ABANT IZZET BAYSAL UNIVERSITY

THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

ROLE OF KOSMOTROPE-CHAOTROPE INTERACTIONS AT MICELLE SURFACES ON THE STABILIZATION OF LYOTROPIC NEMATIC PHASES

MASTER OF SCIENCE

MERİÇ TÜRKMEN

BOLU, DECEMBER 2016

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APPROVAL OF THE THESIS

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December 23, 2016

Prof. Dr. Duran KARAKAŞ .....

Director, **Graduate School of Natural and Applied Sciences**

To my family

DECLARATION

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

MERİÇ TÜRKMEN

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ABSTRACT

ROLE OF KOSMOTROPE-CHAOTROPE INTERACTIONS AT MICELLE SURFACES ON THE STABILIZATION OF LYOTROPIC NEMATIC PHASES
MSC THESIS
MERİÇ TÜRKMEN
ABANT IZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF CHEMISTRY
(SUPERVISOR: ASSOC. PROF. DR. EROL AKPINAR)

BOLU, DECEMBER 2016

Three series of lyotropic quaternary mixtures of ionic surfactants were prepared to investigate the role of kosmotrope-chaotrope interactions at the micelle surfaces on stabilizing the different nematic phases. The ionic surfactants were potassium laurate (KL), sodium dodecylsulfate (SDS) and tetradecyltrimethylammonium bromide (TDTMABr), where KL is a kosmotrope surfactant, and others are chaotrope. Since the first serie consisted of KL/decanol (DeOH)/water/alkali sulfate (lithium sulfate, Li_2SO_4, sodium sulfate, Na_2SO_4, potassium sulfate, K_2SO_4, rubidium sulfate, Rb_2SO_4, and cesium sulfate, Cs_2SO_4), the second serie was obtained from SDS/DeOH/water/alkali sulfate lyotropic mixtures. Other mixtures were prepared by dissolution of some sodium salts of kosmotropic anions (sodium fluoride, NaF, sodium acetate, NaOAc, sodium chloride, NaCl) and of chaotropic anions (sodium bromide, NaBr, sodium nitrate, $NaNO_3$, sodium chlorate, $NaClO_3$, sodium iodide, NaI, sodium thiocyanate, NaSCN, and sodium perchlorate, $NaClO_4$) in the primary mixture of TDTMABr/DeOH/water, separately. The characteristic nematic textures of uniaxial discotic nematic (N_D), biaxial nematic (N_B) and uniaxial calamitic (N_C) were confirmed under polarizing light microscope with and without magnetic field. Laser conoscopy was employed to determine the uniaxial-to-biaixal phase transitions from the temperature dependence of the birefringences of the nematic phases. All experimental results indicated that the interactions at the micelle surfaces play a key role on the stabilization of different nematic phases. Since the kosmotrope-kosmotrope or chaotrope-chaotrope interactions between the head groups of the surfactants and the ions of the electrolytes gave rise to the stabilization of the N_D phase, the opposite characters of these species, i.e. kosmotrope-chaotrope, stabilize the N_B and/or N_C phases. In addition, because two micellar systems, isotropic micellar solutions and lyotropic liquiud crystals, are close contact with each other, we evaluated some parameters of isotropic micellar solutions such as critical micelle concentration (cmc), degree of counterion binding (β), micellization Gibbs energy (ΔG_{mic}) and minimum area per surfactant head group (A_{min}) at constant salt or electrolyte concentration and temperature. These parameters gave useful information on understanding of the interactions at micelle surfaces.

KEYWORDS: Lyotropic nematic phases, uniaxial-to-biaxial nematic phase transition, kosmotrope, chaotrope, interactions at micelle surface, isotropic micellar solutions.

ÖZET

LİYOTROPİK NEMATİK FAZLARIN KARARLI HALE GELMESINDE MİSEL YÜZEYLERİNDEKİ KOZMOTROP-KAOTROP ETKİLEŞİMLERİN ROLÜ
YÜKSEK LİSANS TEZİ
MERİÇ TÜRKMEN
ABANT İZZET BAYSAL ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ
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(TEZ DANIŞMANI: DOÇ. DR. EROL AKPINAR)

BOLU, ARALIK - 2016

Misel yüzeylerindeki kozmotrop-kaotrop etkileşimlerin farklı nematik fazların kararlılığı üzerindeki rolünün incelenmesi için iyonik sürfaktanların liyotropik dörtlü karışımları üç seri olarak hazırlanmıştır. İyonik sürfaktanlar olarak, potasyum laurat (KL), sodyum dodesilsülfat (SDS) ve tetradesil amonyum bromür (TDTMABr) kullanılmıştır. Bu sürfaktantlardan, KL kozmotrop diğerleri ise kaotroptur. Birinci seri, KL/DeOH/su/alkali sülfat (lityum sülfat, Li_2SO_4, sodyum sülfat, Na_2SO_4, potasyum sülfat, K_2SO_4, rubidyum, Rb_2SO_4, ve sezyum sülfat, Cs_2SO_4) ve ikinci seri SDS/DeOH/su/alkali sülfat liyotropik karışımlarından elde edilmiştir. Diğer karışımlar sodyum tuzlarının kozmotropik (sodyum florür, NaF, sodyum asetat, NaOAc, sodyum klorür, NaCl) ve kaotropik (sodyum bromür, NaBr, sodyum nitrat, $NaNO_3$, sodyum klorat, $NaClO_3$, sodyum iyodür, NaI, sodyum tiyosiyanat, NaSCN, ve sodyum perklorat, $NaClO_4$) anyonlarının TDTMABr/DeOH/su ana karışımının içinde ayrı ayrı çözünmesiyle hazırlanmıştır. Tek eksenli diskotik nematik (N_D), çift eksenli nematik (N_B) ve tek eksenli kalamitik (N_C) nematik fazların karakteristik dokuları polarize ışık mikroskopu altında manyetik alan ve manyetik alan olmadığı durumlarda doğrulanmıştır. Nematik fazların çift kırınımlarının sıcaklığa bağımlılığından tek eksenli-çift eksenli faz geçişlerini belirlemek için lazer konoskopisi kullanılmıştır. Tüm deneysel sonuçlar, misel yüzeylerindeki etkileşimlerin farklı nematik fazların kararlılığı üzerinde anahtar bir rol oynadığını göstermiştir. Sürfaktant baş grupları ile elektrolitlerin iyonlarının arasındaki kozmotrop-kozmotrop ve kaotrop-kaotrop etkileşimleri diskotik nematik (N_D) fazını kararlı hale getirirken, zıt iyonik türlerin (örneğin kozmotrop-kaotrop) N_B ve/veya N_C fazını kararlı hale getirmiştir. Ayrıca, her iki miselli sistemin (izotrop miselli çözeltiler ve liyotropik sıvı kristaller) birbirleriyle yakın ilişki içinde olması nedeniyle, kritik misel konsantrasyonu (cmc), karşı-iyon misele bağlanma derecesi (β), miselleşme Gibbs enerjisi (ΔG_{mic}) ve sürfaktant baş grubu başına düşen minimum alan (A_{min}) gibi izotrop miselli çözeltilerden elde edilen bazı parametreler sabit tuz veya elektrolit konsantrasyonu ve sıcaklıkta belirlenmiştir. Bu parametreler liyotropik nematik fazlarda misel yüzeyindeki etkileşimlerin anlaşılması üzerine yararlı bilgiler vermiştir.

ANAHTAR KELİMELER: Liyotropik nematik fazlar, tek eksenli-çift eksenli nematik faz geçişi, kozmotrop, kaotrop, misel yüzeylerindeki etkileşimler, izotropik miselli çözeltiler.

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LIST OF ABBREVIATIONS AND SYMBOLS

ΔG^{o}_{mic}	: The standard Gibbs free energy of the micellization
ΔH^{o}_{mic}	: The standard entalphy of the micellization
ΔS^{o}_{mic}	: The standard entropy of the micellization
A_{min}	: The minimum area per head group of the surfactant molecule at air/water interface
Ch_B	: Biaxial cholesteric phase
Ch_C	: Calamitic cholesteric phase
Ch_D	: Discotic cholesteric phase
cmc	: Critical micelle concentration
H	: Hexagonal phase
htp	: Helical twisting power
I	: Cubic phase
L	: Lamellar phase
LLCs	: Lyotropic liquid crystals
TLCs	: Thermotropic liquid crystals
N	: Nematic phase
N_B	: Biaxial nematic phase
N_C	: Calamitic nematic phase
N_D	: Discotic nematic phase
P	: Pitch
X	: Mole fraction
α	: The degree of counterion ionization from micelle
β	: The degree of counterion binding to micelle
Δn/δn	: Birefringences
$\Delta\chi$	: Diamagnetic susceptibility anisotropy
Γ_{max}	: The maximum total amount of surfactant adsorbed at the air/water interface
η/η_o	: Relative viscosity

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1. INTRODUCTION

Micellar systems of surfactants are mainly known as isotropic micellar solutions and lyotropic liquid crystals. Because both systems consist of same structural units, so-called micelles, they have some similar properties with one another although the latter is more complex than the former one. From the sample preparation point of view, while the isotropic micellar solutions are obtained at low surfactant concentrations, the lyotropic liquid crystalline phases are prepared at high surfactant concentrations. In addition, near the critical micelle concentrations, the micelles, in general, are spherical in shape, however, they grow to give anisometric micelles by increasing the surfactant concentration in the solution, and i.e. lyotropic liquid crystalline samples are now formed. From this respect, the isotropic micellar solutions may be assumed as the precursors of lyotropic phases, especially nematic ones.

Because both micellar systems exhibit some similar properties, we can obtain some information from isotropic micellar solutions to explain the properties of lyotropic liquid crystals (Ute et al., 2009; Akpınar et al., 2016a). For instance, as it was proved, the addition of an electrolyte has same role on both systems, i.e. it causes the micellar growth not in only isotropic micellar solutions but also in lyotropic liquid crystals (Ali and Makhloufi, 1999). So, as it is aimed in this dissertation, we may use some parameters obtained from the isotropic micellar solutions to interpret the effect of the same parameters on lyotropic liquid crystals.

1.1 Lyotropic Liquid Crystals

Liquid crystals are distinct states of matter between crystalline solid and liquid state. As it can be understood from their nomenclature, they exhibit some properties similar to both solid and liquid states. For instance, liquid crystal materials are strongly anisotropic in some of their properties and have a certain degree of fluidity, like solids and liquids, respectively (Chandresakkar, 1992).

Depending on the building blocks, two types of liquid crystals are mainly identified as: (a) thermotropic liquid crystals (TLCs) and (b) lyotropic liquid crystals (LLCs). Since TLCs are composed of molecules, micelles are structural units of LLCs. The micelles are formed by the agglomerations of the amphiphilic molecules above a certain concentration, so-called critical micelle concentration, (Figure 1.1). Indeed, LLCs may be considered as dispersion of the micelles in a solvent.

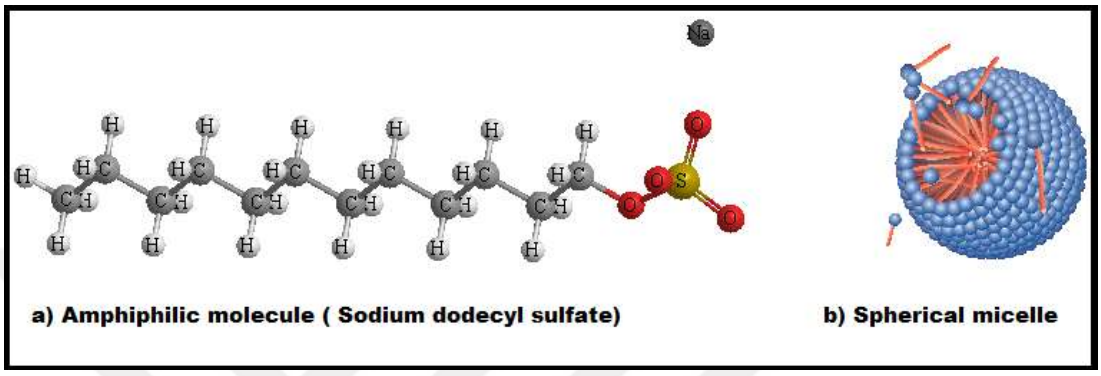


Figure 1.1. Molecular structure of an amphiphilic molecule and representation of a spherical micelle.

TLCs have some potential applications in optical devices such as LCD displays (Yeh and Gu, 1999), however, there are not many devices based on lyotropics. On the other hand, the physico-chemical properties of lyotropics have an interesting interface with biology, and understanding of these properties has been relevant for improving some technological aspects of cosmetics, soaps, food, crude oil recovery and detergent production (Neto and Salinas, 2005). From the production point of view, LLCs differ from the other class of liquid crystals, TLCs. While TLC structures are determined or changed by temperature, LLCs are mixtures of amphiphilic molecules and a solvent under certain temperature and relative concentration of constituents. In other words, the driving forces for the formations of TLCs and LLCs phases are only temperature and both temperature and concentration of ingredients of lyotropic mixtures, respectively.

1.1.1 Lyotropic Liquid Crystalline Structures

Depending on the micelle shapes and different packing of the micelles, LLCs are mainly classified as lamellar (L), hexagonal (H), cubic (I), nematic (N) and cholesteric (Ch). In lamellar LLCs, which are also known as “neat” phases, there are infinitively large bilayers composed by the surfactant molecules which prefer to build up disc-like micelles at low surfactant concentrations.

In this structure, water molecules are trapped between the polar head groups of neighboring layers and the hydrocarbon parts of the surfactants are located in the non-polar part of the bilayers, (Figure 1.2).

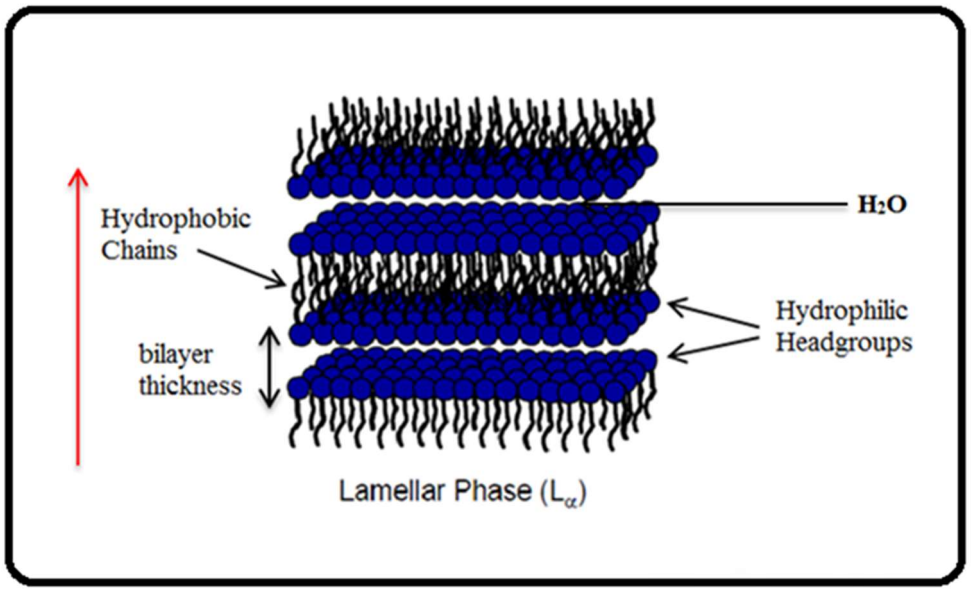


Figure 1.2. Schematic representation of lamellar phase.

In the lamellar phases, the surfactant molecules are packed in one-direction, along the bilayer thickness. So, there is a one-dimensional repeating order in the lamellar phases. Depending on the state of the hydrocarbon chains of the surfactants, within the micelles, the lamellar phases are classified as L_α and L_β. The subscripts α and β correspond to liquid-like disordered and solid-like ordered hydrocarbon chains, respectively. The main difference between these two types of the hydrocarbon chains is related to their conformations. While liquid-like hydrocarbon chains possess lots of different conformations, the solid-like chains exhibit all-trans conformations. The L_β phases are also known as “gel” phases and they are characterized with very high

viscosity and viscoelasticity. Lamellar liquid crystalline phases are used as a food emulsifier, cosmetic products materials, and drug delivery agents in industrial applications (Wang and Marangoni, 2016; Li, et al., 2016; Tiberg and Johnsson, 2011).

Hexagonal (middle) phases are composed of infinitively long cylindrical or rod-like micelles in a hexagonal array, (Figure 1.3). In these phases, cylindrical units are arranged parallel to one another in two dimensions, i.e. there exists two dimensional repeating order in the hexagonal phases.

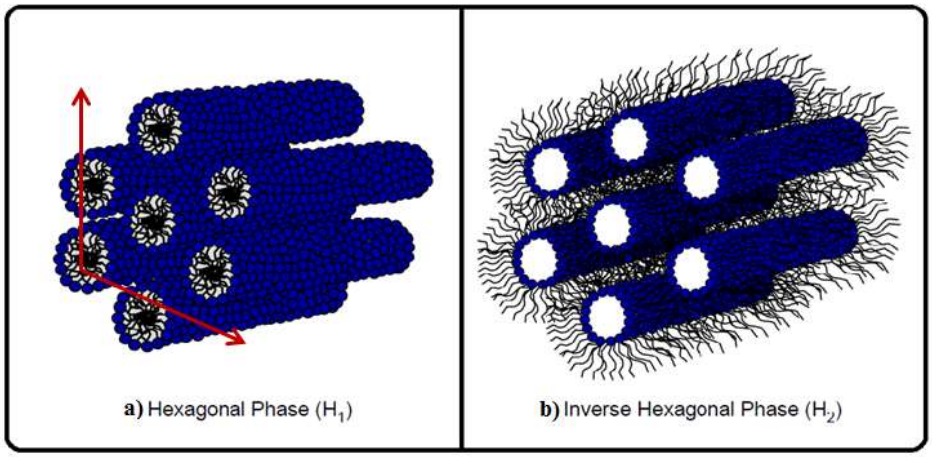


Figure 1.3. Schematic representation of hexagonal phase.

Cubic phases are formed by the arrangement of spherical micelles in three dimensions, i.e. there is a three-dimensional repeating order in these phases. A body centered cubic arrangement is given in (Figure 1.4a) and as it can be seen that the spherical micelles have certain positions in this arrangement and water molecules fill the space between the units. It is known that cubic phases exhibit properties similar to isotropic media in many aspects. Because of this, the cubic phases are also called "viscous isotropic phases". A bicontinuous arrangement is also observed in a cubic phase.

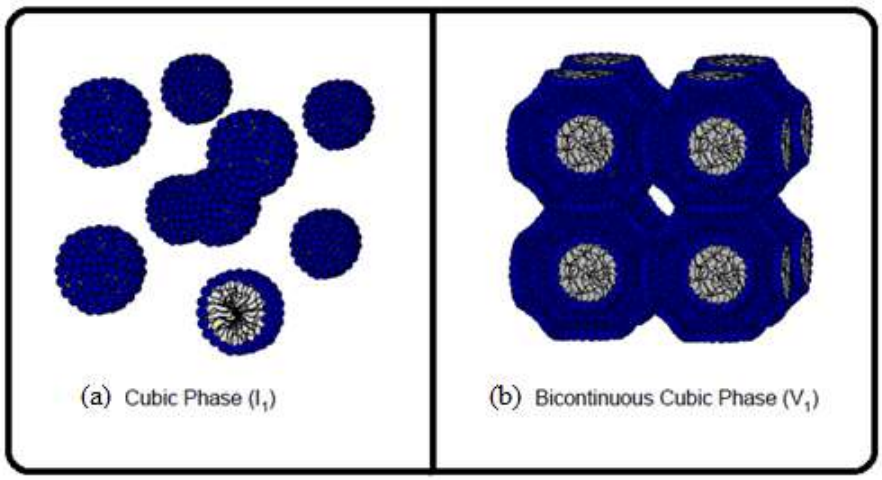


Figure 1.4. Schematic representation of cubic phases.

Hexagonal and cubic lyotropic liquid crystalline phases have applications in drug delivery systems because some drugs are insoluble in blood and addition of a small amount of liquid crystalline sample increases solubility of drugs in blood. They also help to release and transfer drugs in living metabolism systems (Chen et al., 2014; Shah et al., 2001; Chang and Bodmeier, 1997; Fong, et al., 2016).

Among the LLC structures, nematic phases, which are subject of this dissertation, have been studied by several research groups. Their main characteristic property is that their phase director's exhibit preferred alignment with respect to applied external magnetic field direction. As it was reported in the literature Boden et al. (1981), the director alignment is related to the diamagnetic susceptibility anisotropy, $\Delta\chi=\chi_{//}-\chi_{\perp}$, of alkyl chains of the amphiphilic molecules which are the main component of lyotropic liquid crystalline mixtures. In the case of $\Delta\chi>0$ ($\Delta\chi<0$), the director of a nematic phase aligns parallel (perpendicular) to the magnetic field direction. For hydrocarbon chains, $\Delta\chi$, in general, is greater (smaller) than zero in the N_C (N_D) phases, however, the opposite behavior of diamagnetic susceptibility anisotropy was also stated for fluorocarbon chains with respect to the hydrocarbon chains (Boden, 1979). In addition to $\Delta\chi$, another parameter for the classification of the nematic phases is the shape of micelles. In the literature, depending of the micelle shapes, three types of nematic phases were reported, being discotic (N_D), calamitic (N_C) and biaxial (N_B) nematic phases (Galerne et al., 1987; Neto et al., 1985a). From the optical point of view, except N_B phases, other nematics are uniaxials, i.e. while N_B phases have two optical axes, uniaxial nematics have only one.

In addition, it is known that the N_B phase is an intermediate phase located between two uniaxial N_D and N_C phases on the phase diagrams (Yu and Saupe, 1980). And the phase transitions from uniaxial-to-biaxial phase are of second order according to the mean-field theory (Galerne and Marcerou, 1985a). The nematic phases are characterized under polarizing optical microscopy with their characteristic schlieren textures, (Figure 1.5). However, sometimes, to differentiate N_D with N_B and N_C with N_B around the phase transitions is difficult, so the birefringences measurements of the well-aligned lyotropic samples are needed to decide the type of the nematic phases.

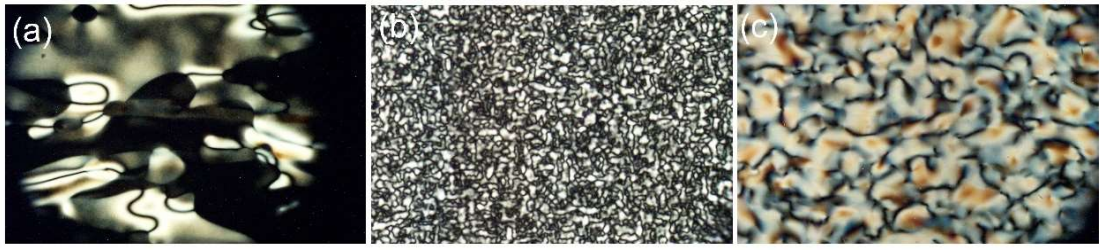


Figure 1.5. Characteristic magnetically non-well aligned textures of lyotropic nematic phases observed under polarising optical microscope: (a) N_D, (b) N_B and (c) N_C.

Similar to the nematic phases, cholesteric phases are classified as Ch_D, Ch_B and Ch_C, being counterparts of nematic phases. Depending on the preparation ways, they are called “intrinsic” and “induced” cholesteric phases. Since, in the former way, they are obtained by directly using L-enantiomers whose DL-racemic mixtures give nematic phases Akpinar et al. (2001); Radley and Cattey (1992), they are prepared by doping a chiral guest agent into a nematic phase in the latter case (Lee and Labes, 1984; Reis et al., 2013). In these phases, the chiral micelles are arranged around a certain axis, so-called helix axis, to form the helical structure. While the preferred alignment of the local director of the individual micelles is a phase director of the nematic phase, the helix axis is the optical director of the cholesteric phases. Two important parameters are used for characterization of cholesteric phases: pitch (P) and helical twisting power (htp) which are mathematically related to each other via $P^{-1} = (\pm)\ htp.x_i$ where P^{-1} is the reciprocal of the pitch (twist) and x_i is the mole fraction of the L-enantiomer or chiral guest molecule in the lyotropic mixture. The characteristic microscopic textures of the cholesteric phases are given in (Figure 1.6).

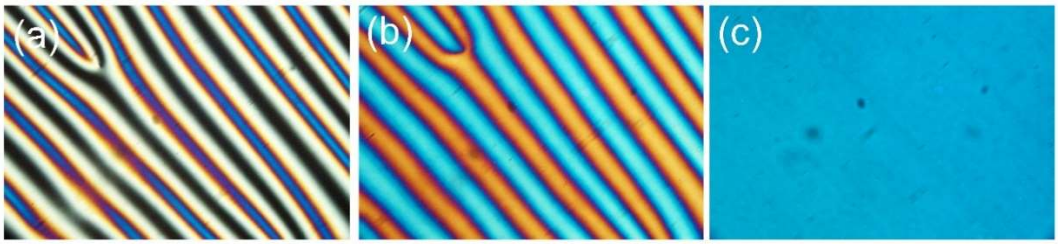


Figure 1.6. Magnetically well-aligned lyotropic cholesteric textures of (a) Ch_D, (b) Ch_B and (c) Ch_C phases. The Ch_C phase is unwounded under the effect of external magnetic field, i.e. helical structure is destroyed and its texture is similar to well-aligned N_C phase. The distance between three paralel lines in (a) and (b) corresponds to the pitch length.

Because the nematic phases are of subject to this dissertation, it would be better to give some information on some models to explain their formation mechanisms, especially biaxial nematic phases.

1.1.2 Lyotropic Nematic Phases and IBM Model

In early studies, the micelle shapes in uniaxial N_D and uniaxial N_C phases were considered as disc-like and cylindrical-like micelles, respectively, (Figure 1.7). It was proposed that the local director of the disc-like (cylindrical-like) micelles prefers to align perpendicular (parallel) to the magnetic field direction. However, after Yu and Saupe (1980) experimentally realized the evidence of the N_B phases for the first time in the ternary mixture of potassium laurate (KL)/decanol (DeOH)/D_2O, the discussions on the N_B phases were started in literature. They constructed the partial phase diagram of this ternary mixture, depending on the concentration of the KL, and it was experimentally observed for the first time that N_B phase was an intermediate phase between other two uniaxial N_D and N_C phases. In 1985, Neto et al. (1985b) investigated the same ternary mixtures in more details. They used the experimental techniques optical microscopy, laser conoscopy and X-ray diffraction and found that the biaxial phase domain was relatively large (~15°C) for appropriate concentrations.

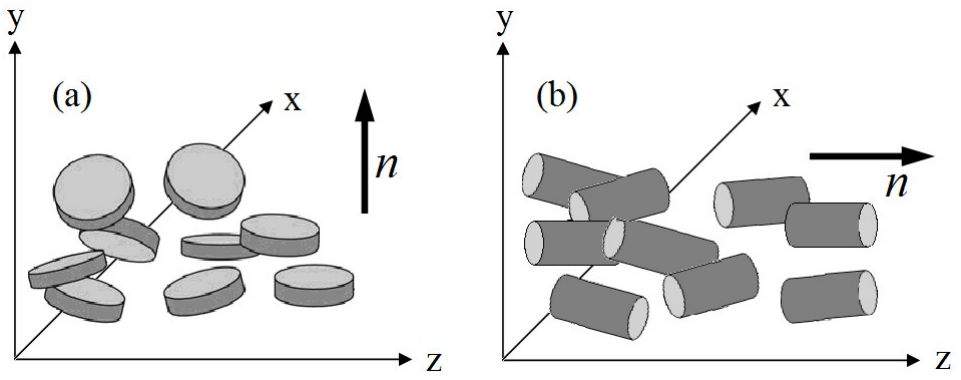


Figure 1.7. Orientations of (a) disc-like and (b) cylindrical micelles perpendicular and parallel to magnetic field direction, H, along z. n (phase director) represents the preferred alignment of the individual micelles with their local directors.

In 1982, Bartolino et al. (1982) presented another ternary mixture of sodium decyl sulfate (SdS)/DeOH/H_2O to make a contribution to the understanding of the biaxial nematic phases. Their study was related to the optical observation on (a) the temperature dependence of the birefringence (Δn) and (b) the variation of the optical sign of oriented samples. They showed that, using phase compensator, uniaxial N_D (N_C) phase had positive (negative) birefringence and the phase transition from N_D to N_C exhibited a discontinuity, i.e. this phase transition is of second order, as stated by Freiser (1990).

Some research groups suggested by rejecting the evidence of the N_B phase that the N_B phase arose from the co-existence of other two uniaxial N_D and N_C phases. In 1984, taking into account Onsager theory, Stroobants and Lekkerkerker proposed a model where cylindrical and discotic objects coexist, giving rise to the biaxial nematic phase (Stroobants and Lekkerkerker, 1984). They attributed their idea to "a mixture of disc-like and cylindrical-like micelles, MCD" model. However, as we will discuss later, some theoretical and experimental studies reported in the literature showed that the MCD types of models had some problems to explain the existence of the N_B phases (Palffy-Muhoray et al., 1985; Sharma et al., 1985; Kooij and Lekkerkerker, 2000).

Some other theoretical studies of binary mixtures of rod-like and disk-like rigid particles presented in the literature. Palffy-Muhoray et al. (1984) studied the phase behavior of the binary nematic liquid crystal mixtures in the absence of the external field by applying the Maier-Saupe mean field theory. They concluded that N_B phase was not thermodynamically stable phase with respect to other uniaxial N_D and N_C

phases and the phase separation should occur. That is, N_B phase was a result of co-existing of two uniaxial N_D and N_B phases, as predicted by MCD model, and the stabilization of N_B phase could be only achieved for some certain materials under external field condition. However, Sharma et al. (1985) showed that there could be a possibility about the biaxial phase being stable by increasing either the isotropic or the anisotropic parts of the interspecies interaction strength.

Although the discussions about the stability of the N_B phase were going on, experimentalist tried to find new lyotropic mixtures presenting the N_B phases. In 1985, Galerne et al, (1985b) introduced a new ternary mixture of rubidium laurate (RbL)/DeOH/H_2O to the literature. They investigated the defect lines (zigzag disclinations) which supported the evidence of biaxial shape micelles in biaxial nematic liquid crystals.

However, until 1985, there was no any useful model to explain existence of the biaxial nematic phases. Eventually, a reliable and an important model was proposed by Neto et al. (1985c), which was supported by also Galerne et al. (1987), for the N_B phases by rejecting the MCD types models. Their model, so-called "intrinsically biaxial micelles model, IBM", is mainly based on two parameters: (a) micelle symmetry and (b) orientational fluctuations. According to the IBM model, the micelles have orthorhombic symmetry, (Figure 1.8a), in all three different nematic phases and the driving force for occurrences of these phases is orientational fluctuations. If we sketch micelles as an object of orthorhombic symmetry, as in (Figure 1.8a), with typical dimensions A', B' and C', we may choose the axes of the coordinate system, fixed in the micelles, as α, β and γ. These orthorhombic micelles exhibit different orientational fluctuations for the formation of N_D, N_B or N_C phases. The orientational fluctuations around the axis perpendicular to the largest micelle surface (along the symmetry axis γ) give rise to the formation of the N_D phase, (Figure 1.8b). In this situation, the micelle size A' is 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 starts to be longer and the small amplitude orientational fluctuations along three axes (1, 2 and 3) leads to the N_B phase, (Figure 1.8c). If the temperature is changed until obtaining the N_C phase, the micelle size along α continues to be longer to favor

the orientational fluctuations around the long micellar axis (paralel to the axis 1), (Figure 1.8d).

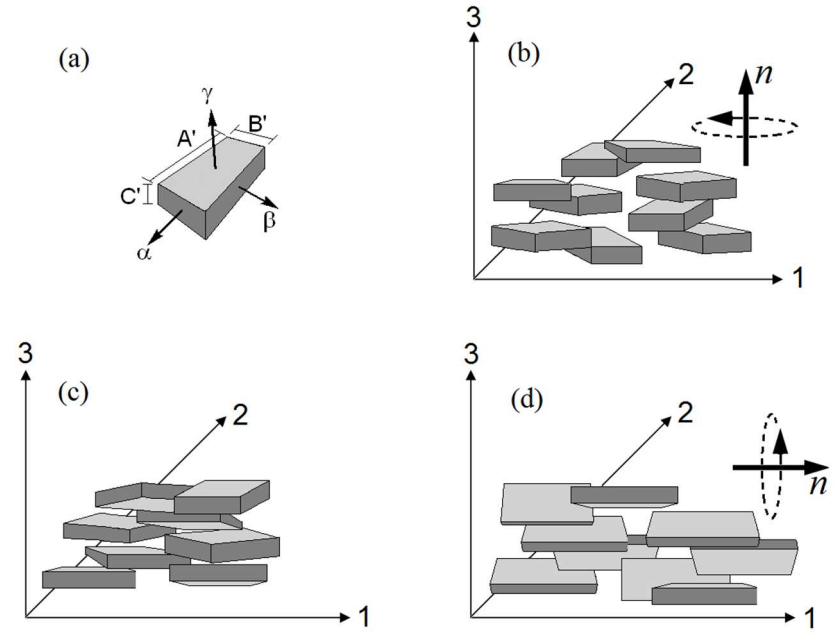


Figure 1.8. (a) Sketch of the orthorhombic micelle in the framework of the IBM model. The detergent amphiphilic bilayer is represented by C'. (b) N_D, (c) N_B and (d) N_C.

Until 1989, since the lyotropic mixtures exhibiting the biaxial nematic phases contained alcohol and surfactant, Oliveira et al. (1989) achieved to find a new mixture of KL/decylammonium chloride/water without alcohol. This new mixture was important because, as was suggested by Melnik and Saupe (1987), if a mixture has KL type surfactant and alcohol there is a possibility of a slow esterification in the mixture. In the study of the reference Oliveira et al. (1989), the researchers investigated the mixtures of KL/DACl/water and KL/DeOH/water, i.e. alcohol free and with alcohol mixtures, respectively, to compare the physico-chemical stability of two types of the mixtures. Their long-term study was 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 stated that the alcohol free mixtures were more stable than the one with alcohol.

In 1990, Vasilevyskaya et al. (1990) investigated two lyotropic mixtures exhibiting biaxial nematic phase. Since one of them, SdS/DeOH/H_2O, was already presented to the literature before by Bartolino et al. (1982), other one, SdS/DeOH/H_2O/Na_2SO_4, was presented for the first time. Their experimental study was based on the measurement of the birefringences of the nematic phases depending on the temperature. They observed that this new system had smaller birefringences value with respect to the conventional lyotropic mixture KL/DeOH/H_2O (Yu and Saupe, 1980). As a result of their study, they concluded that the phase transitions from biaxial to uniaxials arise from the suppression of the rotation of the micelles around the axes. For instance, if the micelles turn around the short axis (long axis) of the micelle, it is possible to obtain the discotic (calamitic) nematic phase. In the case of the biaxial nematic, the rotation of the micelles is completely suppressed. Their conclusion is very similar to the IBM model. However, it is better to use the term "orientational fluctuations" instead of "suppression" to have different nematic phases as it is suggested in the IBM model. In addition, in the case of the biaxial nematic, the rotations of the micelles or orientational fluctuations are not suppressed, instead, the orientational fluctuations with small amplitudes around the three symmetry axes of the orthorhombic micelles are responsible for the formation of the biaxial nematic phases.

Experimental studies and theoretical predictions stated that the biaxial nematic phase is an intermediate phase between two uniaxial nematic ones. Ho et al. (1991) reported an interesting study which was 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 not be an intermediate phase between two uniaxial nematics.

Another interesting study was published by Quist (1995) to investigate novel lyotropic mixture of sodium dodecylsulfate SDS/DeOH/H_2O via NMR spectroscopy. According to the Landau theory, the phase transitions from uniaxials-to-biaxial nematic phase are of second-order. However, Quist proposed that these phase transitions might be first-order. The author attributed the first–order N_D-N_B and N_B-N_C phase transtions to a variation in the aggregate (micelle) shape.

This result is really very interesting, because other experimental and theroretical studies showed that the uniaxial-to-biaxial transitions have to be of second order. In addition, early studies Galerne and Marcerou (1985a) and recent Akpinar et al. (2012a; 2012b), especially obtained from the temperature dependence of the birefringences, showed that these phase transitions are of second order as predicted by mean-field theory (Freiser, 1970).

From the diamagnetic susceptibility anisotropy point of view, taking into account the 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-}. For the biaxial nematics, the diamagnetic susceptibility anisotropy is defined as:

$$\Delta\chi = \chi_{33} - \frac{\chi_{11} + \chi_{22}}{2} \qquad (1.1)$$

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 (Filho et al. 2003; Akpinar et al., 2014). Since Quist (1995) reported two different biaxial nematic phase region with positive and negative diamagnetic susceptibility anisotropy in the phase diagram, however, they did not study on the phase transitions between these N_{B+} and N_{B-}. This type of phase transition was investigated by de Melo Filho et al. (2003) in the novel lyotropic mixture of tetradecyltrimethylammonium bromide (TDTMABr)/DeOH/ H_2O by measuring the deuterium quadrupolar splittings via Nuclear Magnetic Resonance. The results indicated that while the phase transition between N_{B+} and N_{B-} is of first-order, the uniaxials-to-biaxial transitions are of second order in the agreement with the mean-field theory and in contrary with the Quist's study.

Summarily, until 2003, the biaxial phase was identified in totally just eight lyotropic mixtures. Unfortunately no further new lyotropic mixtures presenting biaxial nematic phase was reported in the literature between 2003 and 2012, Akpinar and Neto et al. (2012a; 2012b; 2015; 2016a; 2016b) discovered novel lyotropic mixtures in recent years and they stated new aspects or factors that affect the formation of the biaxial nematic and cholesteric phases and the biaxial phase domain.

1.2 Isotropic Micellar solutions

In the frame of this dissertation, we aimed to interpret lyotropic liquid crystalline properties of ionic surfactants supporting by some parameters obtained from their isotropic micellar solutions (Ute et al., 2009). From this respect, it would be better to give some basic information on the micellization of the surfactant molecules in water.

1.2.1 Micellization

Surfactants have various applications in not only research but also technological fields. A large number of studies have been reported on their characteristic properties in various micelles, emulsions, vesicles, lyotropic liquid crystals, etc. via several techniques (Moulik, 1996; Maiti et al., 2007; Zhai et al., 2005; Siperstein and Gubbins , 2003). In those studies, researchers mainly concentrated on their micellization process taking into account some factors such as temperature, additives, pH etc. (Khoshnood et al., 2016; Lewis, et al., 2016; Rose, et al., 2015). As given in (Figure 1.1), surfactants are mainly composed of hydrophilic (water-loving) and hydrophobic (water-hating) parts and they exhibit different properties in water. These two parts play an important role on the nature of surfactants. For instance, while hydrophilic parts determine the surfactants to be anionic, cationic, zwitterionic or non-ionic, hydrophobic ones do as one linear or two linear chains as branched, (Figure 1.9)

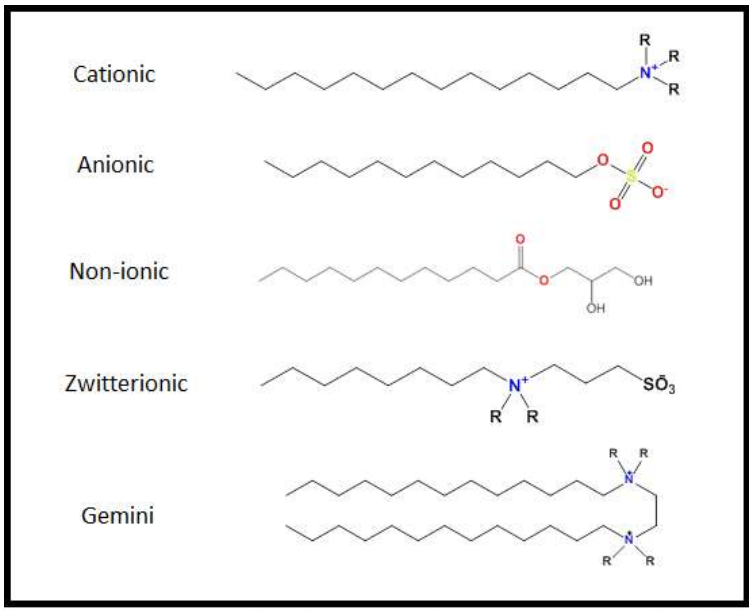


Figure 1.9. Examples of surfactant types by head group classification.

Surfactant molecules show different properties in bulk and at surface. When they are dissolved in water at low surfactant concentrations (i.e. before micellization), they adsorb at the air/water interface with their hydrophobic parts oriented towards the air and their hydrophilic parts are in contact with water molecules at the interface. If the concentration of surfactant molecules is increased enough to saturate the surface of the solution, hydrophobic parts of surfactant molecules try to be located on the surface of water reaching the maximum surface concentration. When all surface of solution is saturated with surfactant molecules by increasing the concentration, monomers of surfactant molecules aggregate into water to form the micelles, i.e. micellization starts at the critical micelle concentration. In general, there exists a dynamic equilibrium between the surfactant monomers, which absorb at the air/water interface and present in the water, and micelles as shown in (Figure 1.10). From the energy point of view, the monomers in the bulk increase the free energy of the system because their hydrophobic parts are surrounded by the water molecules which cause the breaking the ordered hydrogen bonding structure of the water molecules, (Figure 1.11). Then, the surfactant monomers are transferred into the micelles by decreasing the free energy of the whole system (aqueous solution). Indeed, this is known as "hydrophobic effect", which is basis of the micelle formation.

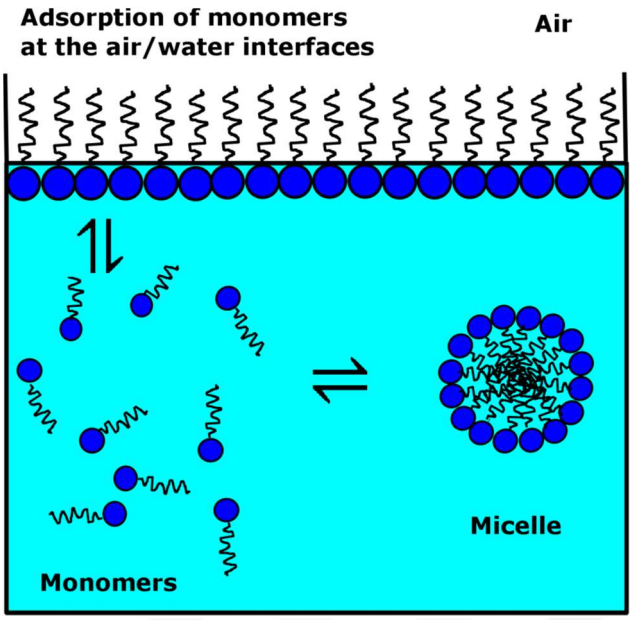


Figure 1.10. Schematic representation of the three states in which surfactant molecules reside in water, i.e. monomers adsorb at the air/water interface, monomers in the bulk solution and micelles (Holmberg, 2002).

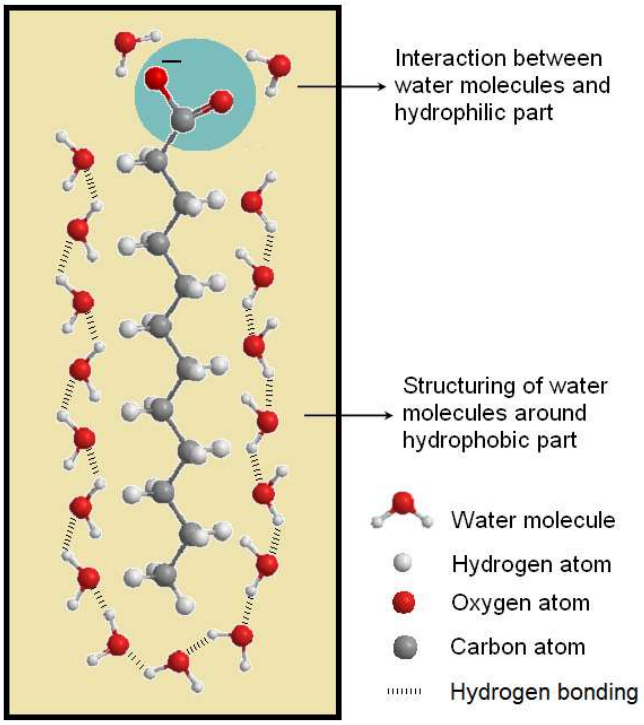


Figure 1.11. Structuring of the water molecules around the hydrophilic and hydrophobic parts of a surfactant molecule.

For aqueous solutions of the surfactants, micellization is an important phenomenon and some parameters that affect the micellization, especially the critical micelle concentration, are of the subject for the studies in the literature. By this way, novel micellar systems may be developed under certain conditions for their various potential applications in industry.

1.2.2 Critical Micelle Concentration

One of the most important parameter for the aqueous isotropic micellar solutions is critical micelle concentration (*cmc*) at which micelles are formed (Shinoda, 1963). The critical micelle concentration is a characteristic property for each surfactant molecules and some experimental techniques are used to determine the *cmc*s of the surfactants from the break point of any physical property of the solution as a function of surfactant concentration (Dominguez et al., 1997; Garcia-Mateos et al., 1990; Chattopadhyay and London, 1984; Lin et al., 1999; Salem et al., 2016). As shown in (Figure 1.12), most of the physical properties of the solution show sharp changes at the critical micelle concentration.

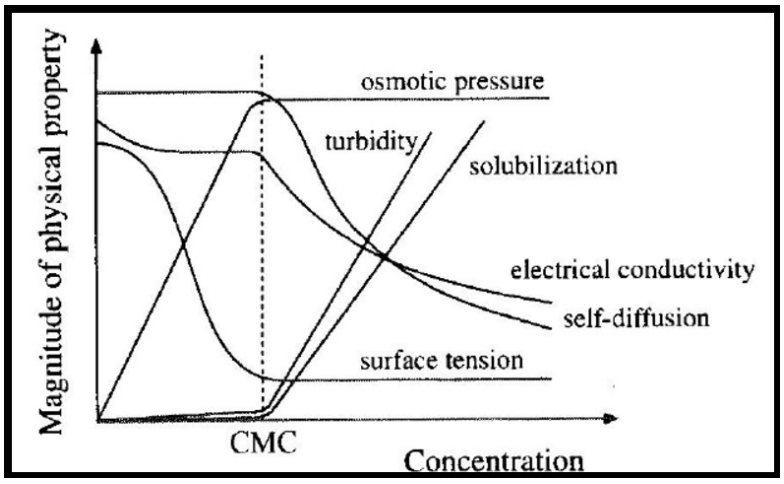


Figure 1.12. Schematic representations of some physical properties which exhibit a sudden change or discontinuity near the critical micelle concentration (cmc). Figure 1.12 is reproduced from (Hamley, 2000).

The main factors that affect the micellization, i.e. the critical micelle concentration, are (a) temperature, (b) structure of surfactant molecule, (c) surfactant counterions and (d) electrolyte added into the binary solutions of the surfactant/water.

1.2.2.1 Temperature

The understanding of the effect of temperature on the cmc of surfactants in aqueous medium is not so easy and it is really quite complex. Experimental results in the literature stated that, for the ionic surfactants, by increasing the temperature, their cmc value firstly decreases until reaching to a minimum value then cmc value increases. In other words, the temperature dependence of cmc of the ionic surfactants give U-shaped curve, (Figure 1.13) (Kang et al., 2001). This process can be explained as follows (Kumar et al., 2000): the hydration of hydrophilic groups by free water molecules is lowered in aqueous media as the temperature is increased and the micellization is more favored, i.e. the critical micelle concentration decreases. On the other hand, the further increase in temperature results in the disruption of the structured water molecules, which surround the hydrophobic groups of surfactant molecules, and, in this case, the micellization is unfavored, i.e. the critical micelle concentration increases.

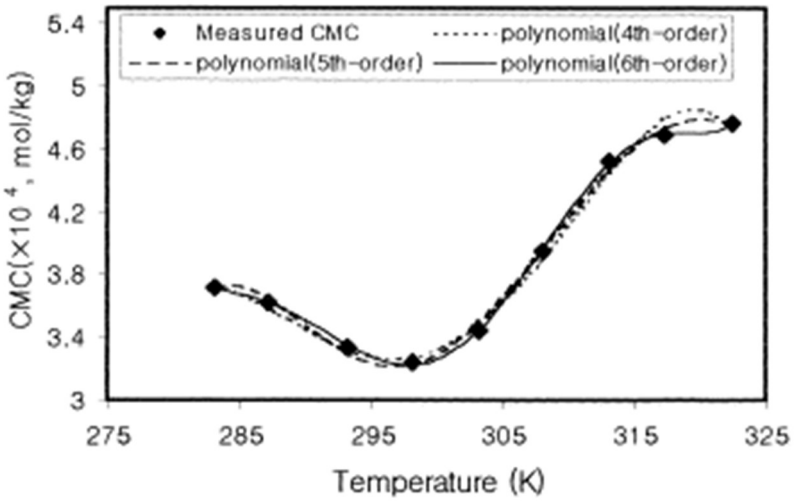


Figure 1.13. Fits of the 4th, 5th, and 6th polynomial functions to the cmc–temperature data for the OTAC/water. (Kang et al., 2001).

1.2.2.2 Structure of Surfactant

Because the surfactants have two different parts, hydrophilic and hydrophobic ones, they affect the critical micelle concentration differently. In general, surfactants have linear alkyl chain and the critical micelle concentration depends on the surfactant alkyl chain length. When two surfactant molecules consist of same head groups or hydrophilic parts, the longer the alkyl chain length leads to the reduction of the critical micelle concentration. The alkyl chain length dependence of the critical micelle concentration may be estimated by the following equation (Klevens, 1953).

$$\log C_{cmc} = A - Bm \qquad (1.2)$$

where 'A' and 'B' are constants for the particular homologous series and temperature, respectively (Shinoda et al. 1963). For most of surfactant molecules, A and B values vary from 1.4 to 1.8 and 0.22 to 0.30, respectively. This equation is valid for surfactants containing maximum 16 carbon atoms in their alkyl chains, however, it cannot be applicable for the surfactants containing more than 16 carbon atoms (Griess, 1955). The effect of the surfactant alkyl chain length on the critical micelle concentration may be attributed to the coiling of the monomers by minimizing the hydrophobic interactions of unassociated molecules (Mukerjee, 1967).

From the hydrophilic parts point of view, surfactants may be ionic, non-ionic or zwitterionic. So, the critical micelle concentration changes with respect to the types of head groups of the surfactants. Ionic surfactants have greater cmc values than non-ionic surfactants containing equivalent hydrophobic groups and zwitterionic surfactants appear to have slightly smaller cmc than ionics with the same number of carbon atoms in hydrophobic groups. In addition, if the surfactant molecules contain more than one hydrophilic group, the critical micelle concentration shows larger value than those with one hydrophilic group. The critical micelle concentration also depends on the functional head groups. For example, the order of decreasing critical micelle concentration in some n-alkyl ionic surfactants has been noted by Klevens (1953) as follows:

$$Ammonium\ salts > carboxylates > sulfonates > sulfates$$

1.2.2.3 Surfactant Counterions

After the surfactant molecules form the micelles, some of their counterions are bound to the micelles. When the counterion binding to the micelle increases, it favors the micelle formation, i.e. the higher the degree of counterion binding, the smaller the cmc value (Sahara and Harada, 2016). The degree of counterion binding is highly dependent on polarizability, charge and hydrated radius of counterions (Bunton et al., 1991; Almgren and Rydholm, 1979; Larsen and Tepley, 1974). While the counterion binding increases with the polarizability and the charge, it decreases with the hydrated radius.

1.2.2.4 Electrolyte

The addition of an electrolyte to an aqueous solution of ionic surfactants decreases their cmc. The decrease in cmc values is a result of the increase in screening of the repulsions between the surfactant charged head groups by the addition of electrolyte or salt. It was stated that organic salts reduce cmc value efficiently with respect to inorganic ones. The effective or hydrodynamic radius of the cation of the inorganic salts plays an important role on the cmc.

The cmc increases as the hydrodynamic radius of the cation increases because of efficient penetration of the smaller cation between the head groups at micelle surfaces, which screen the electrostatic forces and cmc is reduced. For instance, when the inorganic sulfate salts of Li, Na, K and Cs ions, where Li ion has the highest hydrodynamic radius among them, are added into a binary isotropic micellar solution of sodium dodecyl sulfate (SDS)/water, cesium sulfate reduces the cmc more than the lithium sulfates (Goddard et al., 1953). It was experimentally found that the effect of salt added on cmc is expressed by the following equation (Corrin and Harkins, 1947; Rosen, 2004).

$$\log CMC = a \log C_I + b \qquad (1.3)$$

where ‘a’ and ’b’ are the constants for a given ionic head at a particular temperature and C_I is the total counterion concentrations in equivalents per liter.

1.2.3 Thermodynamic of Micellization

Thermodynamic parameters of micellization are expressed by the difference between the thermodynamic parameters of surfactant in the monomeric state and those in the micellar state. It can be calculated from the temperature dependence of the cmc and degree of counterion binding to the micelle (β), which is related to the degree of ionization of counterions (α) by $\alpha=1-\beta$. In general, cmc and α or β are evaluated from conductivity method (Jiang, et al., 2005; Tarus et al., 2003). A plot of conductivity (κ) of an ionic surfactant against its concentration in aqueous solution gives a linear curve. When the concentration reaches to the cmc value, a break on the curve at cmc is observed and, above the cmc, a linear dependence of κ with the concentration continues with different slope, (Figure 1.14). The break on the plot arises from the binding of some of the counter-ions of the ionic surfactant to the micelle.

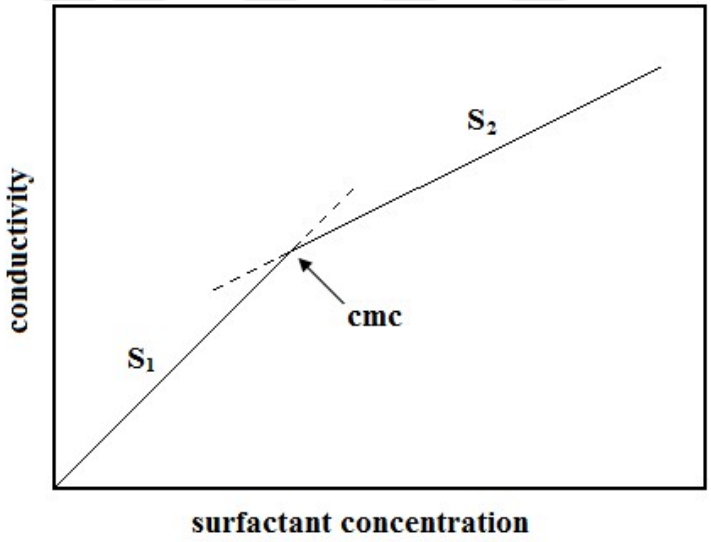


Figure 1.14. Conductivity (κ) versus surfactant concentration plot with slopes of premicellar (S_1) and postmicellar (S_2) regions.

The ratio of slopes of postmicellar region to premicellar region on the cmc plot corresponds the value of α (Myers, 1992).

$$\alpha = \frac{S_2}{S_1} \tag{1.4}$$

The α takes the value $0 \leq \alpha \leq 1$ and then degree of counter-ion binding to the micelle for an ionic surfactant can be evaluated ($\beta=1-\alpha$). The micellization thermodynamic parameters for ionic surfactants, the standard Gibbs free energy of micellization (ΔG^o_{mic}), the standard enthalpy of micellization (ΔH^o_{mic}) and the standard entropy change (ΔS^o_{mic}), can be calculated from the values of cmc and β via following equations

$$\Delta G^o_{mic} = (1+\beta)RTl \quad _{cmc} \tag{1.5}$$

$$\Delta H^o_{mic} = -(1+\beta)RT^2\left(\frac{\partial lnX_{cmc}}{\partial T}\right) \tag{1.6}$$

$$\Delta S^o_{mic} = \frac{(\Delta H^o_{mic} - \Delta G^o_{mic})}{T} \tag{1.7}$$

where X_{cmc} is expressed as the mole fraction of the surfactant at the critical micelle concentration.

1.2.4 Adsorption of Surfactants at Air/water Interface

As we mentioned before, surfactants adsorb at air/water interface by reducing the surface tension of water. This reduction of the surface tension of water continues until reaching to the critical micelle concentration and the surface tension remains constant after the critical micelle concentration, i.e. it does not change with further increase in the surfactant concentration. The Gibbs adsorbed isotherm gives information on the maximum total amount of surfactant adsorbed on the surface (Γ_{max}) and the affinity of the surfactant towards the surface of the solution.

For dilute surfactant solutions, Γ_{max} can be evaluated from the surface tension measurements by the Gibbs equation (Azum et al., 2016; Tadros, 2014).

$$\Gamma_{max} = -\frac{1}{nRT}\left(\frac{\partial\gamma}{\partial lnC}\right)_T \quad (1.8)$$

where γ is the surface tension in $N.m^{-1}$, C is the total concentration of the surfactant solution, T is the absolute temperature in Kelvin, R is the perfect gas constant (8.314 $J.mol^{-1}.K^{-1}$), and n is the ionic species, respectively. For 1:1 ionic surfactants such as potassium laurate, sodium dodecylsulfate in the absence of any other solutes, n is equal to 2. In the case of ionic surfactants in the presence of strong electrolytes, n is taken as 1 (Tadros, 2014; Myers, 1992; Mchedlov-Petrossyan, 2014). The linear part of γ-lnC plot is taken for the calculation of Γ_{max} (Chauhan et al., 2014). The Γ_{max} is used to calculate another important parameter for the isotropic micellar solutions, so-called the minimum area per head group of the surfactant molecule at the air/water interface, when the surface is saturated by the surfactant molecules. The following equation gives the relation between Γ_{max} and A_{min}.

$$A_{min} = \frac{10^{16}}{N_A\Gamma_{max}} \quad (1.9)$$

where N_A is the Avogadro's number.

2. AIM AND SCOPE OF THE STUDY

Lyotropic nematic phases have been the subject of a large number of studies in the literature for years (Yavuz et al., 2014; Freiser, 1970; Alben, 1973; Yu and Saupe, 1980; Akpinar et al., 2012b; Braga, et al., 2016). From their optical axes point of view, nematic phases are classified as "uniaxial" and "biaxial". Uniaxial phases (discotic nematic phase, N_D, and calamitic nematic phase, N_C) have one optical axis; the biaxial phase (N_B) has two distinct optical axes. It was experimentally verified (Yu and Saupe, 1980; Akpinar et al., 2012b) that, in general, the lyotropic biaxial nematic phase is located between two uniaxial N_D and N_C on the phase diagrams. Furthermore, polarizing optical microscopy (Braga, et al., 2016) and laser conoscopy (Galerne and Marcerou, 1983) measurements showed that uniaxial-to-biaxial phase transitions are of second order as predicted by mean-field theory (Freiser, 1970; Alben, 1973).

In recent studies, some important factors that affect the stabilization of different lyotropic nematic phases have been reported in the literature. These studies helped to understand what kinds of parameters play a role on the stabilization of nematic phases, especially the biaxial one, in terms of sample preparation. Among them, it was shown that the doping of the lyotropic mixture of dodecytrimethylammonium bromide (DDTMABr)/salt/dodecanol/water (Akpinar et al., 2015) with different Hofmeister anions was efficient to stabilize the biaxial nematic phase. It was observed in that study that the interactions of the chaotrope head groups of DDTMABr with different Hofmeister anions at the micelle surfaces have a key importance to stabilize different nematic phases. In addition, the effect of alkyl-chain length of long-chain alcohols on obtaining both biaxial nematic (Akpinar et al., 2012a) and biaxial cholesteric (Reis et al., 2013) phases was also investigated.

In our previous study we had some hints about the specific electrostatic interactions at the micelle surface or in its vicinity to obtain different nematic phases from the quaternary lyotropic mixtures of potassium laurate (KL)/alkali sulfates/undecanol (UnDeOH)/water. In that study, although we showed that the stabilization of the nematic phases highly depends on the interactions of kosmotrope head group of KL surfactant molecule with kosmotrope and chaotrope alkali cations, we could not investigate those interactions by using a chaotrope surfactant molecule

to generalize the role of kosmotrope-chaotrope interactions between the ionic surfactants and ions of strong electrolytes added into the lyotropic mixtures. It is known that one of the most important interactions at the micelle surfaces of ionic surfactants is the Coulombic repulsion between the charged head groups of the surfactants. This interaction is very effective not only at short distances but also at long distances between the charged species. The Coulombic interactions are also important in the intermicellar region.

For the micelle formation, the Coulombic repulsions have to be screened by counterions of the ionic surfactants and/or the ions of electrolytes added into the solution. Depending on the screening the repulsions between the heads of the amphiphilic molecules at the micelle surfaces, the surfactants are less or more packed in the micelle and different nematic phases may be stabilized. So, if we change the degree of the interactions at the micelle surfaces, it would be highly possible to obtain the nematic phases desired. The basic way to do this is to change the degree of the interactions existing between the head groups of the surfactants and their counterions.

As it is known, two different features are attributed not only to ionic head groups of the surfactants but also to ionic species (ions of electrolytes and counterions of the surfactants) existing in micellar systems. They are "kosmotrope" or "chaotrope", based on Collins' water-matching concept (Collins, 2004; Collins et al., 2007). For instance, if we take into account the ions that we used in the framework of the present study: Li^+, Na^+, F^-, OAc^- and Cl^- are classified as kosmotrope ions while K^+, Rb^+, Cs^+, Br^-, NO_3^-, ClO_3^-, I^-, SCN^- and ClO_4^- are chaotrope ones (Salis and Ninham, 2014; Leontidis, 2002; Abezgauz, et al., 2010). Surfactants are also classified as kosmotrope and chaotrope surfactants, according to their head groups (Vlachy, et al., 2009; Marcus, 2009). It was reported in the literature that potassium laurate, KL (Vlachy, et al., 2009), (sodium dodecylsulfate, SDS (Vlachy, et al., 2009), and tetradecyltrimethylammonium bromide (Marcus, 2009), TDTMABr) is (are) known as a kosmotrope (chaotrope) surfactant(s).

The feature of the interaction between ionic species in the micellar vicinity affects the packing of the surfactants in micelles. If both ionic species, head groups and ions, have the same feature, they produce the closest ion pairs (Collins, 1996). This leads to the close packing of the surfactants in the micelle, and the micellar growth (Sein and Engberts, 1995; Oelschlaeger et al., 2010). On the other hand, if they exhibit opposite features, they are bound to each other loosely, giving rise to the formation of smaller micelles. These situations have been reported in the literature for both micellar solutions Aswal and Goyal (2000); Neto and Salinas (2005); Israelachvili (1991) and lyotropic nematic mesophases Dawin et al. (2009) with ionic surfactants. So, in isotropic micellar solutions, kosmotrope-kosmotrope or chaotrope-chaotrope head groups-ions interactions favor the stabilization of bigger micelles. In the case of lyotropic mixtures showing the nematic liquid crystalline phases, these types of interactions result in the stabilization of just the N_D phase. To obtain the N_B and/or N_C phase, kosmotrope-chaotrope interactions should be dominant, according to our recent studies (Akpinar et al., 2015). But, the question that remains is how to choose suitable pairs of surfactant-electrolyte to obtain, especially, the biaxial nematic phase. To answer this question, it would be better to take into account some micellization parameters obtained from isotropic micellar solutions and compare them with those from lyotropics. This approach can be accepted because, although the nematic phase of lyotropic liquid crystals is more complex than the isotropic micellar solutions, the latter may be considered as the precursor of the former one at low surfactant concentrations. Hence, it should be expected that the information obtained from isotropic micellar solutions might be applicable to understand some points in lyotropic nematic phases.

In this study, we aimed to understand the role of kosmotrope-chaotrope interactions at the micellar surfaces on the stabilization of the three lyotropic nematic phases by finding some hints from the investigation of different isotropic micellar solutions (first part of the paper). In the second part, we studied three different novel lyotropic mixtures: (a) KL/decanol (DeOH)/water/alkali sulfate, (b) SDS/DeOH/water/alkali sulfate and (c) TDTMABr/DeOH/water/sodium salt. In (a) and (b), Li_2SO_4, Na_2SO_4, K_2SO_4, Rb_2SO_4 and Cs_2SO_4 were used as alkali sulfates. For series (c), NaF, NaOAc, NaCl, NaBr, $NaNO_3$, $NaClO_3$, NaI, NaSCN and $NaClO_4$, were chosen as sodium salts of some kosmotrope and chaotrope anions.

3. MATERIALS AND METHODS

3.1 Chemicals

All chemicals were purchased from Sigma, Merck, Aldrich, Carlo Erba and Alfa-Aesar in high purities (>99%). Surfactant molecule potassium laurate was synthesized by the neutralization of lauric acid with potassium hydroxide, KOH, in absolute ethanol at room temperature of about 25ºC under strong mixing by magnetic stirrer according to the procedure given in Reference (Berejnov, et al., 2000; Akpinar, et al., 2016). The neutralization of all lauric acid was confirmed by IR spectroscopy from the disappearance of broad –OH peak of carboxylic acid and appearance of carboxylate (−COO−) peak. Otherwise, i.e. if KL includes some amount of non-neutralized lauric acid, the biaxial phase domain and uniaxial-to-biaxial phase transition temperatures may be affected.

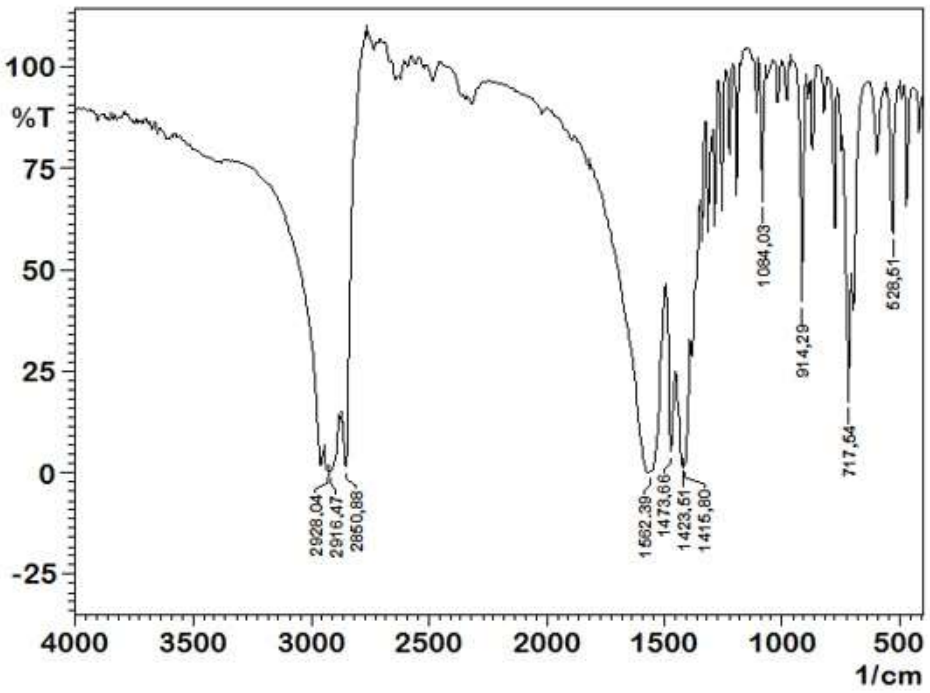


Figure 3.1. FT-IR spectroscopy of potassium laurate molecule.

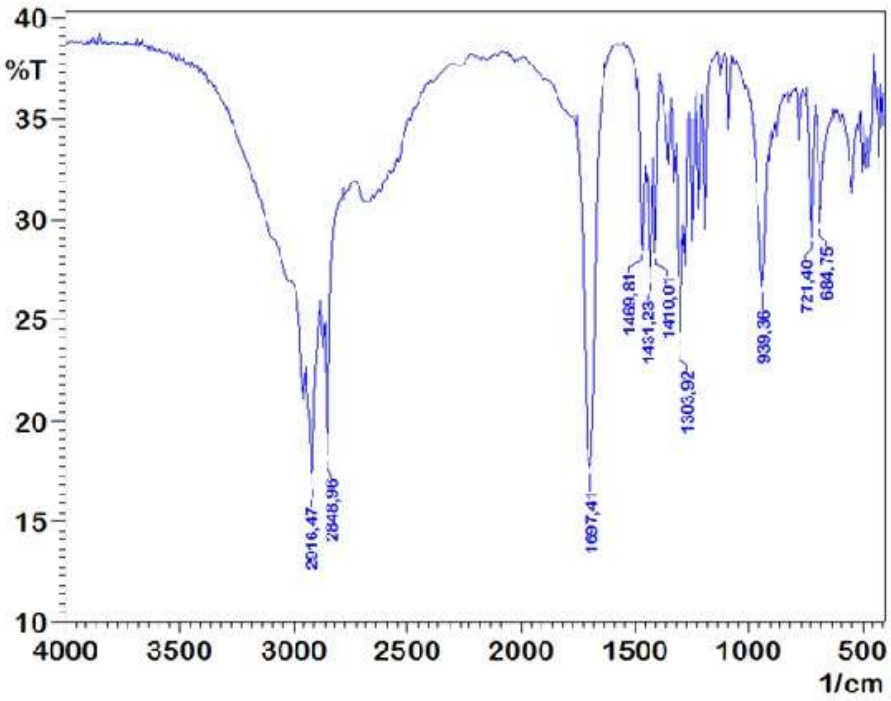


Figure 3.2. FT-IR spectroscopy of lauric acid molecule.

Ultrapure water for all measurements was provided by Millipore Direct-Q3 UV, which produces a water having 18.2 MΩ.cm of resistivity at 25ºC.

3.2 Preparation of Lyotropic Samples

Lyotropic liquid crystalline mixtures were prepared by weighing the mixture components in appropriate amounts into the well-closed test tubes and then well homogenized by applying vortex and centrifuging occasionally. Because well-oriented nematic samples under magnetic field are needed for all measurements, i.e. polarizing optical microscopy and laser conoscopy, a small amount (1 μL per 1 g of the mixture) of water-based ferrofluid (Ferrotec) was added to the samples.

3.3 Polarizing Optical Microscopy

In the polarizing optical microscope (Nikon Eclipse E200POL, Japan) measurements, a small amount of the mixture was placed in a 0.2 mm flat microslide. Both ends of the microslide were closed with a photopolymer on which UV-light was applied to prevent water loss. Then, the microslides were placed in a precise temperature control unit (Linkam LTS120E with a temperature stability of, at least, 0,1ºC) with water circulation (Polyscience SD07R with an accuracy of ±0.04ºC) to provide the homogenous heat distribution in the temperature control unit.

3.4 Laser conoscopy

Laser conoscopy was used to measure the temperature dependence of the birefringences of the three nematic phases, and to calculate the symmetric-tensor invariants. Samples were put between two 2.5 cm of optical glasses (Helma), separated by a 2,5 mm of O-ring (Helma). The temperature was controlled by a Lakeshore 335 model temperature controller (with Pt102 sensor and an accuracy of ±0.001ºC). The laser conoscopy set-up is schematically given in (Figure 3.3). The typical conoscopic patterns of the nematic phases were observed as in (Figure 3.4). These patterns were used to calculate the birefringences of the nematic phases by a specific computer software.

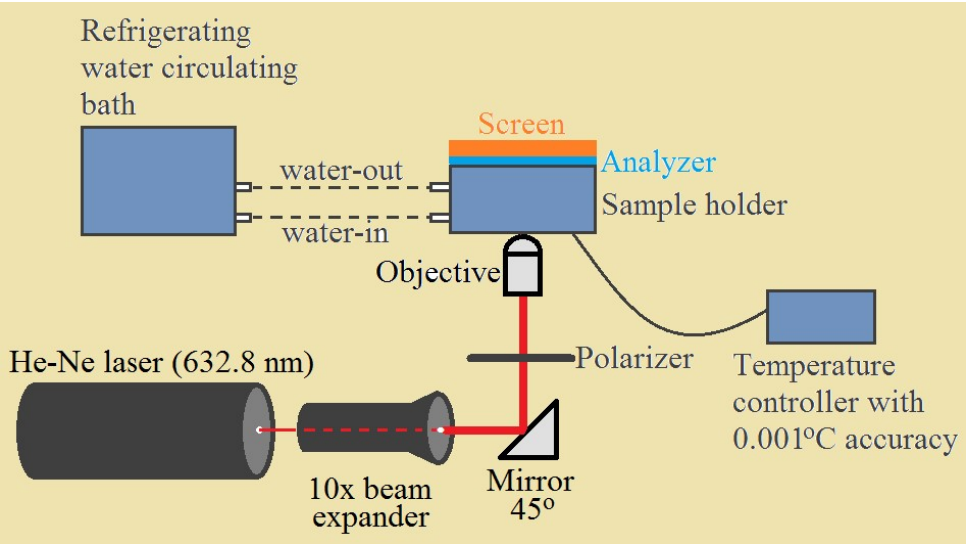


Figure 3.3. The experimental set-up of laser conoscopy.

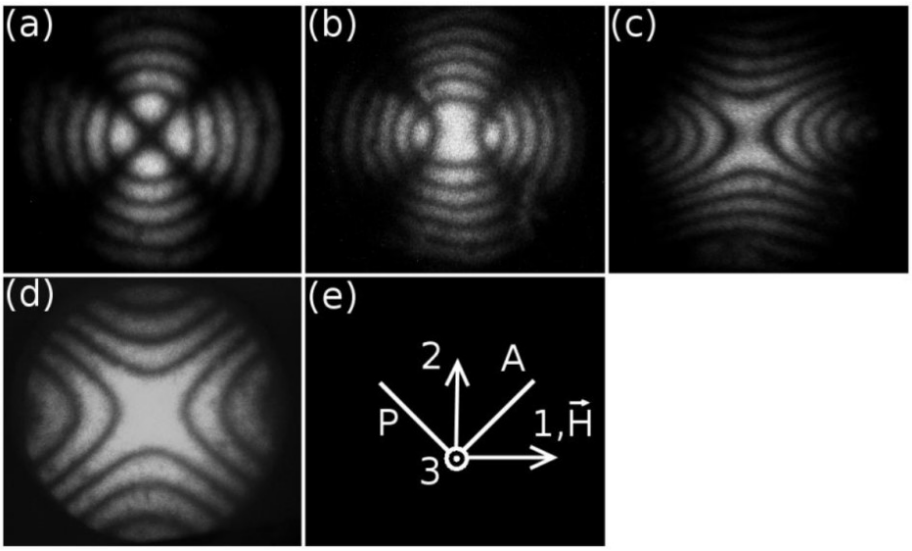


Figure 3.4. Typical conoscopic patterns of (a) N_D, (b) N_B near the N_D to N_B transition (c) N_B; and (d) N_C, (e) geometry of the experiment: P, A and are the directions of the polarizer, analyzer and the applied magnetic field, respectively.

3.5 Electrical Conductivity

Electrical conductivity measurements were carried out in a Mettler Toledo S470 SevenExcellence conductivity meter at 40.0ºC. The dip-type conductivity cell was placed in a homemade aluminum sample holder in which water circulates for providing stable temperature (±0.1ºC). The cell constant was determined as 1.03 cm^{-1} with standard dilute KCl solutions. The conductivities were measured as a function of the surfactant concentration by the successive addition of standard solutions of 1.1545 mol/kg of KL and 0.3849 mol/kg of SDS (0.1743 mol/kg of TDTMABr) into both 8 g of pure water and into 3 mmol/kg (6 mmol/kg) of alkali sulfates (sodium salts) prepared in 8 g of water, existing in the conductivity cell, separately. To keep the water loss at the minimum acceptable level, the conductivity cell was kept closed, except during the addition of the standard solution. For each surfactant/water/salt ternary isotropic solutions, the conductivities were measured at 50 different total surfactant concentrations, until reaching the corresponding concentration of 2.5 times the critical micelle concentration.

3.6 Surface Tensiometry

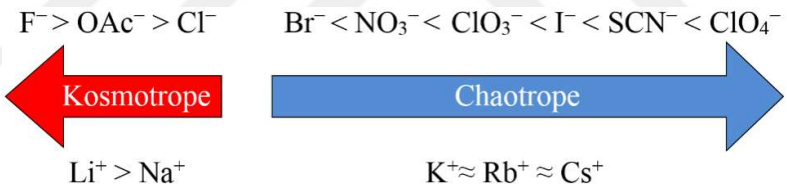
Surface tension measurements were carried out in an Attension tensiometer (Model 701) by platinum ring detachment method at 40.0±0.1 ºC. On the Surface tension (γ) versus ln surfactant concentration (lnC) plot, a minimum was observed for each surfactant. This is a common situation for ionic surfactants Zhang et al. (2013), especially for SDS (Umlong and Ismail, 2007; Chauhan et al., 2014). The tensiometer enables us to evaluate the surface tension (γ) within ±0.1 mN/m, obeying the Du Nouy principle, which indicates that the force (F) to lift the ring from the surface of a liquid is related to the surface tension of that liquid by the relation (Azum et al., 2016):

$$F = 2\pi (r_1 + r_2) \gamma, \qquad (3.1)$$

where r_1 and r_2 are the radius of inner ring and outer ring of the liquid film respectively. The concentration of a solution was varied by the aliquot addition of standard surfactant solution of known concentration to a known volume of solvent in the vessel. The standard solutions were prepared by dissolving, separately, 0.3442 g of KL in 5 g of water (0.2888 mol/kg), 1.0415 g of SDS in 10 g of water (0.3612 mol/kg) and 0.600 g of TDTMABr in 2.140 g of water. For ternary mixtures of surfactant/salt/water, the standard solutions were added into 100 mL (30 mL) of 3 mmol alkali sulfates for SDS (KL) system and 100 mL of 6 mmol sodium salt for TDTMABr one. For each set of experiments, the ring was cleaned by heating it in an ethanol flame. The measured surface tension values were plotted as a function of the logarithm of the surfactant concentration to calculate the maximum surface excess concentration of the surfactant, Γ_{max}, at the saturation and the minimum area per surfactant head group, A_{min}.

4. RESULT AND DISCUSSION

The present study consists of two parts. The first part presents the results of the aqueous isotropic micellar ternary solutions of the ionic surfactants/water/salt at constant temperature and salt concentration. The second one brings the results of lyotropic liquid crystalline phases of three different quaternary mixtures of ionic surfactant/DeOH/water/salt. The ionic surfactants are potassium laurate (KL) - kosmotrope; and sodium dodecylsulfate (SDS) and tetradecyltrimethylammonium bromide (TDTMABr) – chaotrope (Vlachy, et al., 2009). To investigate the role of the interactions between the head groups of the surfactants and the ions/counterions at the micelle surfaces, Hofmeister anions and cations, which are also classified as kosmotrope and chaotrope, were used (Collins, 2004; Collins et al., 2007). Among the anions (cations), F^-, OAc^- and Cl^- (Li^+ and Na^+) are classified as kosmotrope, Br^-, NO_3^-, ClO_3^-, I^-, SCN^- and ClO_4^- (K^+, Rb^+ and Cs^+) are chaotrope (Leontidis, 2002; Abezgauz et al., 2010). The kosmotrope and chaotrope order of these Hofmeister ions are, in general, given as follows (Leontidis, 2002; Wen et al., 2014):



However, at this point, we would like to mention some controversies on the order of the Hofmeister anions in the literature. In some studies (Trompette et al., 2010), Cl^- ion is reported as a chaotrope ion while others accept it as kosmotrope. (Santos and Levin, 2010). This may be attributed to its viscosity coefficient B, which is also used to classify the ions as kosmotrope and chaotrope. This coefficient is evaluated from the salt concentration (c_{salt}) dependence of the relative viscosity (η/η_o) of salt solutions, according to the relation:

$$\eta/\eta_o = 1 + A\sqrt{c_{salt}} + Bc_{salt} \qquad (4.1)$$

where A is an “electrostatic” parameter (Salis and Ninham, 2014). If an ion has positive (negative) viscosity coefficient, it is classified as kosmotrope (chaotrope) ions. The viscosity coefficient of the Cl^- ion is very small −0.007 L/mol (Trompette et

al., 2010). This means that the Cl^- ion behaves as kosmotrope or chaotrope depending on the kosmotrope or chaotrope degree of the surfactant head group. In other words, if the head group is highly chaotrope (kosmotrope), it may exhibit kosmotrope (chaotrope) feature.

This discussion is important to interpret our results with the TDTMABr system in lyotropics. The highly chaotropic TDTMABr interacting with the Cl^- ion presented similar results compared to other two kosmotrope F^- and OAc^- ions. It is the result of a weak interaction between the head group of the surfactant and the Cl^- ion. In addition, it was also stated that Cl^- is a border-line case between the kosmotrope and chaotrope ions in the Hofmeister series (Leontidis, 2002).

Another important point that we have to take into account is how the ionic species form ion pairs. Since the closest ion pairs are the result of strong interaction, weak interaction between them causes loosely formed ion pairs. Moreira and Froozabadi (Moreira and Firoozabadi, 2010) reported a theoretical study about the specific ion effects on micellization of ionic surfactants. In that study, authors proposed a molecular thermodynamic modeling taking into account the kosmotrope and chaotrope interactions between the ionic species. Here, we will summarize some of their conclusions related to the present study for a better understanding. For a given solvent, ions may form four different pairings (Conway, 1981; Marcus, 1985). If two ions form “contact ion pairs”, they share only one primary solvation shell, which is common for both ions, but no solvent molecules exist between them. If they share only one layer of solvent molecule, in addition to their own primary solvation shells, they produce “solvent-shared ion pair”. The third type of the ion pair is “solvent-separated ion pair”. In this case, the ions (anions and cations) have their own primary solvation shells and they are in contact with each other via these shells. In the last case, two ions are dissociated and form freely “unpaired solvated ions”. According to some studies Moreira and Firoozabadi (2010); Conway (1981), the most common ion pairing is the solvent-shared ion pair. As we are dealing with the interactions between the surfactant head groups and the counterions and/or ions added to the mixtures, two possibilities must be considered (Moreira and Firoozabadi, 2010).

If the head groups of the surfactant molecule and the counterions exhibit a similar character, kosmotrope or chaotrope, their hydration shells overlap to produce a larger cosphere, as a result of strong interactions between them. This causes a strong screening effect on the repulsions between the head groups, which leads to a closer packing of the surfactants in the micelles. This leads to the formation of bigger micelles. The second possibility indicates a smaller overlap of the head group and the counterion hydration shells, as a result of the opposite character of the head groups and the counterions (chaotrope/kosmotrope or kosmotrope/chaotrope). This leads to the formation of smaller micelles.

Sulfate (sodium) salts of the Hofmeister cations (anions) were added separately to the lyotropic mixtures and isotropic micellar solutions of the KL and SDS (TDTMABr), which have (has) negatively (positively) charged head groups. With this strategy, we examined how the kosmotrope-kosmotrope, chaotrope-chaotrope and kosmotrope-chaotrope interactions play a role on the micellization parameters in the isotropic micellar solutions and whether there is a direct relation between these parameters and the stabilization of the different lyotropic nematic phases.

4.1 Isotropic Micellar Solutions

Some experimental (Kajari et al., 2009) and theoretical (Collins, 2004; Collins, 1996; Clarke and Lupfert, 1999) studies showed that ions produce closest ion pairs if they exhibit similar character, i.e. kosmotrope-kosmotrope and chaotrope-chaotrope. However, if they have opposite character (kosmotrope-chaotrope) they are loosely bound to each other. In addition to the interactions between the head groups and counterions/ions, we have to take into account those between the counterions and ions present in the mixture. For instance, in our case, K^+ counterion from KL is a chaotrope ion and it weakly interacts with the highly kosmotrope SO_4^{2-} ion from the alkali sulfate salts added. Thus, SO_4^{2-} ion cannot remove some of K^+ counterion bound to the micelle surfaces. It is expected that additional kosmotrope ions (Li^+ and Na^+) present in the isotropic micellar solutions of kosmotrope surfactant KL (a) give rise to the formation of bigger micelles, reducing the area per surfactant head group at the micelle surfaces, as a result of strong kosmotrope-kosmotrope interactions between these ions

and the head group of the KL (leading to the micellar growth), and (b) favor the micellization, i.e. decrease the critical micelle concentration. In the case of chaotrope ions (K^+, Rb^+ and Cs^+), they exhibit weak interactions with the head groups of KL, and their effects remain limited with respect to the kosmotrope ones.

(Table 4.1) shows some micellization parameters obtained from both electrical conductivity and surface tension measurements for KL/water/salt mixtures at constant alkali sulfate concentrations (0.003 mol/kg) and temperature of 40.0ºC. Note that, because each alkali sulfate has two alkali cations, total concentrations of the cations are taken as 0.006 mol/kg. The lowest temperature and the highest salt concentration were chosen for optimum conditions. In other words, to keep the water loss at a minimum level and to prevent the formation of hydrated crystals as a result of the strong interactions between the salts and the surfactants, the experimental conditions were chosen at these salt concentration and temperature. For instance, KL produces lithium laurate (LiL), which has low solubility in water, where Li^+ is replaced with the counterion K^+, and LiL is precipitated below 40.0ºC and above the salt concentration of alkali sulfates at 0.003 mol/kg.

The critical micelle concentrations (cmc) of KL/water/alkali sulfate and SDS/water/alkali sulfate isotropic solutions were evaluated from the specific conductivity (κ) versus the total surfactant concentration (C) plot, in (Figure 4.1) and (Figure 4.2), respectively. The break point observed on the κ-C plot corresponds to the cmc of the surfactants. The degree of counterion dissociation (α) was obtained from the ratios of slopes of the postmicellar (S_2) and premicellar (S_1) linear plots ($\alpha=S_2/S_1$), which is used to calculate the degree of counterion binding (β) values ($\beta=1-\alpha$).

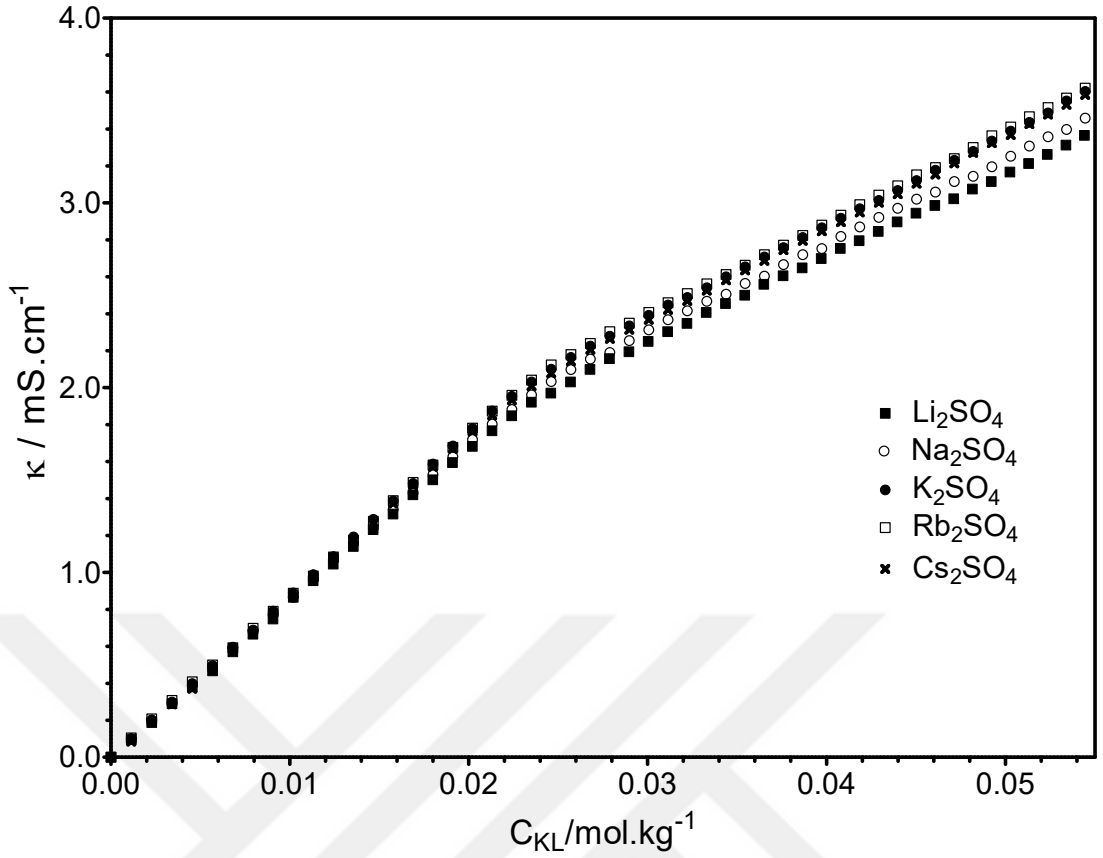


Figure 4.1. Specific conductance as a function of the total surfactant concentration of alkali sulfate salts for the isotropic micellar solutions of KL/water/alkali salt at constant salt concentration and temperature of 40.0ºC. All curves, post- and premicellar regions, have regressions >0.999.

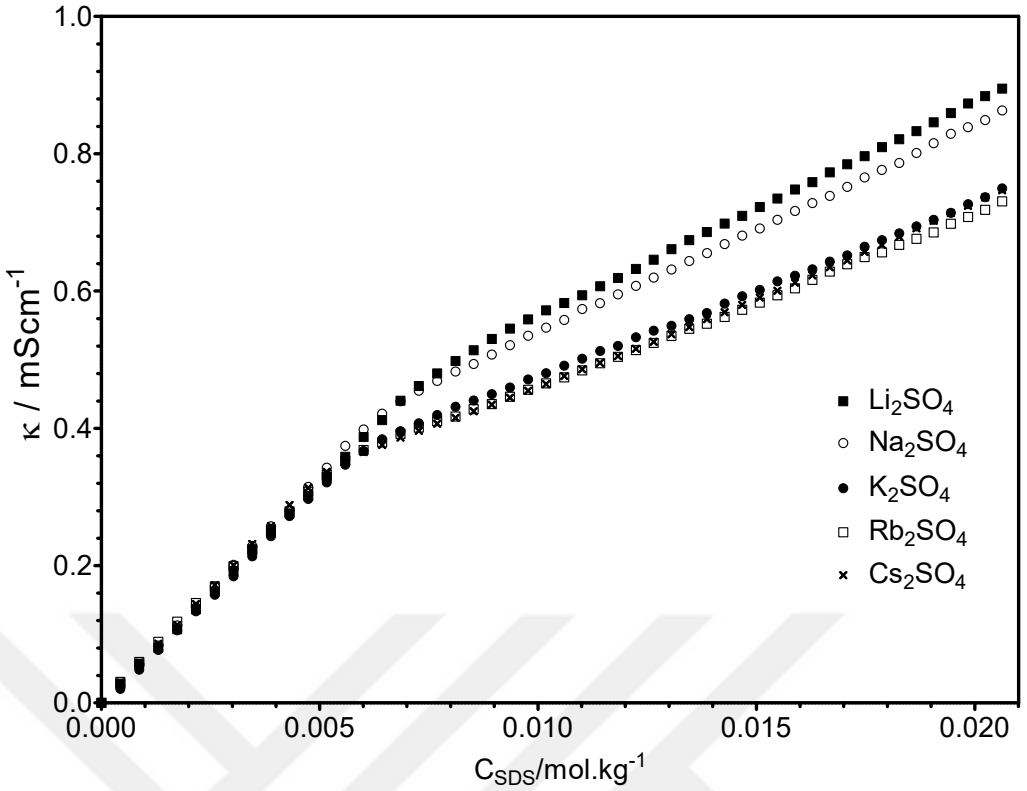


Figure 4.2. Specific conductivity as a function of the total surfactant concentration of alkali sulfate salts for the isotropic micellar solutions of SDS/water/alkali salt at constant salt concentration and temperature of 40.0ºC. All curves, post– and premicellar, have regressions >0.999.

The micellization Gibbs free energy, $\Delta_{mic}G$, of a surfactant molecule can be calculated by equation 1.6 (page 21) in the absence of any electrolyte. In our case, the micellar solutions include strong electrolytes, so $\Delta_{mic}G$ values were calculated according to the following equation 4.2 (Phillips, 1955; Bojan and Bešter-Rogac, 2009).

$$\Delta_{mic}G = RT[lnX_{cmc} + \beta \ln(X_{cmc} + X_{salt})] \qquad (4.2)$$

where R is the ideal gas constant (8.3145 $J.K^{-1}.mol^{-1}$), X_{cmc} and X_{salt} are the mole fractions of the surfactant at the cmc and alkali sulfates in the mixture, respectively, and T is the absolute temperature. The cmc, β and $\Delta_{mic}G$ values obtained for KL/water/alkali and SDS/water/alkali sulfate are given in (Table 4.1). The decrease in the cmc values from Li^+ to Cs^+ follows the order of the Hofmeister series, i.e. $Li^+ < Na^+ < K^+ \approx Rb^+ \approx Cs^+$ for KL/water/alkali sulfate and $Li^+ > Na^+ > K^+ \approx Rb^+ \approx Cs^+$ for SDS/water/alkali sulfate. These orders can only be interpreted by the different condensation or binding of the cations on the micelles as a result of their interactions with the kosmotrope (chaotrope) head group of the KL (SDS).

This means that, while the highest kosmotrope ion Li^+ forms the closest ion pairs with KL at the micelle surface, the chaotrope K^+ (or Rb^+ or Cs^+) cannot be bound to micelle surface efficiently. In the former (latter) case, the repulsions between the head groups are more (less) screened, which favors (does not favor) the micelle formation. This situation can be also seen by analyzing other micellar parameters β and $\Delta_{mic}G$. Higher β values of Li^+ indicate that it is efficiently bound to the micelle surface with respect to other cations, and the more negative $\Delta_{mic}G$ favors micellization. As it is expected, opposite behavior is seen for the SDS molecule because it has a chaotrope head group. That is, alkali sulfates oppositely affect the cmc, β and $\Delta_{mic}G$ of the SDS system with respect to the KL system, as a result of the relatively strong (weak) interactions between SDS and chaotrope (kosmotrope) ions K^+, Rb^+ and Cs^+ (Li^+ and Na^+).

This result is surprisingly in good agreement with the results obtained with the lyotropic liquid crystalline mixtures of both KL/DeOH/water/alkali sulfate and SDS/DeOH/water/alkali sulfate, as we will show in the following. Furthermore, a similar order for adsorption of alkali metal cations on metal oxides was observed (Piasecki et al., 2010), i.e. $Li^+ > Na^+ > K^+ \approx Rb^+ \approx Cs^+$. Although this type of adsorption is different from the condensation or binding of alkali metal ions on the micelles, same effect for potassium, rubidium and cesium ions was observed and they exhibited different behavior from lithium and sodium ions as we obtained in the present study.

Table 4.1. Critical micelle concentration (cmc), degree of counterion bindings (β) and micellization Gibbs free energy ($\Delta_{mic}G$) obtained from the electrical conductivity measurements for the isotropic micellar solutions of KL/water/alkali sulfate and SDS/water/alkali sulfate at 40.0ºC.

Surfactant		Salt				
		Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4
KL	cmc/mmol kg^{-1}	22.93	23.53	24.47	24.50	24.55
	β	0.45	0.44	0.43	0.43	0.43
	$\Delta_{mic}G$/kJ mol^{-1}	−29.27	−28.98	−28.64	−28.64	−28.63
SDS	cmc/mmol kg^{-1}	7.54	6.55	5.57	5.12	5.00
	β	0.52	0.55	0.61	0.62	0.62
	$\Delta_{mic}G$/kJ mol^{-1}	−34.80	−35.90	−37.92	−38.56	−38.58

* Errors are within ±2%, ±7% and ±2% in cmc, β and $\Delta_{mic}G$ for KL solutions, respectively; ±4%, ±3% and ±2% in cmc, β and $\Delta_{mic}G$ for SDS solutions.

The degree of the interactions between the surfactant head groups and the ions may also be evaluated from the pre-micellar domain. It is known that, before micellization, surfactant molecules exist at the water-air interface, where the surfactant head groups are in contact with the water molecules. If the repulsion between the head groups is large (small), it is expected that small (large) amounts of surfactant molecules are located at the air-water interface. Thus, the area per hydrated surfactant head group (A) may vary depending on the intensity of this repulsion, i.e. the bigger the repulsion, the larger the A values. In the vicinity of the critical micelle concentrations of the surfactants, the surfactant molecules saturate the surface of the liquid and, at this stage, the surfactant concentration at the air-water interface reaches its maximum level, while the surface per surfactant molecule head reaches its lowest value. Then, further increase in the concentration of the surfactant causes the formation of the micelles. At this point, we will assume that the minimum area per surfactant head group (A_{min}) at the air-water interface saturated by the surfactant molecules is the same as at the micelle surface after the micellization. In this framework, this assumption may help us to understand the relative effect of the ions in the micellar solutions and lyotropic liquid crystalline phases.

From the surface tension measurements, the maximum surface-excess concentration (Γ_{max}) and the minimum area per surfactant head group (A_{min}) were evaluated and they are given in (Table 4.2) for KL/water/alkali salt and SDS/water/alkali sulfate isotropic solutions.

Table 4.2. Maximum surface-excess concentration (Γ_{max}) and the minimum area per surfactant head group (A_{min}) at the saturation of the air-liquid interface for the KL/water/alkali sulfate and SDS/water/alkali sulfate isotropic dilute micellar solutions at 40.0ºC.

Surfactant		Salt				
		Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4
KL	$\Gamma_{max}/10^{-10}$ mol cm^{-2}	4.84	3.67	2.97	3.02	2.98
	A_{min}/Å^2	34.4	45.4	55.9	55.1	55.8
SDS	$\Gamma_{max}/10^{-10}$ mol cm^{-2}	2.92	3.55	4.12	4.13	4.11
	A_{min}/Å^2	56.9	46.7	40.3	40.2	40.4

*Errors are within ±5% (±2%) and ±5% (±2%) in Γ_{max} and A_{min} for KL (SDS) solutions, respectively.

The Γ_{max} is a measure of the adsorption of a surfactant molecule at the air-liquid interface and, hence, the higher the Γ_{max} is attributed to the higher surface activity (Azum et al., 2016). In other words, a higher the Γ_{max} means efficient packing of the surfactant molecule at the interface. This process, as expected, is accompanied by a decrease in the minimum area per surfactant head group. Going from Li^+ to Cs^+, the Γ_{max} (A_{min}) decreases (increases) in the KL/water/alkali sulfate, however, it increases (decreases) in the SDS/water/alkali salt. In addition, K^+, Rb^+ and Cs^+ exhibited, within the experimental error, similar effects on both Γ_{max} and A_{min} values.

These results indicate that the head groups of the KL molecules are in closer contact with Li^+ rather than K^+, which is attributed to the strong interactions between the kosmotrope surfactant head groups and kosmotrope Li^+ ion. The KL molecular packing degree at the air-liquid interface with Li^+ ion is bigger than that with K^+. An important result obtained from the surface tension measurements is that KL and SDS exhibited opposite behavior with kosmotrope and with chaotrope ions, similarly to the electrical conductivity results.

We also investigated the effect of sodium salts of some Hofmeister anions exhibiting both kosmotrope and chaotrope characters on the chaotrope surfactant TDTMABr with positively charged head group. The results obtained from the electrical conductivity and surface tensiometry are summarized in (Table 4.3). Although we have studied mixtures with nine different anions (F^-, OAc^-, Cl^-, Br^-, NO_3^-, ClO_3^-, I^-, SCN^- and ClO_4^-) in the laser conoscopy measurements of lyotropic liquid crystalline mixtures, it was not possible to obtain results of the electrical conductivity and surface tension for I^- and ClO_4^- ions. This happened because we observed precipitates in their diluted isotropic micellar solutions, as previously reported (Maiti et al., 2007; Anacker and Ghose, 1963; Underwood and Anacker, 1987). This is most probably related to the exhange of some part of the counterion of TDTMABr (Br^-) with these two ions, seperately, to give relatively less water soluble tetradecyltrimethylammonium iodide (TDTMAI) and tetradecyltrimethylammonuim perchlorate ($TDTMAClO_4$) at the working temperature and salt concentration. This may be attributed to the similar extent of the chaotrope character of the head group of $TDTMA^+$, I^- and ClO_4^-.

Table 4.3. Critical micelle concentration (cmc), degree of counterion binding (β) and micellization Gibbs free energy ($\Delta_{mic}G$) from the electrical conductivity measurements and the maximum surface excess surfactant concentration (Γ_{max}); and the minimum area per surfactant head group (A_{min}) obtained from the surface tension measurements for the isotropic micellar solutions TDTMABr/water/salt with some Hofmeister anions. The salt concentrations are 0.006 mol/kg and the temperature is 40.0ºC.

	Salt						
	NaF	NaOAc	NaCl	NaBr	$NaNO_3$	$NaClO_3$	NaSCN
cmc/mmol kg^{-1}	3.55	3.47	2.99	2.68	2.40	1.86	0.41
β	0.66	0.67	0.68	0.72	0.72	0.65	0.71
$\Delta_{mic}G$/kJ mol^{-1}	−40.00	−40.41	−41.06	−42.37	−42.60	−41.81	−47.42
$\Gamma_{max}/10^{-10}$ (mol cm^{-2})	3.94	3.52	2.71	1.94	1.92	1.87	2.66
A_{min}/$Å^2$	42.6	47.3	61.4	85.6	86.3	89.0	62.5

*Errors were within ±4%, ±2%, ±2%, ±3% and ±3% in cmc, β, $\Delta_{mic}G$, Γ_{max} and A_{min} values, respectively.

Similarly to the results of chaotrope surfactant SDS, chaotrope surfactant TDTMABr with kosmotrope anions (F^-, OAc^- and Cl^-) exhibited higher cmc than with chaotrope ones (Br^-, NO_3^-, ClO_3^- and SCN^-). This means that micellization is more favored with the chaotrope anions, which indicates negatively higher micellization Gibbs energy and higher ion binding to the micelle surface (i.e., higher β). As can be seen, the mixtures with the chaotrope anions have larger negative $\Delta_{mic}G$ values than those with the kosmotrope ones. If we compare the β values, chaotrope anions are efficiently bound to the TDTMABr micelles with respect to the kosmotrope ones. However, the ClO_3^- ion, except its cmc value, does not obey the Hofmeister series, which was also stated in the literature (Abezgauz et al., 2010).

At this point, before passing on the discussion of the results of the lyotropic liquid crystalline mixtures, we will summarize all data obtained from both electrical conductivity and surface tension measurements of KL, SDS and TDTMABr. All results indicated that the types of ions and head groups, i.e. their kosmotrope and chaotrope features, play an important role on the micelle formation in isotropic micellar solutions. It is essential to take into account how the ionic species produce ion pairs at the micelle surfaces.

This is a key point to explain the role of interactions in both isotropic micellar solutions and, as discussed in the following, in lyotropic nematic mesophases.

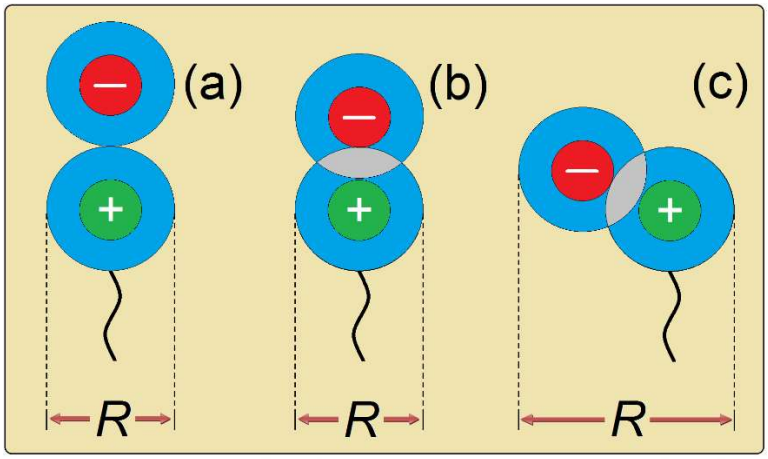


Figure 4.3. Sketch of the formation of possible headgroup-counterion/ions pairing at the micelle surface.

In (figure 4.3), for instance, the positively (negatively) charged headgroup (counterion/ion) is represented by green (red). Since blue regions show the hydration shell around the head groups, grey ones correspond to the region where two hydration shells overlap. R is total diameter of the cosphere. This figure is adapted from Figure 4 of Reference (Moreira and Firoozabadi, 2010).

If we compare the A_{min} values of KL and SDS systems (Table 4.2), the head group of KL forms a smaller head-group area with both kosmotrope ions Li^+ and Na^+ than all chaotrope ones K^+, Rb^+ and Cs^+. However, in the SDS system, completely a opposite situation was observed, i.e. the head group of SDS forms a bigger head-group area with kosmotrope ions Li^+ and Na^+ than chaotrope ones K^+, Rb^+ and Cs^+. As expected, if two ionic species have a similar character (kosmotrope-kosmotrope or chaotrope-chaotrope), the ion pair between the head groups and the counterions exhibits strong interactions, as schematically shown in (Figure 4.3c). However, for kosmotrope-chaotrope interactions, the ion pairing shown in (Figure 4.3a) or (Figure 4.3b) is most likely to be formed (Moreira and Firoozabadi, 2010). If the opposite character between the ionic species is large, they may produce an ion pair as shown in (Figure 4.3a). However, if they have a relatively less opposite character, their ion pairing may be as shown in (Figure 4.3b).

Consequently, taking into account the A_{min} values, KL head groups produce closer ion pair with kosmotrope ions, as shown in (Figure 4.3c). In this way, the kosmotrope counterions/ions enters between two adjacent surfactant head groups. This leads to the efficient screening of the electrostatic repulsions between the head groups, which causes micellar growth (highly packing of the surfactant in the micelle by reducing the A_{min}) in both isotropic micellar solutions and lyotropic liquid crystalline phases stabilization of N_B and/or N_D Akpinar et al. (2015) and N_D and/or lamellar phases are favored (Dawin et al., 2009; Boden, et al., 1995). In contrast, KL head groups cannot be efficiently bound by chaotrope ions, which indicates the formation of smaller micelles (loosely packing of the surfactant molecules in the micelle by enhancing the A_{min}) in the micellar solutions and the stabilization of the N_C phase in lyotropic liquid crystalline mixtures should be expected as we observed in our previous study supported by both laser conoscopy and X-ray diffraction (Akpinar et al., 2015).

For chaotrope SDS, a completely opposite behavior is observed, which is in good agreement with the results obtained from the KL mixture. At this point, a question may arise: if the interactions between KL and SDS head groups with kosmotrope and chaotrope counterions/ions are described as above, why do TDTMABr and KL exhibit a similar trend (from the interactions point of view), but SDS does not, although it is a chaotrope surfactant like SDS (Table 4.3)? This question may be answered taking into account the structure of the head groups. Acetate, methylsulfate and tetramethylammonium ions may be chosen as model structures to understand the interactions of KL, SDS and TDTMABr, respectively, head groups with the ionic species. The surfactant alkyl chain length has no effect on the classification of surfactants as kosmotrope and chaotrope (Vlachy et al., 2008), i.e. just head groups are important on those classifications. Then, in those three molecules, and additional $-CH_3$ group was shown as an alkyl chain length of each surfactant molecule, (Figure 4.4).

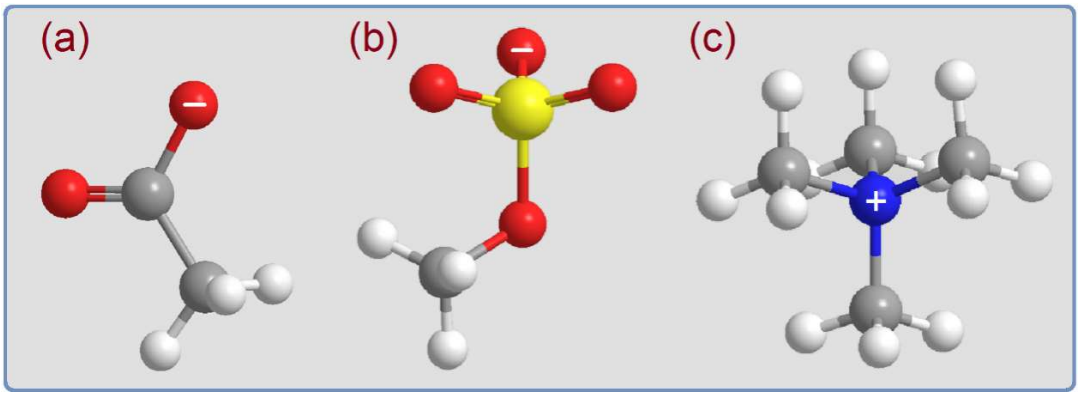


Figure 4.4. Molecular structures of (a) acetate, (b) methylsulfate and (c) tetrametylammonium ions. Grey: carbon; white: hydrogen; red: oxygen; yellow: sulfur; blue: nitrogen.

Let us start the discussion by comparing the ions acetate and methylsulfate. Note that the π-electrons of a double bond −C=O in acetate, (Figure 4.4a), (two double bonds −S=O in sulfate, (Figure 4.4b) are delocalized among the carbon atom and the two oxygen atoms (sulfur and three oxygen atoms). This means that the negative charge is equally distributed on the head group of acetate (methylsulfate), i.e. KL (SDS), assumed being −1/2 (−1/3) on each oxygen atom. In other words, it may be thought that the negative charge is distributed on the spherical head groups of the KL and SDS, as shown in (Figure 4.3).

It means that the counterions/ions added can be strongly or loosely bound from each side of their head groups, depending on the kosmotrope and chaotrope characters of both ionic species. However, in the case of tetramethylammonium ion, the positive part of the ion, $-N^+$, is surrounded by four apolar $-CH_3$ groups, except along the perpendicular direction to the head group, (Figure 4.4c). Because of this, TDTMABr is more chaotrope than SDS. In addition, if we take into account two adjacent TDTMABr molecules they are most likely to be packed from the $-CH_3$ groups in their head groups, which may exhibit van der Waals attractions. Thus, it is expected that a counterion/ion primarily approaches to the TDTMABr head group along the perpendicular direction, since these ionic species have negative charge on their surfaces.

From kosmotrope to chaotrope ions, TDTMABr and KL have similar trends, i.e. A_{min} increases. As it was stated in ref. Bridges et al. (2007), kosmotrope ions are hydrated by water molecules as much as possible, depending on their degree of kosmotrope character. In other words, for monovalent ions, the smaller (larger) the ion, the higher (higher) the kosmotrope (chaotrope) character. So, we may say that KL is highly kosmotrope, while TDTMABr is highly chaotrope. NMR studies Leontidis (2002); Hedin et al. (2000) indicated that it is very difficult to remove water molecules from the hydration shell of kosmotrope ionic species (ions or ionic head groups), however, chaotrope ones are easily dehydrated. Thus, kosmotrope ions can remove water molecules from the chaotrope head groups efficiently. Because both Li^+ and KL are highly kosmotrope, Li^+ cannot efficiently remove water molecules from the hydration shell of KL (dehydration). So, when a highly kosmotrope ion Li^+ is added into KL solutions they share their water shells. So, it is expected that they form the ion pair shown in (Figure 4.3c), which causes the higher packing of the surfactants in the micelles of both isotropic solutions and lyotropic nematic phases (i.e. the smaller $A_{min,}$ see Table 4.2). This is a natural result of strong kosmotrope-kosmotrope interactions. In the case of chaotrope SDS, even if kosmotropic Li^+ ion may remove water molecules from the sulfate head groups to form thinner hydration shell, the repulsions between the adjacent SDS head groups have to increase because of negative charge, which is distributed on three oxygen atoms. This causes the increase of the surfactant head group area, A_{min}, at both the air-water interface and the micelle surface.

On the other hand, chaotrope ions K^+, Rb^+ and Cs^+ cannot remove water molecules from the hydration shell of SDS. Instead, they share their hydration shells to form closer ion pairing as a result of strong chaotrope-chaotrope interactions (i.e. smaller A_{min}) (Table 4.2). When kosmotrope ions F^-, OAc^- and Cl^- are added to the TDTMABr mixtures, at constant ion concentration, the dehydration of the head group occurs and the adjacent TDTMABr molecules are packed at the solution surface (air-water interface) and in the micelles (i.e. smaller A_{min}). When chaotrope ions Br^-, NO_3^- and ClO_3^- are added to the mixture, they form closest ion pairs (Figure 4.3c) and exhibit larger surfactant head group area (larger A_{min}), (Table 4.3). As seen in (Table 4.3), from the highly kosmotrope one F^- to relatively highly chaotrope one ClO_3^- A_{min} increaseas a result of the increase in the degree of chaotrope-chaotrope interactions. SCN^- has greater chaotrope character than $ClO_3^-$and although their effects on the cmc

values obey the Hofmeister series, SCN^- causes the dramatic decrease in the A_{min} value in the TDTMABr mixture, see (Table 4.3). This may be attributed to the structure of the SCN^- ion. In general, for monoatomic and polyatomic monovalent ions that were used in our study, it is assumed that they have spherical-like shape, with their hydration shells. However, this assumption is not reasonable for the SCN^- ion. Due to its resonance structures, SCN^- and its hydration shell, has a rod-like shape. So, it may approach the head group of TDTMABr along the perpendicular direction of $-N^+$, as shown in (Figure 4.3b). Then the van der Waals attractions between the head groups of TDTMABr (as discussed before) will be dominant. This results in the decrease of both cmc and A_{min} values, see (Table 4.3).

4.2 Lyotropic Liquid Crystalline Samples

Three series of lyotropic ternary mixtures were prepared. These mixtures were composed of KL/DeOH/water, SDS/DeOH/water, and TDTMABr/DeOH/water. Since KL and SDS are anionic surfactants, the Hofmeister cation (Li^+, Na^+, K^+, Rb^+ and Cs^+) sulfates were added to the ternary mixtures of KL and SDS, separately. In the case of TDTMABr, which has a positively charged head group, sodium salts of the Hofmeister series (F^-, OAc^-, Cl^-, Br^-, NO_3^-, ClO_3^-, I^-, SCN^- and ClO_4^-) were chosen to study the effect of the interactions at the micelle surface on the formation of the different nematic phases. The phase compositions and the nematic phase types observed are given in (Table 4.4, 4.5 and 4.6).

Table 4.4. Composition of the lyotropic mixtures obtained from doping the ternary mixture KL/DeOH/water with alkali sulfates (M_2SO_4). X corresponds to the mole fraction per cent. N-Phase shows the type of lyotropic nematic phase present in each mixture as a function of temperature.

Mixture	M_2SO_4	X_{KL}	X_{DeOH}	X_{H_2O}	$X_{M_2SO_4}$	N-phase
k1	Li_2SO_4	3.124	1.206	95.597	0.073	N_D
k2	Na_2SO_4	3.124	1.206	95.597	0.073	N_D
k3	K_2SO_4	3.124	1.206	95.597	0.073	N_D–N_B– N_C
k4	Rb_2SO_4	3.124	1.206	95.597	0.073	N_D–N_B– N_C
k5	Cs_2SO_4	3.124	1.206	95.597	0.073	N_D–N_B– N_C

Table 4.5. Composition of the lyotropic mixtures obtained from doping the ternary mixture SDS/DeOH/water with alkali sulfates (M_2SO_4). X corresponds to the mole fraction per cent. N-phase shows the type of lyotropic nematic phase present in each mixture as a function of temperature.

Mixture	M_2SO_4	X_{SDS}	X_{DeOH}	X_{H_2O}	$X_{M_2SO_4}$	N-phase
s1	Li_2SO_4	3.218	0.892	95.785	0.105	N_C
s2	Na_2SO_4	3.218	0.892	95.785	0.105	N_D–N_B– N_C
s3	K_2SO_4	3.218	0.892	95.786	0.104	N_D
s4	Rb_2SO_4	3.218	0.892	95.785	0.105	N_D
s5	Cs_2SO_4	3.218	0.892	95.785	0.105	N_D

Table 4.6. Composition of the lyotropic mixtures obtained from doping the ternary mixture TDTMABr/DeOH/water with sodium salts of some monovalent anions (NaA). X corresponds to the mole fraction per cent. N-phase shows the type of lyotropic nematic phase present in each mixture as a function of temperature.

Mixture	NaA	$X_{TDTMABr}$	X_{DeOH}	X_{H_2O}	X_{NaA}	N-phase
t1	NaF	3.929	0.942	94.832	0.297	N_C
t2	NaOAc	3.929	0.942	94.832	0.297	N_C
t3	NaCl	3.929	0.942	94.832	0.297	N_C
t4	NaBr	3.929	0.942	94.832	0.297	N_D–N_B– N_C
t5	$NaNO_3$	3.929	0.942	94.832	0.297	N_D–N_B– N_C
t6	$NaClO_3$	3.929	0.942	94.832	0.297	N_D–N_B
t7	NaI	3.929	0.942	94.832	0.297	N_D–N_B
t8	NaSCN	3.929	0.942	94.832	0.297	N_D
t9	$NaClO_4$	3.929	0.942	94.833	0.296	N_D

The lyotropic nematic phases were characterized under polarising optical microscope and their textures were similar to ones given in (Figure 1.5) (page 6). When the uniaxial N_D (N_C) phases were aligned under external magnetic field (0.44 kG), they exhibited homoetropic (planar) alignment, i.e. the phase directors of the N_D (N_C) phases aligned perpendicular (parallel) to the magnetic field direction. The lyotropic uniaxial-to-biaxial phase transitions were determined by laser conoscopy, which enables us to precisely determine the temperature dependence of the birefringences of the nematic phases. It is important to stress that a key point in laser conoscopy experiments 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 (Akpinar et al., 2012b). (Figure 4.5, 4.6 and 4.7) show the laser conoscopy results of KL/DeOH/water/alkali sulfate, SDS/DeOH/water/alkali sulfate and TDTMABr/DeOH/water/sodium salt lyotropic mixtures, respectively.

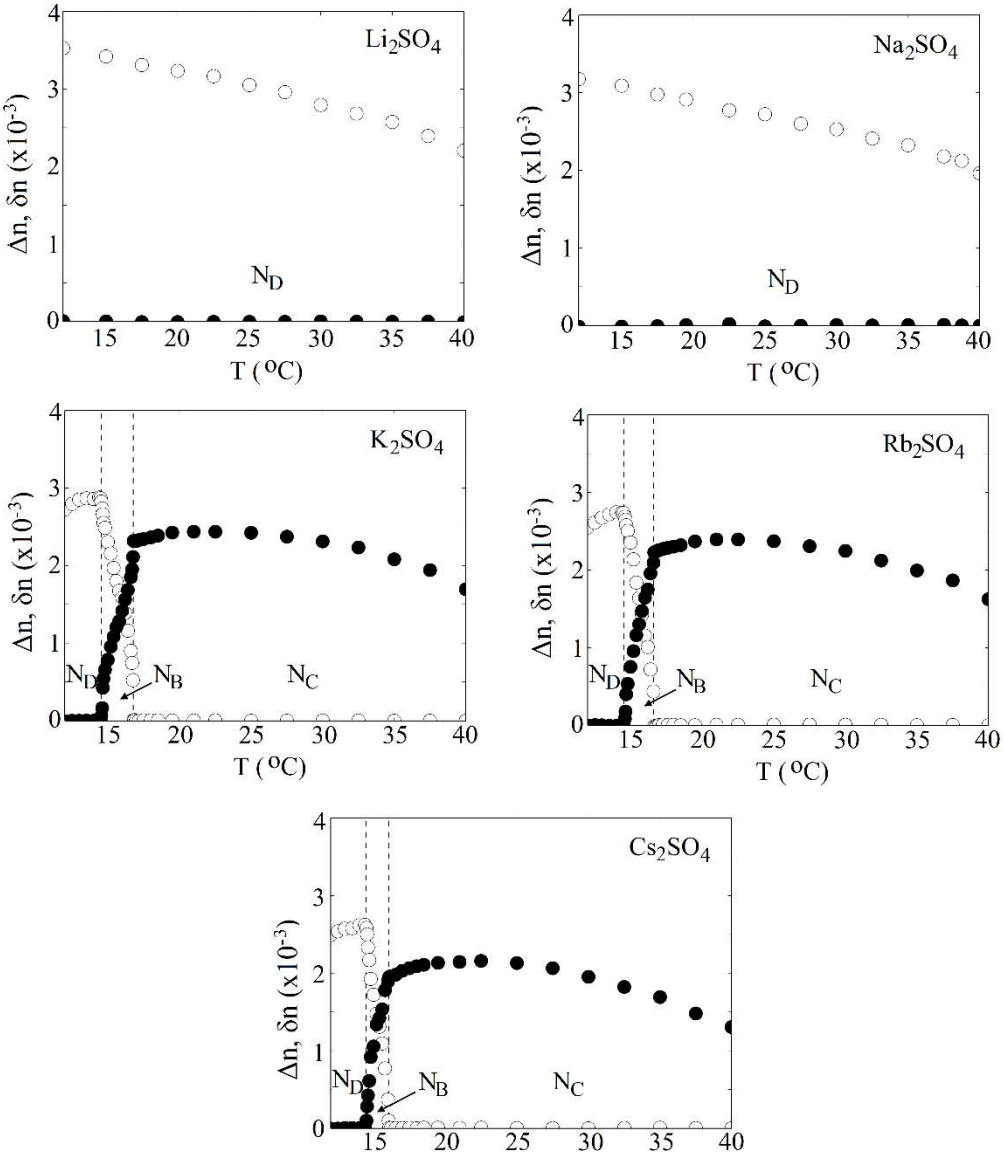


Figure 4.5. Temperature dependence of the birefringences of the lyotropic mixture KL/DeOH/water/ alkali sulfates. 2P: biphasic region. The biphasic regions are beyond the scope of this study.

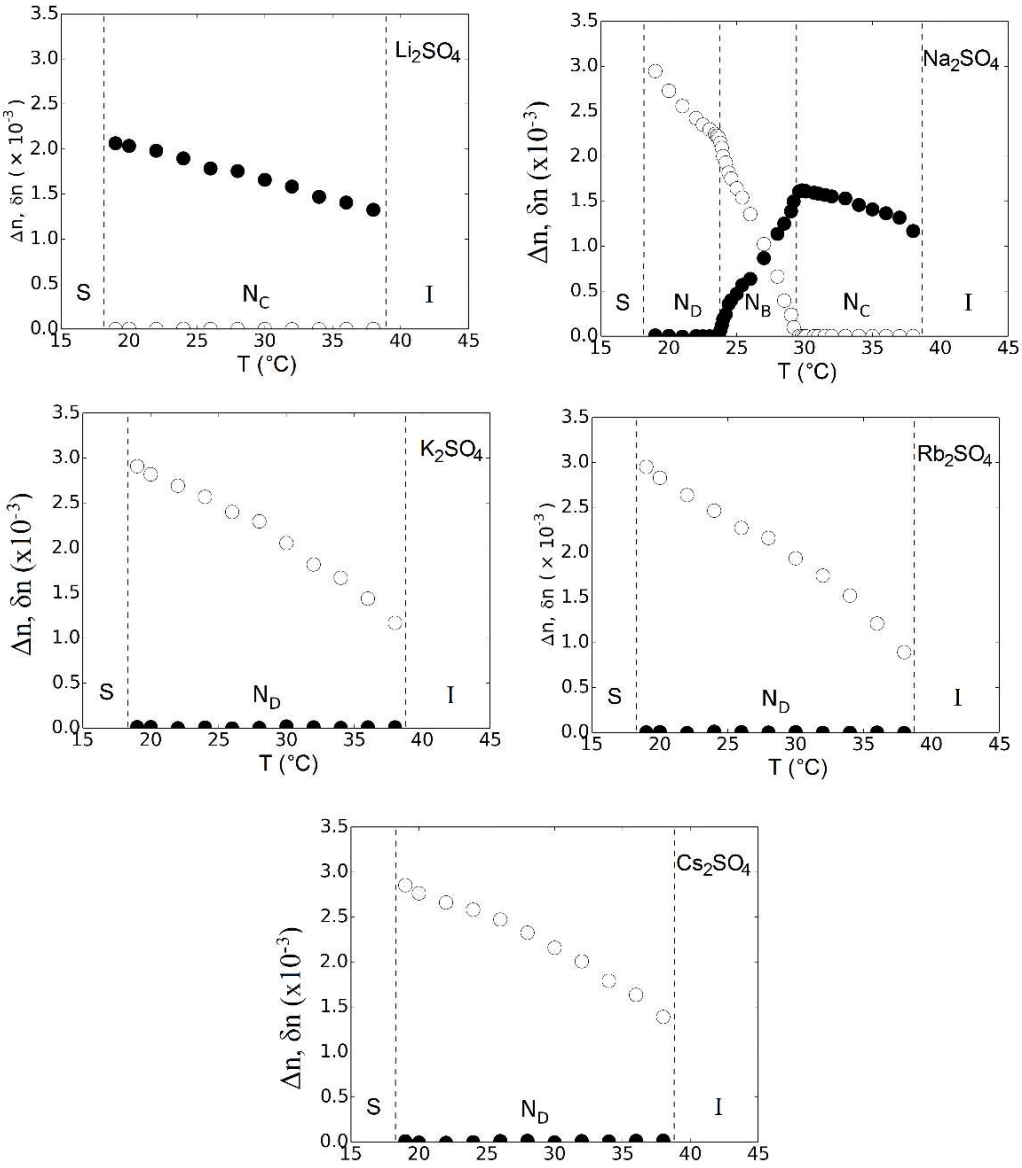


Figure 4.6. Temperature dependence of the birefringences of the lyotropic mixture SDS/DeOH/water/ alkali sulfates. 2P: biphasic region. The biphasic region is beyond the scope of this study. I: isotropic phase.

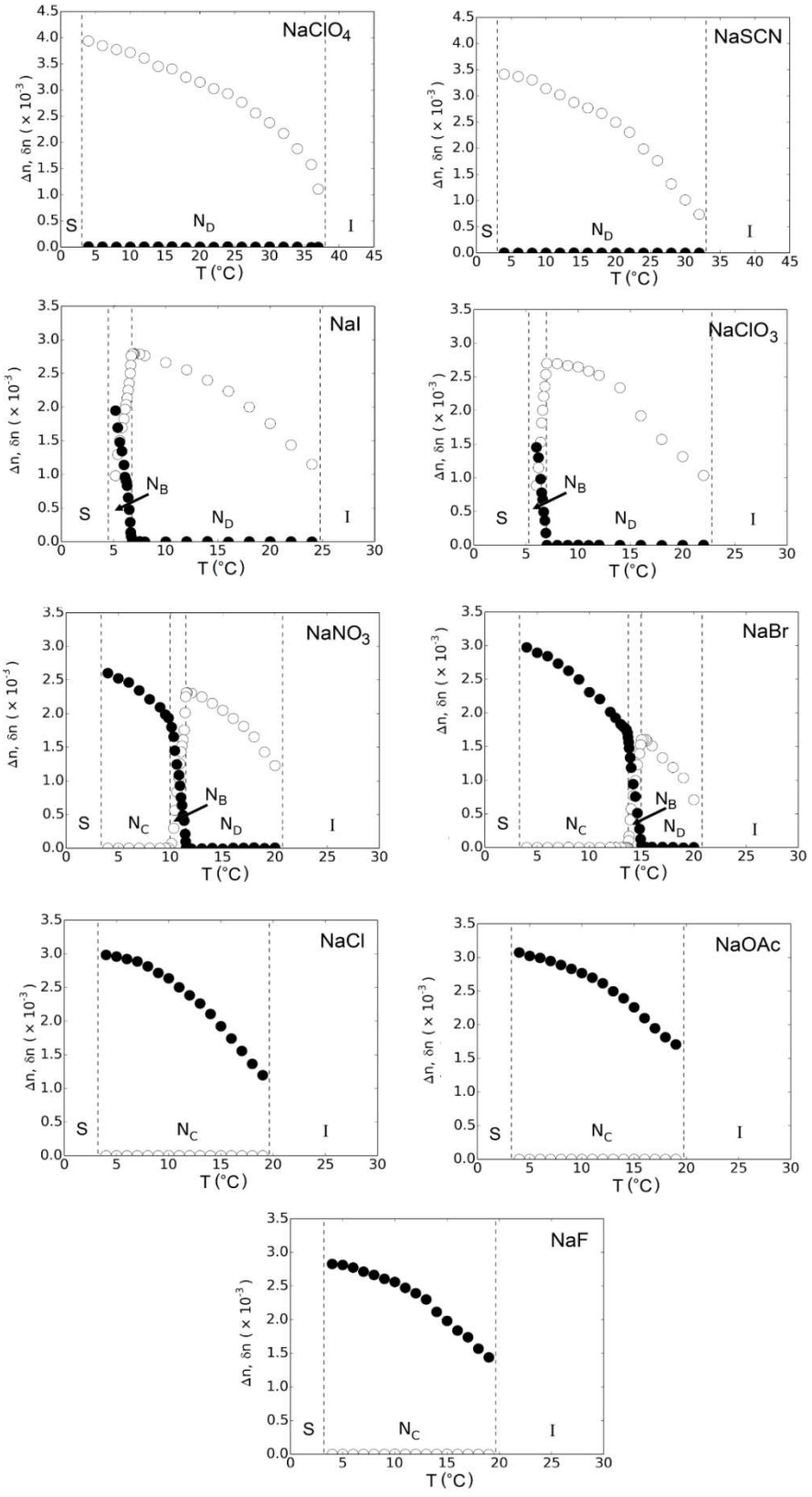


Figure 4.7. Temperature dependence of the birefringences of the lyotropic mixture TDTMABr/DeOH/water/ sodium salts 2P: biphasic region. The biphasic region is beyond the scope of this study. I: isotropic phase.

Let us start the discussion of the laser conoscopy results for the kosmotrope surfactant KL mixture (Figure 4.5). The kosmotrope ions Li^+ and Na^+ stabilize just the N_D phase. The chaotrope ions K^+, Rb^+ and Cs^+ stabilize the three nematic phases, depending on the temperature. Mixtures with these chaotrope ions exhibited similar topologies of the phase diagrams (about the same uniaxial-to-biaxial phase transitions temperatures and temperature range of the biaxial phase domains). Taking into account the maximum birefringence values in the N_D phase region, they decrease from the Li^+ to the K^+ mixtures, and remain approximately constant for the Rb^+ and Cs^+ mixtures. These results agree with those obtained in isotropic micellar solutions in this study. Moreover, they agree with the studies of the effect of alkali metal ions on DNA conformation transition in water Wen et al. (2014) and their adsorption on metal oxides (Piasecki et al., 2010). It is known that the interactions of the ions/counterions with the head group of the surfactants at the micelle surfaces highly depend on the hydrodynamic radius (r_h) of the ions bound to the micelle surfaces. The r_h values of Li^+, Na^+, K^+, Rb^+ and Cs^+ are 3.40, 2.76, 2.32, 2.28 and 2.28 Å Ropers et al. (2003), see Table 4.7, respectively. So, it can be understood why K^+, Rb^+ and Cs^+ ions exhibited similar results on the KL/DeOH/water/alkali sulfate lyotropic mixture. The highest birefringence value in the N_D phase slightly decreased from $3.5x10^{-3}$ (Li^+ mixture) to $2.7x10^{-3}$ (K^+ mixture), and remained almost constant for the Rb^+ and Cs^+ mixtures. This indicates that, if the negatively charged kosmotrope head group of KL strongly (loosely) interacts with the kosmotrope (chaotrope) ions, bigger (smaller) micelles are formed, which give rise to the stabilization of N_D (N_B and/or N_C). It is important to stress that the length of the main amphiphile present in the mixture fixes the double-layer dimension. The micellar growth considered here refers to the increase of the micelle flat surface, perpendicular to the bilayer. Thus, if the kosmotrope and chaotrope interactions between the surfactant head groups and counterions/ions are dominant at the micelle surfaces, the stabilization of N_B phase is more favored.

In the case of the chaotrope surfactant, with negatively charged head group (SDS) the opposite effect of the alkali sulfate on the nematic-phase type was observed with respect to the kosmotrope KL, see (Figure 4.6). As can be seen from (Figure 4.6) and (Table 4.5), SDS micelles stabilizes just the N_C phase with highly kosmotrope Li^+; three nematic phases with kosmotrope Na^+; and just the N_D phase with chaotrope ions K^+, Rb^+ and Cs^+. If we take into account the laser conoscopy results of the mixtures

with the chaotrope ions given in (Figure 4.6), they exhibited similar values of the highest birefringences and temperature range of the N_D phase domain. This is in good agreement with the results of the kosmotrope KL mixtures. Changing the surfactant kosmotrope character by chaotrope, the interactions between the opposite species (in the case of SDS, chaotrope head group - kosmotrope ions) are responsible for the stabilization of the N_B phase. Consequently, comparing the two systems, KL/DeOH/water/alkali sulfate and SDS/DeOH/water/alkali sulfate, the interactions at the micelle surfaces play a key role on the stabilization of different nematic phases. To obtain a mixture presenting the lyotropic biaxial nematic phase, a surfactant exhibiting opposite character with respect to its counterion or ions of electrolytes added into the mixture has to be chosen, i.e. a kosmotrope (chaotrope) surfactant and chaotrope (kosmotrope) counterions/ions.

KL and SDS have negatively charged head groups, which interacts with the cations of the salts/counterions at the micelle surfaces. TDTMABr is also a chaotrope surfactant like SDS, but has a positively charged head group, which is bound by the anionic counterions at the micelle surfaces. Sodium salts with negatively charged anions were added to the mixture TDTMABr/DeOH/water. The laser conoscopy results of TDTMABr mixtures are given in (Figure 4.7). Among the chaotrope anions added to the mixtures, the most chaotrope one is ClO_4^- and the least chaotrope one is Br^-. It is expected that, while the ClO_4^- exhibits close contact with the head group of TDTMABr, Br^- is weakly bound to the micelle. If we take into account the results obtained from the other two lyotropic series investigated, ClO_4^- stabilizes the N_D phase; the N_B and/or N_C phase are more favored in the case of the doping with Br^-, as we observed in (Figure 4.7). Highly chaotrope ions ClO_4^- are tightly bound to the micelles surface and screen efficiently the surfactant head groups. This process favors the formation of big micelles and, consequently, highest maximum birefringences values (~$4.0x10^{-3}$). If the less chaotrope ions were replaced by the ClO_4^-, the maximum values of the birefringences in the N_D phase decreased to ~$1.6x10^{-3}$. In the case of the kosmotrope anions (F^-, OAc^- and Cl^-), they cannot form close contact with the chaotrope head groups of the surfactant TDTMABr, thus just N_C phase is stabilized (i.e., smaller micelles).

Although we examine the interactions between the surfactant head groups and the ions added at the micelle surfaces, we have also to take into account those between the counterions and the ions that have the same charge with respect to the surfactant head groups. For instance, in both KL and SDS mixtures (TDTMABr), the highly kosmotrope SO_4^{2-} (Na^+) ion of alkali salts (anions) remains away from the micellar surfaces. In the KL system, since the highly kosmotrope Li^+ and Na^+ ions are bound to the micelle surface, the kosmotrope SO_4^{2-} ion does not remove the K^+ counterions of the surfactant from the micelle surfaces. Thus, these two ions added to the lyotropic mixture behave as additional "counterions" bound to the micelle surfaces. They favor more flat and bigger micelles, which mainly stabilizes the N_D phase. This idea is confirmed by their birefringences values. As discussed before, higher birefringences indicate the presence of bigger micelles.

The mixture doped with the highly kosmotrope Li^+ ion shows the maximum birefringences of ~$3.5x10^{-3}$ in the N_D phase region whereas the doping with the less chaotrope ion Cs^+ (≈K^+ and Rb^+) exhibits that of ~$2.5x10^{-3}$. This means that the additional ions Cs^+, K^+ and Rb^+ do not form closest ion pairs with the sulfate ion and it is expected that most of them remain in the intermicellar region, hydrated by water molecules. With respect to the doping of the KL/DeOH/water mixture with Li^+ or Na^+, a small amount of these ions are bound to the micelle surfaces. On the other hand, the same mixture doped with Cs^+, K^+ and Rb^+ gave the three nematic phases, and the ions are partly binding to the micelle surfaces. In the case of the SDS mixtures (chaotrope head groups) a different behavior with respect to the KL mixtures is exepcted, with the addition of alkali salts. SDS head groups are mainly bound to the chaotrope Cs^+, K^+ and Rb^+ ions. There is a replacement of the kosmotrope Na^+ counterion of SDS due to: (a) the strong interaction between the SDS head groups and the chaotrope ions added to the mixture, and (b) the removal of the Na^+ counterions from the micelle surface by the kosmotrope sulfate ion of alkali salts added to the mixture. The latter case is supported by the maximum birefringence observed in the N_D phase region. Kosmotrope Na^+ ions from Na_2SO_4 in the lyotropic mixtures investigated favor the stabilization of the three nematic phases. These mixtures exhibited almost the same maximum birefringence in the N_D phase (~$3.0x10^{-3}$) compared to those from mixtures with chaotrope K^+, Rb^+ and Cs^+ sulfates. This result may be attributed to the removal of some Na^+ counterions from SDS, being substituted by chaotrope ions.

However, these ions do not behave as additional counterions, as it was observed in the KL mixtures. In other words, there is an opposite situation in the SDS mixtures with respect to that of KL mixtures, as a result of the kosmotrope-chaotrope interactions between the head groups and counterions/ions added. These results show one more time that the kosmotrope-chaotrope interactions are important to stabilize the different nematic phases.

Let us analyze now the system with TDTMABr. The counterion of TDTMABr molecule (Br^-) presents a chaotrope character and its interaction with the kosmotrope Na^+ ions of the added salts may be omitted. Then, we can just take into account the interactions of the anions of the sodium salts with the head groups of the surfactant at the micelle surfaces. The kosmotrope ions do not interact with the head group of TDTMABr as efficiently as the chaotrope ones. So, this doping does not promote an increase of the birefringences by the efficient screening of the repulsions between head groups to stabilize the N_B and/or N_D phase. Only the N_C phase is present, similarly to the ternary mixture of TDTMABr/DeOH/water. In the case of chaotrope ions (Br^-, NO_3^-, ClO_3^-, I^-, SCN^- and ClO_4^-), the maximum birefringences in the N_D phase increase 2.5 times from Br^- to ClO_4^- (Figure 4.7). This behavior may be attributed to the increasing in the number of ions bound to the micelle surfaces. This is in good agreement with the results of the KL mixtures, supporting also the results of the SDS mixtures. In other words, the salt ions added to the mixtures behave as "additional counterions" to reduce more the electrostatic repulsion between the head groups of the surfactants. As a consequence, bigger micelles are formed and N_B and/or N_D phases are more favored (as observed for KL and TDTMABr mixtures), with higher maximum birefringences. In addition, if the interactions between the counterions and ions (that have the same charge as the surfactant head groups) are dominant, as a result of their kosmotrope-kosmotrope and chaotrope-chaotrope characters, part of the counterions may be replaced by ions of opposite charge with respect to that of the surfactant head groups. This implies that the number of counterions remains unchanged and the maximum birefringences are approximately constant. See, e.g., the case of the SDS system (Table 4.1) and the N_D phase domain in (Figure 4.6). Kosmotrope SO_4^{2-} from alkali sulfate salts cannot (can) remove the chaotrope (kosmotrope) K^+ (Na^+) counterions of KL (SDS) from the micelle surfaces to the intermicellar- or water- region. The Na^+ ions of sodium salts cannot remove the

chaotrope Br^- counterions of the TDTMABr from the micelle surfaces. Hence, we may say that the interactions between counterions of the surfactants and ions (oppositely charged with respect to those counterions) added to the mixtures play an important role in the stabilization of the nematic phases, especially the N_B.

The laser conoscopy enables us to calculate the symmetric nontrivial invariants of the nematic order parameter σ_2 and σ_3 (Galerne and Marcerou, 1983; Neto and Salinas, 2005). These two invariants 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 $-{\sigma_2}^{3/2} < \sigma_3 < {\sigma_2}^{3/2}$. This description of the nematic phases leads to some assumptions about the symmetry, shape and shape anisotropy of the micelles in the three nematic phases, which were synthesized in the "intrinsically biaxial micelles model, IBM" (Neto and Salinas, 2005). This model is mainly based on two assumptions: (a) micelles have orthorhombic symmetry in the three nematic phases and (b) different orientational fluctuations trigger the stabilization of the three nematic phases. If the orientational fluctuations are full rotations around the axis perpendicular to the largest micelle surface (perpendicular to the main-surfactant bilayer), the N_D phase is stabilized. 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 maximum optical birefringences in the nematic phases and, consequently, the bigger the invariants σ_2 and σ_3 (Neto and Salinas, 2005). The plot of σ_2 versus σ_3 for three quaternary lyotropic mixtures are given in (Figure 4.8, 4.9 and 4.10).

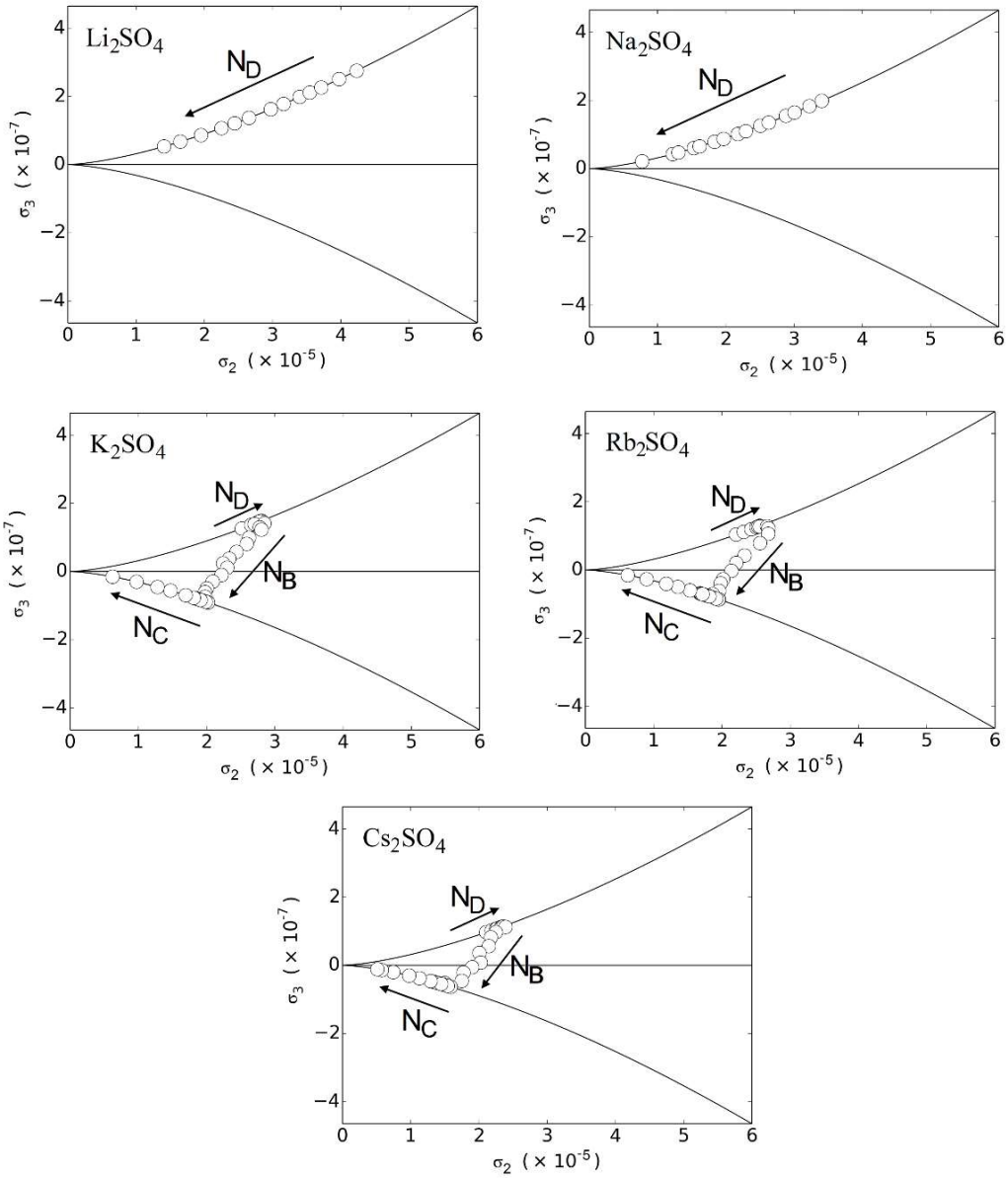


Figure 4.8. The plot of σ_3 versus σ_2 of the lyotropic mixtures KL/alkali sulfates/DeOH/H_2O/.

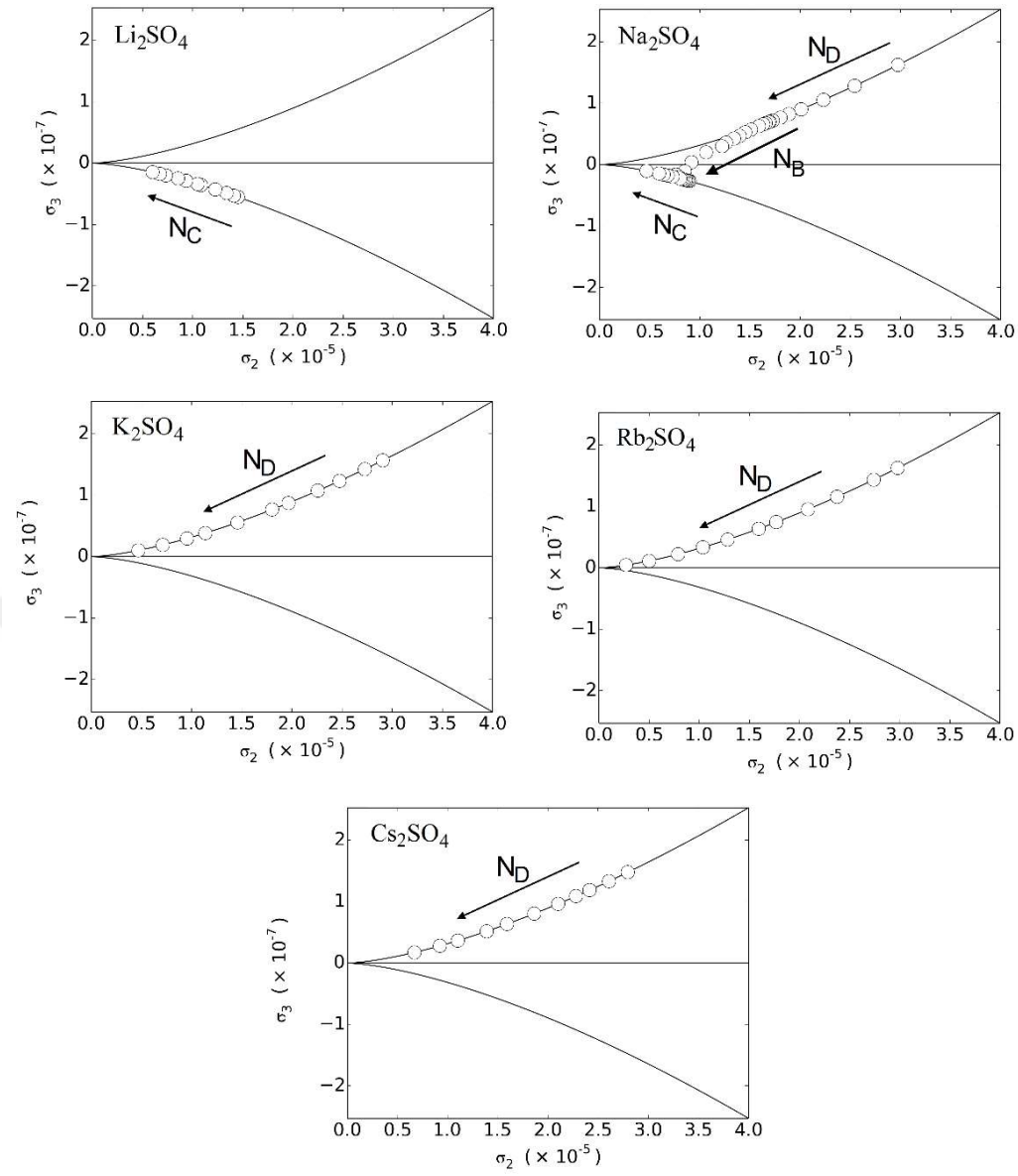


Figure 4.9. The plot of σ_3 versus σ_2 of the lyotropic mixture SDS/ alkali sulfates/DeOH/H_2O.

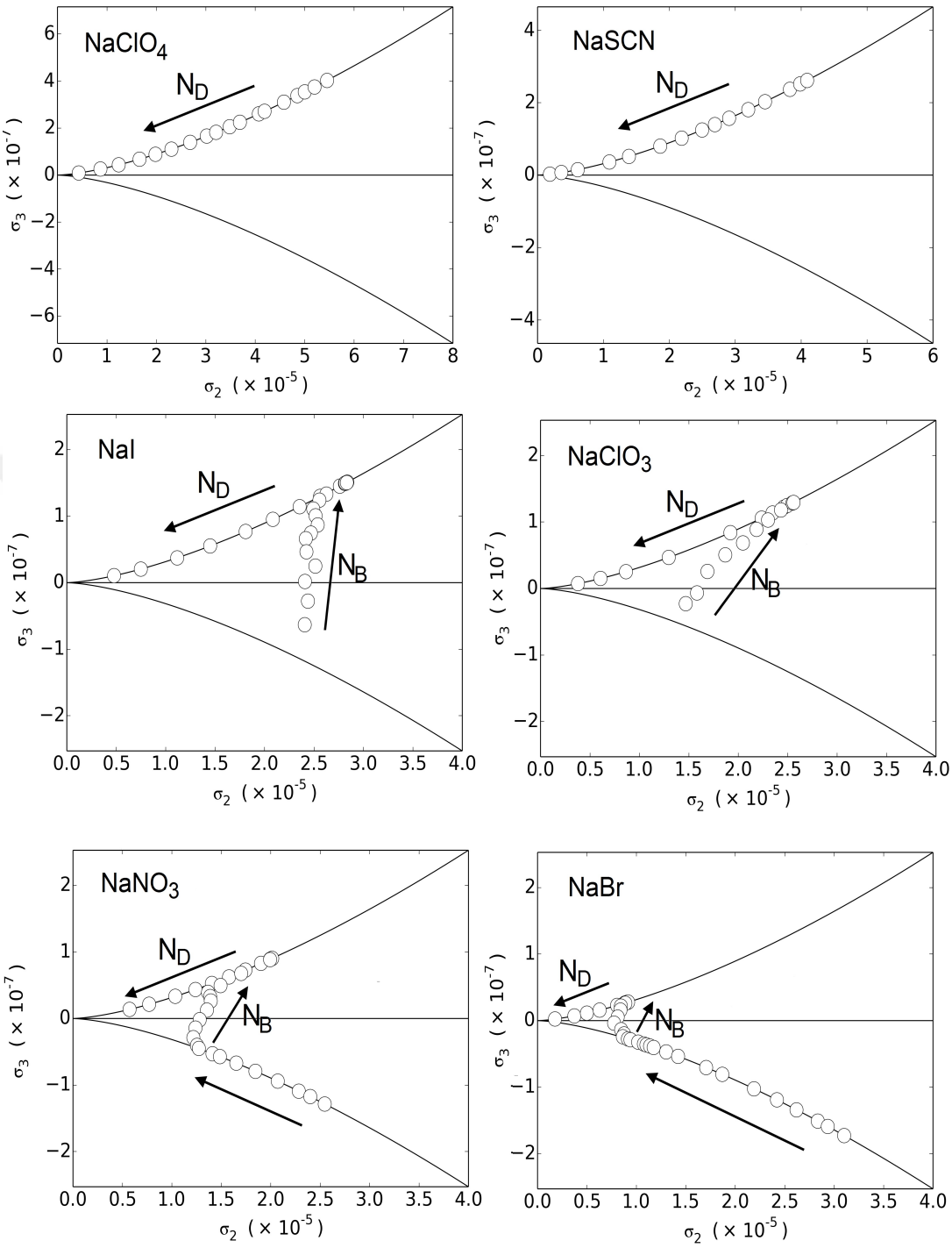


Figure 4.10. Continuing on the next page.

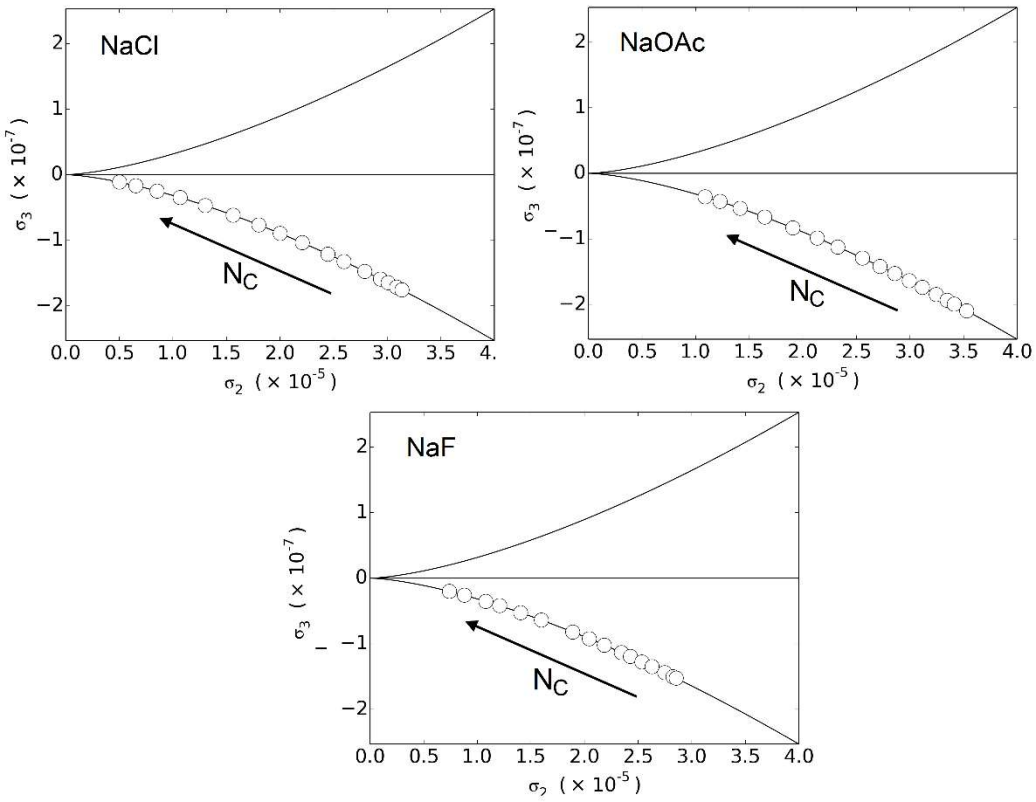


Figure 4.10. The plot of σ_3 versus σ_2 of the lyotropic system TDTMABr/sodium salts/DeOH/H_2O.

If we take into account the results of both isotropic micellar solutions and lyotropic nematic mixtures, there are close relations between them. In both cases, the salts affect micelle formation and micelle shape anisotropy. This study is another evidence of the usefulness of the information obtained from the isotropic micellar solutions to more complex systems (like lyotropic liquid crystals (Dawin et al., 2009). All the results shown here for isotropic micellar solutions and lyotropic liquid crystalline phases revealed that the relative effects of the Hofmeister ions are governed by the surface charge density (σ) of the ionic species and the hydrodynamic radius (r_h). This study also shows that the important contribution to the specific interactions between the head groups and the counterions/ions arise from, primarily, the surface charge density of the ionic species, see (Table 4.7).

Table 4.7. Pauling radius, r_p, (anions from (Babu and Lim, 1999); cations from (Fritz and Gjerde, 2009)), hydrodynamic radius, r_h, (anions from (Marcus, 1997); cations from (Fritz and Gjerde, 2009) and surface charge density, σ, (anions from (Leontidis, 2002) of the Hofmeister ions. The σ values of the alkali metal cations were calculated as given in Ref. (Leontidis, 2002), according to the equation $\sigma = ze/4\pi(r_p)^2$, where z=+1 and e is 1.602×10^{-19} C.

*From Ref. (Wang et al., 2010)

Ion	r_p / Å	r_h / Å	σ / C.m^{-2}
Li^+	0.60	3.40	3.541
Na^+	0.96	2.76	1.383
K^+	1.33	2.32	0.720
Rb^+	1.48	2.28	0.582
Cs^+	1.69	2.28	0.446
F^-	1.33	2.12	0.720
OAc^-	1.62	2.17	0.485
Cl^-	1.81	2.24	0.389
NO_3^-	1.79	2.23	0.397
Br^-	1.96	2.31	0.331
ClO_3^-	2.00	2.33*	0.318
SCN^-	2.13	2.42	0.281
I^-	2.20	2.46	0.263
ClO_4^-	2.50	2.61	0.221

5. CONCLUSIONS

In this study we investigated the role of kosmotrope/chaotrope specific interactions between the head groups of the surfactant molecules and the counterions/ions at the micelle surfaces on the stabilization of lyotropic nematic phases. For this purpose, some novel lyotropic quaternary mixtures (surfactant/DeOH/water/strong electrolyte or salt) were prepared. The uniaxial to biaxial phase transitions were determined from the temperature dependences of the birefringences in the nematic phases via laser conoscopy. It was observed that the stronger kosmotrope-kosmotrope or chaotrope-chaotrope interactions are related to the stabilization of the N_D phase. Conversely, weak interactions between the ionic species (head groups and ions) are related to the stabilization of the N_C phase. This happens in the case of strong kosmotrope surfactant head groups (ions) and strong chaotrope ions (surfactants head groups). Relatively weak interactions between weak kosmotrope and weak chaotrope species seem to be related, mainly, to the stabilization of the N_B phase.

From the sample preparation point of view, to obtain lyotropic mixtures showing the desired nematic phases, the surfactants and counterions/ions of electrolytes have to be chosen with respect to their kosmotrope and chaotrope characters. As a general trend, to obtain a N_D (N_C) phase it is preferred to make a mixture with strong kosmotrope-kosmotrope or chaotrope-chaotrope (highly weak kosmotrope-chaotrope) interactions between the heads of the main surfactant and ions/counterions.

To obtain the N_B phase, it is preferred to make a mixture with species that show relatively weak kosmotrope-chaotrope interactions. The present study shows that some parameters of isotropic micellar solutions of surfactants should be taken into account for the selection of optimum surfactant-electrolyte/counterion pairs to obtain lyotropic nematic phases, especially the N_B one.

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List of Publications :

(1) Akpinar E, **Turkmen M**, Canioz C, Neto AMF (2016) "Role of kosmotrope-chaotrope interactions at micelle surfaces on the stabilization of lyotropic nematic phases", European Physical Journal E: Soft Matter and Biological Physics, 39(11):107(1-16).

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