordering.

In 1985, a reliable model was proposed by Neto and co-workers [41,78], assuming that the micelles in all the three nematic phases in lyotropics have orthorhombic symmetry. They investigated the uniaxial and biaxial nematic phases of the mixture KL/DeOH/D_2O by X-ray diffraction and observed that the micelles in all the nematic phases are locally biaxial, arranged in a pseudo-lamellar structure. This means that in the three nematic phases, the micelles are similar from the point of view of the local symmetry. Their model, so-called "intrinsically biaxial micelles model, IBM", is mainly based on two pillars: (a) micelle symmetry and (b) orientational fluctuations of the micelles. According to the IBM model, the micelles have orthorhombic symmetry, as shown in Figure 4a, in all three different nematic phases and different orientational fluctuations are responsible for the stabilization of the three nematic phases. Figure 4a shows a sketch a micelle as an object of orthorhombic symmetry, with typical dimensions A′, B′ and C′. The axes of the local coordinate system fixed in the micelle are α, β and γ. These orthorhombic micelles exhibit different orientational fluctuations for the stabilization of the N_D, N_B or N_C phases. The orientational fluctuations around the axis perpendicular to the largest micelle surface (along axis y) give rise to the N_D phase, as shown in Figure 4b. In this situation, the micelle size A′ approximately equal to B′ (A′~B′). By changing temperature to reach the transition from

N_D to N_B, the micelle size along the symmetry axis α increases, and the small-amplitude orientational fluctuations along the three axes (x, y and z) lead to the N_B phase. If the temperature is changed until obtaining the N_C phase, the micelle dimension along α continues to increase, which favors the orientational fluctuations around the local α micellar axis (along the z axis).



(a) (b) (c) (d)

Figure 4. (**a**) Sketch of the orthorhombic micelle in the framework of the IBM model (Reference [79]). The detergent amphiphilic bilayer is represented by C′. According to the IBM model, based on the different orientational fluctuations, the formations of (**b**) ND, (**c**) NB, and (**d**) NC phases. $\vec{n}$ represents the director of the ND and NC phases."

A neutron scattering study reported by Hendrikx et al. [80] in 1986 supported the IBM model. In that study, authors experimentally showed that the micelles of the N_C phase are statistically biaxial.

Until 1989, since the lyotropic mixtures exhibiting the biaxial nematic phases contained alcohol and surfactant, Oliveira et al. [9] achieved to find a new mixture of KL/decylammonium chloride (DACl)/water, alcohol-free. This new mixture was important because, as suggested by Saupe et al. [81], if a mixture has surfactant and alcohol, there is a possibility of a slow esterification occur in the mixture. In the study of the [9], researchers investigated the mixtures of KL/DACl/water and KL/DeOH/water, i.e., alcohol-free and with alcohol mixtures, respectively, to compare the physical-chemical stability of both types of mixtures. Their long-term studies were based on the birefringence and X-ray diffraction measurements. It was shown that the phase-transition temperatures, birefringences and microscopic structures changed with time in the case of the mixtures including alcohol. However, for the alcohol-free mixtures, especially the X-ray diffraction results of the nematic phases, revealed that the alcohol-free mixtures were more stable than the one with alcohol.

In 1991, Vasilevyskaya et al. [82] investigated a new lyotropic mixture exhibiting the biaxial nematic phase SdS/DeOH/H_2O/Na_2SO_4. Their experimental study was based on the measurement of the birefringences of the nematic phases, as a function of the temperature. They observed that this new system had much smaller birefringence values with respect to the conventional lyotropic mixture KL/DeOH/H_2O [1]. As a result of their study, they concluded that the phase transitions from biaxial to uniaxial arise from different orientational fluctuations of the micelles around their axes. Their conclusion is similar to those from the IBM model.

Experimental and theoretical studies stated that the biaxial nematic phase is an intermediate phase between two uniaxial nematic ones. Ho et al. [83] reported an interesting study related to a new lyotropic mixture of sodium lauroyl sulfate/hexadecanol (HDeOH)/water, exhibiting a biaxial nematic phase in the case of diluted solutions. They obtained this biaxial phase after applying the sonication process on a gel-like phase. They showed, surprisingly that a biaxial phase could be found in a different place in the lyotropic phase diagram, not as an intermediate phase between two uniaxial nematics. Another interesting study was published by Quist [84] to investigate novel lyotropic mixture of sodium dodecylsulfate SDS/DeOH/H_2O via NMR spectroscopy. Based on the Landau theory, the phase transitions from uniaxial to biaxial nematic phase transitions are of second-order. However, Quist proposed that these phase transitions might be of first-order. The author attributed the first–order N_D-N_B and N_B-N_C phase transitions to a variation in the aggregate (micelle) shape. This result is really very interesting, because other experimental and theoretical studies showed that the uniaxial to biaxial transitions have to be of second-order. In addition, early [40] and recent [13,15] studies, especially obtained from the temperature dependence of the birefringence, showed that these phase transitions are of second-order, as predicted by mean-field theory [16,18].

From the diamagnetic-susceptibility anisotropy (Equation (1)) point of view, considering the diamagnetic susceptibilities along three two-fold symmetry axes being χ_{33}, χ_{22} and χ_{11}, the biaxial nematics are identified with positive and negative $\Delta\chi$, N_{B+} and N_{B-}.

$$\Delta\chi = \chi_{33} - \frac{\chi_{11} + \chi_{22}}{2}. \tag{1}$$

In the case of $\Delta\chi > 0$ ($\Delta\chi < 0$), the largest (smallest) diamagnetic susceptibility is larger (less) than the average of the diamagnetic susceptibilities of other axes and the biaxial phase aligns parallel (perpendicular) to the magnetic field direction [84,85]. Quist [84] reported a study with these two biaxial nematic phases, with positive and negative diamagnetic-susceptibility anisotropy in the phase diagram; however, they did not study an eventual phase transition between these N_{B+} and N_{B-} phases. Moreover, from the symmetry point of view, there is no transition between them. This type of "phase transition" was investigated by de Melo Filho et al. [85] in the novel lyotropic mixture of tetradecyltrimethylammonium bromide (TDTMABr)/DeOH/H_2O by measuring the deuterium quadrupolar splitting, via Nuclear Magnetic Resonance. In 2009, van den Pol et al. [36] reported a model-system to experimentally obtain the biaxial phase in colloidal dispersions of board-like particles. According to theory and simulations, the particles have the dimensions $L/W \approx W/T$, where L, W and T are length, width and thickness, to obtain a biaxial nematic phase [48,50,86]. They used goethite particles as a model-system with $L/W = 3.1$ and $W/T = 3.0$, and investigated the properties of the model-system by small angle x-ray scattering, under the effect of external magnetic field. Their results indicated the evidence of the biaxial nematic phase. Indeed, their model system is similar to what is proposed by the IBM model in terms of the micelle shapes and, from this respect, the study in [36] supports the IBM model.

As reviewed above, despite the evidence of the stability of the biaxial nematic phase in lyotropics, some studies still reject the existence of this phase. Indeed, these controversies arise from the absence of enough number of lyotropic mixtures in the literature showing this phase and the missing thermotropic counterpart.

In the next sections, we will discuss how to stabilize the lyotropic biaxial nematic phase from the sample preparation point of view. In other words, we will show which experimental conditions have to be fulfilled to prepare a lyotropic mixture presenting this phase.

3. Recent Experimental Studies on the Stabilization of the Lyotropic Biaxial Nematic Phase

Lyotropic mixtures are prepared by dissolution of a surfactant molecule in water (mainly). In some cases, a cosurfactant and/or an electrolyte are/is added to that binary solution. Indeed, while the former provides both the decrease in the repulsions between similarly charged headgroups of the surfactants at the micelle surfaces and the increase in the attractive forces (van der Waals) between the surfactant alkyl chains in the interior of the micelles, the latter one just reduces the repulsions between the headgroups. Because of this, modifications at the micelle surfaces and in the micelles shape anisotropy play a key role to obtain not only uniaxial nematic phases but also the biaxial one. Thus, we will review our recent experimental results focusing, mainly, in the modifications at micelle surfaces and in the micelles shape anisotropy.

3.1. Effects of Alkyl-Chain Lengths of Surfactant and Cosurfactant

Surfactant molecules consist of two different parts, hydrophilic water-soluble head groups and hydrophobic water-insoluble alkyl tails or chains. By the same way, cosurfactants have water-insoluble parts and polar water-soluble parts attached. In general, long-chain alcohols, such as 1-decanol, are added to the lyotropic mixtures as cosurfactants.

In 2012, we studied the effect of the alkyl-chain length of the alcohols in the mixture of KL/K_2SO_4/alcohol/water [11]. We constructed a partial phase diagram by changing the number of carbon atoms in the alcohol-chain length from 8 (1-octanol) to 16 (hexadecanol), as shown in Figure 5. The laser conoscopy technique, which is a very accurate method to measure the birefringences of the nematic phases [87], was applied to determine the uniaxial to biaxial nematic phase transitions from the temperature dependences of the birefringences. The results indicated that there is a strong relation between the alkyl-chain length of the surfactant and that of the alcohol. As the alkyl-chain length of the alcohol gets longer (shorter), the N_C (N_D) phase is stable and at intermediate alkyl chain length there exists the possibility to obtain the N_B one. In general, at constant mixture composition, the N_B phase is stabilized when the $n = m \pm 2$, where m (n) is the number of carbons in alkyl chain of the main surfactant (co-surfactant) molecule.

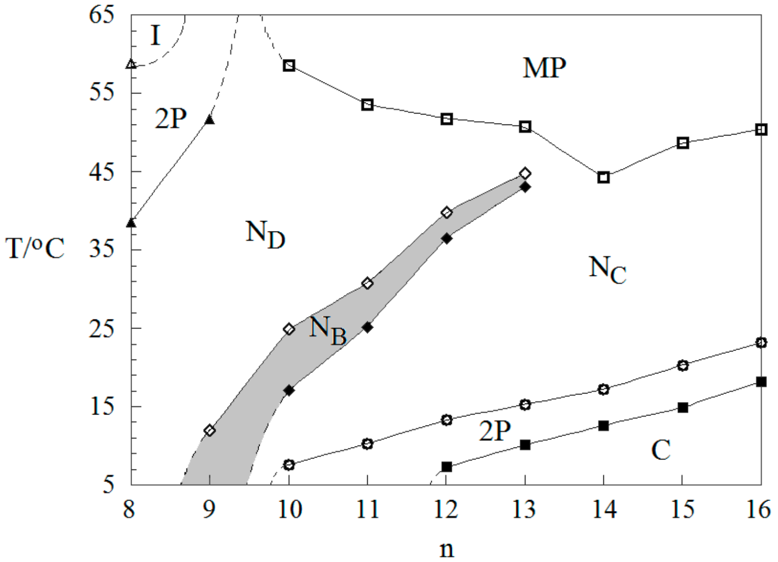


Figure 5. Partial phase diagram of KL/K_2SO_4/alcohol/water mixtures [11]. n is the number of carbon atoms in the alkyl chain of the alcohol molecules. I, 2P, MP and C represent an isotropic phase, two-phase region, multi-phase region and crystalline-like phase, respectively. Solid and dashed lines are only guides. The grey region shows the biaxial nematic phase domain.

In a more recent study [15], we have also investigated the relation between the alkyl-chain length of the surfactant and the alcohol in a different experimental design. In this case, we examined the effect of the surfactant alkyl-chain length on the stability of the different nematic phases, at constant alcohol chain-length and mixture composition. The mixtures chosen were potassium alkanoates/Rb_2SO_4/DeOH/water and sodium alkylsulfates/Na_2SO_4/DeOH/water. The experimental techniques employed were the laser conoscopy, polarizing optical microscopy and small-angle x-ray scattering. In both systems, it was observed that as the number of the carbon atoms in the surfactant alkyl-chain length increases (decreases), the stabilization of the N_D (N_C) phase is favored. Here, again, for the intermediate level of the relation between the alkyl-chain length of the surfactant and the alcohol, the N_B is stabilized. It was also observed that the $n = m \pm 2$ rule is still applicable, except that the concentration of the surfactant, which is the main component of the lyotropic mixtures, is bigger than that of alcohol.

3.2. Effect of Interactions between Head Groups and Ions of Electrolytes

Lyotropic systems are also known as micellar systems because their building blocks (or basic units) are micelles. The micellar systems consist of three main regions: (a) intermicellar region, (b) interfacial region and (c) micelle core. The intermicellar region includes water, some counterions of the surfactants and, if an electrolyte is added to the mixture, the ions of the electrolytes, and free surfactant molecules. The micelle cores consist of the hydrocarbon part, i.e., the alkyl chain of the surfactants. The interfacial region is a region at the micelle surfaces where the head groups of the surfactants, some counterions, ions of electrolytes and structured water are present. In the previous section, we have dealt with the modifications in the micelle core by examining the relative effect of the alkyl-chain lengths of the surfactant and of the alcohol. In this section, we discuss the effect of the modifications at the micelle surfaces, i.e., in the interfacial region.

The interaction of alkali ions with the head groups of the surfactant molecules on obtaining the different nematic phases, especially biaxial one, was investigated [88]. In this study, two different lyotropic mixtures were examined, KL/alkali sulfate/undecanol/water, as shown in Figure 6, and sodium dodecylsulfate (SDS)/alkali sulfate/dodecanol/water, as shown in Figure 7, where alkali sulfates are Li_2SO_4, Na_2SO_4, K_2SO_4, Rb_2SO_4 and Cs_2SO_4. In Figure 6 the optical birefringences are given. The refraction indices along the x, y and z axes of the laboratory coordinate system are n_x, n_y and n_z, and the birefringences are defined as: $\delta n = \left|n_z - n_y\right|; \Delta n = \left|n_x - n_z\right|$. The magnetic field is applied along the z axis. In the N_D phase, $n_x = n_z \neq n_y$, in the N_C phase $n_x = n_y \neq n_z$, and in the N_B phase $n_x \neq n_z \neq n_y$.

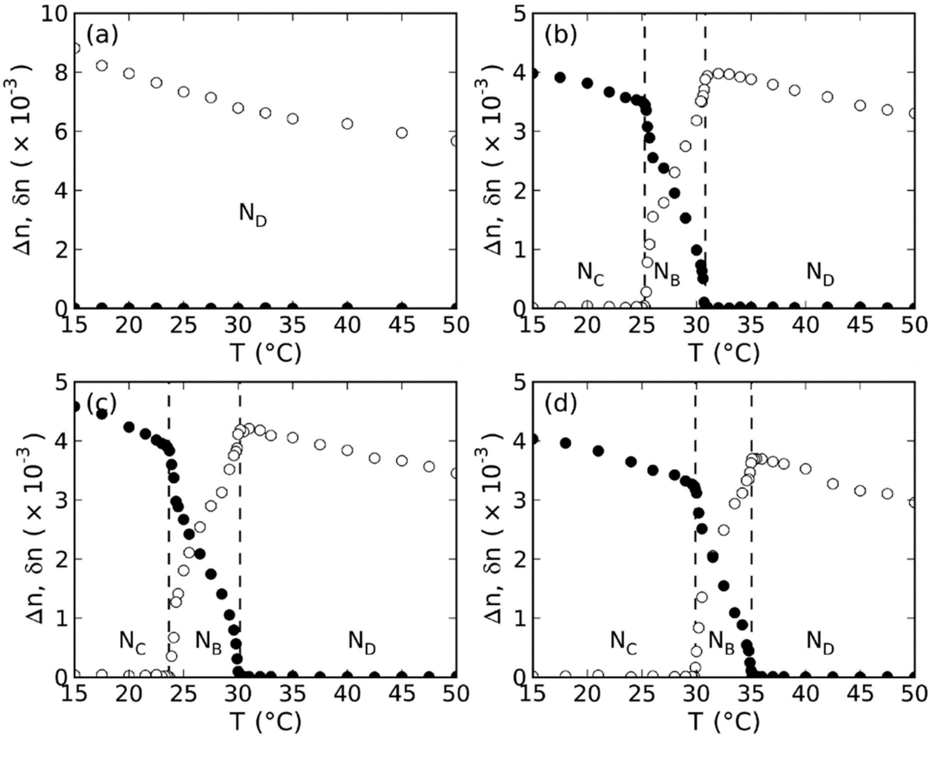


Figure 6. Temperature dependences of the birefringences of the mixtures KL/alkali sulfate/UndeOH/water, including (**a**) Na_2SO_4, (**b**) K_2SO_4, (**c**)Rb_2SO_4 and (**d**) Cs_2SO_4, separately. (○) and (•) represent δn and Δn, respectively [88].

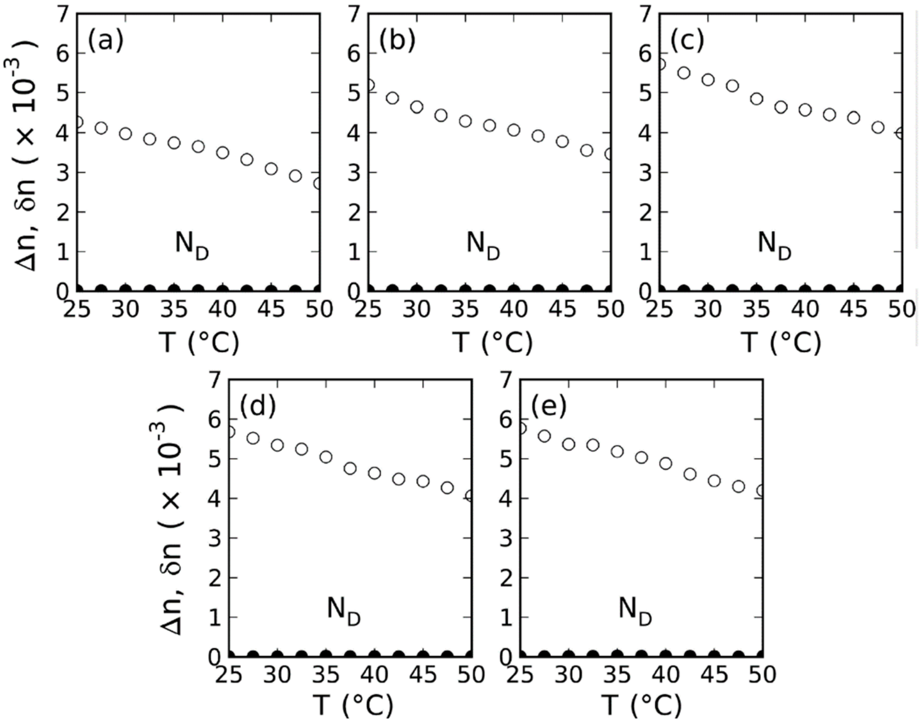


Figure 7. Temperature dependences of the birefringences of the mixtures SDS/alkali sulfate/DDeOH/water, including (**a**) Li_2SO_4, (**b**) Na_2SO_4, (**c**) K_2SO_4, (**d**)Rb_2SO_4 and (**e**) Cs_2SO_4, separately. (○) and (●) represent δn and Δn, respectively [88].

As seen in Figure 6, except for Na_2SO_4, three nematic phases were obtained for K_2SO_4, Rb_2SO_4 and Cs_2SO_4 and the biaxial temperature ranges were about the same, ~5–6 °C. The mixture with Na_2SO_4 has higher birefringence in the N_D region (about twice higher) with respect to those from the other salts. Although we did not observe the biaxial regions for SDS mixtures, as shown in Figure 7, we extracted some useful information from those samples, which were in good agreement with the results of the KL mixtures. While the sample with Li_2SO_4 and Na_2SO_4 exhibited maximum birefringence of ~4.0×10^{-3} and ~5.0×10^{-3}, respectively, K_2SO_4, Rb_2SO_4 and Cs_2SO_4 presented similar birefringence values of ~6.0×10^{-3}, in the N_D phases of the lyotropic host mixture SDS/DDeOH/water. The ~50% increase in the birefringence value, going from Li_2SO_4 to K_2SO_4, was really significant because the birefringences are related to the micelle size and shape anisotropy. The higher the birefringences the bigger the micelle shape anisotropy. Moreover, the amount (or degree) of structured water around the ions of the salts provides a different electrostatic capability to them against the head groups of the surfactants in the micelle interface that plays an important role on the stabilization of the different nematic phases. Indeed, this effect arises from the chaotropic and kosmotropic properties of the ions/counterions. Small ions have relatively high surface-charge density [89] and they exhibit high tendency to be hydrated by a large amount of free water molecules (water-structuring or kosmotropic ions [90–92]) with the negatively greater enthalpy of hydration with respect to bigger ions [90–92]. On the contrary, big ions show opposite behaviour with respect to small ones and they are less hydrated (water-breaking or choatropic ions [90–92]). The kosmotropic and chaotropic properties of the ions are in close relation with the hydrodynamic radius of the ions, R. Comparing two ions with different physical (ionic) radius, r_s and r_b ($r_s < r_b$), and same electrostatic charge, as stated above, smaller ions are surrounded by a higher amount of structured water molecules with respect to the bigger ions, as shown in Figure 8. If two ions with $r_s \neq r_b$ and $R_s \approx R_b$, it is expected that they show similar kosmotropic or chaotropic character. This can be seen in our experimental results given in Figures 6 and 7. While the sequential ordering of the ionic radii of the alkali ions is Li^+ (0.59) < Na^+ (0.99) < K^+ (1.37) < Rb^+ (1.52) < Cs^+ (1.67), their hydrodynamic radii sequence is Li^+ (3.40) >Na^+ (2.76) >K^+ (2.32) ≈ Rb^+ (2.28) ≈ Cs^+ (2.28), where the numbers between parentheses are the ionic and hydrodynamic radius of the ions in Å [93]. In Figures 6 and 7, it was observed that K_2SO_4, Rb_2SO_4 and Cs_2SO_4 affected the phase topology of the nematic-host phases in the similar way because their alkali ions have almost same hydrodynamic radii. At first sight, it seems that the birefringences of the nematic phases could be related to the hydrodynamic radius of ions. Although, for instance, K^+ ion has smaller hydrodynamic radius than Na^+, the mixture with K^+ has lower birefringences in the N_D phase with respect to the one with Na^+ in KL system (Figure 6a,b). However, in the case of SDS system, as shown in Figure 7b,c, there is an opposite situation for the same ions. Remembering that KL is kosmotropic and SDS is chaotropic type surfactants, the head groups of the surfactants KL and SDS interact with strongly kosmotropic Na^+ and chaotropic K^+ ions, respectively, to produce strongly bound ion-pairs at the micelle surfaces, which leads to the formation of larger micelles. X-ray diffraction studies indicated that the larger the micelles the higher the birefringences [15]. Consequently, it would be better to conclude that the larger value of the birefringences is attributed to the formation of tightly bound ion-pairs at the micelle surfaces.

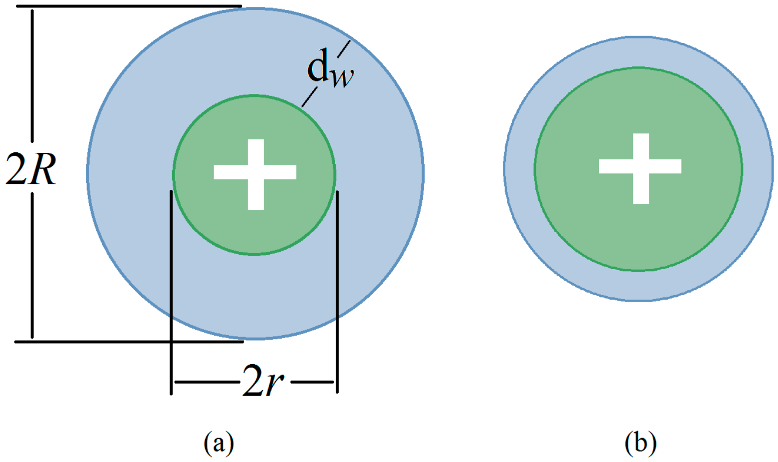


Figure 8. Comparative representation of ionic (2*r*) and hydrodynamic (2*R*) diameter of small kosmotropic (**a**) and the bigger chaotropic ions (**b**) with the same electrostatic charge. d_w is the thickness of the water layer.

The results discussed in [88] may be considered as preliminary. For this reason, complementary investigations were needed to understand the effect of the specific interactions between the ionic species at the micelle surfaces on the stabilization of the lyotropic nematic phases, especially the biaxial. Sodium salts of some Hofmeister ions were added [12] to the host lyotropic mixture of dodecyltrimethylammonium bromide (DTMABr)/dodecanol (DDeOH)/water. The results showed that the interactions between the positively charged head group of DTMABr, trimethylammonium, and the Hofmeister series kosmotropic (SO_4^{2-}, F^-, Cl^-), and chaotropic (Br^-, NO_3^-, I^-, ClO_4^-) anions play an important role on stabilizing the lyotropic nematic phases. The relatively strong interactions of the trimethylammonium head group, which has a chaotropic property, with the most chaotropic anions ClO_4^- promoted the stabilization of just the N_D phase. The higher the kosmotropic (chaotropic) character of the anions the bigger the N_C (N_D) temperature domain.

Although the results of [12] provided useful results about the stabilization the different nematic phases, it was necessary to generalize the role of specific interactions on the micelle's surfaces in terms of the kosmotropic and chaotropic properties of both the surfactant head groups and the counterions/ions. For this purpose, three surfactant molecules were selected, two of them with chaotropic head groups (one positively charged, the other negatively charged) and one with a negatively charged kosmotropic head group. The chaotropic surfactants were sodium dodecylsulfate (SDS) and tetradecyltrimethylammonium bromide (TTMABr), and the kosmotropic one potassium laurate (KL). Three mixtures were prepared, SDS/alkali salt/dodecanol/water, TTMABr/sodium salt/DeOH/water and KL/alkali salt/DeOH/water. The alkali salts (sodium salts) were Li_2SO_4,

Na_2SO_4, K_2SO_4, Rb_2SO_4 and Cs_2SO_4 (Na_2SO_4, NaF, NaCl, NaBr, $NaNO_3$, $NaClO_4$ and NaSCN). The results [14] indicated that when the surfactant head groups and the ions bound to them at the micelle's surface exhibit the same property in terms of the chaotropic or kosmotropic character, the ionic species shows highly-strongly bound ion pairs (Figure 9a), which lead to the stabilization of the N_D phase. If they form highly-loosely bound ion pairs (Figure 9b), the N_C phase is stabilized. For the ion pairs formed by the intermediate level of the interactions between the head groups and the ions, the N_B is favored, as shown in Figure 9c.

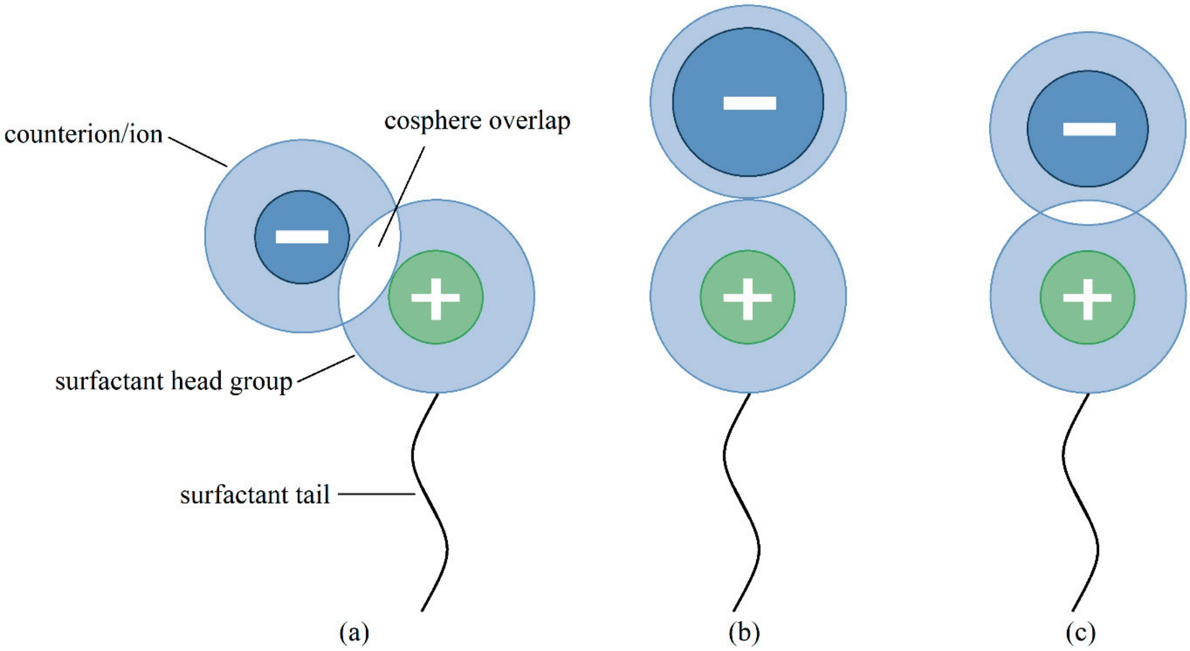


Figure 9. Formation of the ion pairs, considering the interactions between the positively charged kosmotropic surfactant head group and (**a**) kosmotropic, (**b**) chaotropic, (**c**) weakly chaotropic or kosmotropic counterion/ion. This phenomenon was described by Moriera and Froozabadi in Ref [94]. For a surfactant with chaotropic head group, similar situation is in question, except that it produces tightly bound ions pairs with a chaotropic ions and loosely bound ion pairs with a kosmotropic ions, as in the (**a**) and (**b**), respectively.

At this point, it would be better to discuss how the surfactant molecules aggregate in the micelles as a result of the formation of tightly/loosely bound ion-pairs at the micelle surfaces. When an ion is strongly bound to the head group of a surfactant, it screens the Coulombic repulsions between the head groups and the surfactant molecules are packed well in the micelles. In this case, the micelle surface curvature is flatter with respect to the one appeared with loosely interacting head group-ion pairs. This situation applies to strong kosmotrope-kosmotrope or chaotrope-chaotrope interactions between the ionic species. As the surfactant head groups and the ions presence the opposite kosmotrope/chaotrope characters, the repulsions between the head groups are screened less and the micelle surface curvature starts to increase. Thus, in the case of lyotropic nematic phases, from N_C to N_D phase passing through the N_B phase by changing the temperature, the surfactant head groups are packed well at the micelle surfaces leading to the growth in the micelle size and the micelle surface curvature decreases.

3.3. Effect of Localization of Weak Electrolytes at Micelle's Surface

Another effect of the modifications on the micelle's surface in the stabilization of uniaxial and biaxial nematic phases is the location of the dopant molecules (e.g., strong or weak electrolytes) on the micelle's surface. It is known that when a strong electrolyte is added to a lyotropic mixture, its oppositely charged ions with respect to the surfactant head groups produce highly bound ion pairs as a result of strong Coulombic attractions on the micelle's surface. This gives rise to the packing of the surfactant molecules within the micelles and the growth of the micelle size in the A′-B′ plane of the orthorhombic micelles (Figure 4a). This process leads to the stabilization of N_D and/or N_B phase. In the case of weak electrolytes, as expected, the interactions of polar parts of these electrolytes with the surfactant head groups are not as strong as those of ions from the strong electrolytes. At first sight, it might be assumed that this situation is due to the difference in the solubilities of strong and weak electrolytes. We chose some weak electrolytes with –OH and –COOH polar parts [13] to investigate this hypothesis. The experimental results indicated that there exists no direct relation between the solubilities of those weak electrolytes in water and their effectiveness for stabilizing the uniaxial and biaxial nematic phases. In contrast to the solubility, the acidity constants, K_a, of the dopant molecules (i.e., weak electrolytes) emerged as an important parameter in obtaining different types of nematic phase. If a dopant molecule with $pK_a < 7$ is chosen, it is highly possible to stabilize three nematic phases. However, in the case of $pK_a > 7$ and exactly the same amount of dopant with $pKa < 7$, the mixture with the dopant molecule exhibit the same nematic phase type that the mixture without the dopant. In other words, the dopant with $pK_a > 7$ does not change the type of the nematic phase of the host mixture. This situation was attributed to the different location of the dopant molecules in the micelles and their effectiveness of screening the repulsions between the ionic head groups of the surfactants.

4. Conclusions

These recent studies have provided advances on the understanding of the biaxial nematic phase stabilization. We may conclude that the choosing the optimum mixture constituents is a key point to stabilize different nematic phases. Parameters as the relative alkyl chain lengths of surfactant and alcohols and occurrence of strong or weak interactions between the ionic species at the micelle surfaces have to be considered in the preparation of a lyotropic mixture aiming the obtaining of particular nematic phases. The following conclusions may be helpful for experimentalists to obtain the lyotropic mixture presenting uniaxial and/or biaxial nematic phases:

- Considering the relative alkyl chain length of both surfactant (m) and alcohol (n), the higher (smaller) the value of the m (n), when compared with the value of n (m), the larger the phase domains of the N_D and N_B (N_C) [11,15]. Indeed, this situation is a result of the molecular segregation of the surfactant and alcohol molecules in the micelles. Remember that according to the IBM model proposed for the stabilization of three lyotropic nematic phases, micelles are assumed to have an orthorhombic symmetry and there exist two main parts in the micelles: the flattest part in the plane perpendicular to the surfactant long molecular axis (A′-B′ plane in Figure 4a) and the curved part at the rims of the micelles. Our results [11,15] indicated that there is a possibility that more alcohol molecules tend to be located in the curved parts of the micelle when the value of n gets bigger. Consequently, if we have a lyotropic mixture with an alcohol as a cosurfactant exhibiting just N_D (N_C), and one wants to stabilize the N_B phase, we have to change the alcohol by another with shorter (longer) alkyl chain length with respect to that of the main surfactant.
- In the case of the specific interactions between head groups of the surfactants and the counterions/ions of strong electrolytes, in terms of their kosmotropic and chaotropic characters, choosing the surfactant and the electrolyte with slightly opposite (strongly same) character may help to stabilize a lyotropic mixture of the N_B (N_D) phase. Strongly opposite characters of both ionic species, head groups and the ions present in the mixture, stabilizes the N_C phase [12,14].
- The researchers have been using, in general, KL/DeOH/water mixtures to prepare lyotropic mixtures presenting the biaxial nematic phase. However, sometimes the reproducible results could not be obtained. As known, the purity of the KL is very important to obtain the reproducible experimental results. In early studies, the researchers reported in the synthesis of the KL molecule

"KL was synthesized by neutralization of lauric acid with KOH". Here, the term "neutralization" does not include the control of the pH. However, Berejnov et al. showed that the neutralization of all lauric acid to give KL is a crucial point to have reproducible results for any mixture of the surfactant KL [95]. To do so, the reaction pH is kept at ~10.8. Otherwise, if the pH is less than 10.8, some amount of lauric acid may remain in the solution without neutralizing, and then excess of lauric acid and DeOH presence in the lyotropic mixture may cause the esterification of lauric acid. Melnik and Saupe proposed a slow esterification reaction between the alcohol and KL; however, most probably this reaction occurs between the alcohol and lauric acid, instead of the soap [81]. Thus, we can say that the experimentalists have to consider the purity of the KL to have chemically stable lyotropic mixtures.

Consequently, if we have a chance to give "a receipt" to experimentalists for preparation of a lyotropic mixture presenting the biaxial phase, the followings may be considered:

- check the purities of the surfactant and other ingredients of the lyotropic mixture,
- consider the relative alkyl chain lengths of both surfactant and alcohol molecules,
- choose the surfactant head groups and counterions/ions of electrolytes with oppositely kosmotrope or chaotrope characters.

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