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Role of kosmotrope-chaotrope interactions at micelle surfaces on the stabilization of lyotropic nematic phases

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Abstract. Three lyotropic quaternary systems 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. The first system consisted of KL/decanol (DeOH)/water/alkali sulfate and the second of SDS/DeOH/water/alkali sulfate. The third system was prepared by adding sodium salts of chaotropic or kosmotropic anions to the primary mixture of TDTMABr/DeOH/water, separately. The characteristic textures of discotic nematic (N_D), biaxial nematic (N_B) and calamitic nematic (N_C) phases were identified under polarizing light microscope. Laser conoscopy was employed to determine the uniaxial-to-biaxial phase transitions. The kosmotrope-kosmotrope or chaotrope-chaotrope interactions between the head groups of the surfactants and the ions of the electrolytes led to the stabilization of the N_D phase. On the other hand, kosmotrope-chaotrope interactions stabilize the N_B and/or N_C phases.

1 Introduction

Lyotropic nematic phases have been the subject of a large number of studies in the literature for years [1–6]. 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 theoretically proposed [2,3] and experimentally verified [4,5] 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 [6] and laser conoscopy [7] measurements showed that uniaxial-to-biaxial phase transitions are of second order as predicted by mean-field theory [2,3].

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 [8] 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 [9] and biaxial cholesteric [10] 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

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and/or the ions of electrolytes added into the solution. Depending on the screening, the repulsion between the heads of the amphiphilic molecules at the micelle surfaces, the surfactants are less or more packed 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 [11,12]. 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; and K^+, Rb^+, Cs^+, Br^-, ${NO_3}^-$, ${ClO_3}^-$, I^-, SCN^- and ${ClO_4}^-$ are chaotrope [13–15]. Surfactants are also classified as kosmotrope and chaotrope surfactants, according to their head groups [16,17]. It was reported in the literature that potassium laurate, KL [16] (sodium dodecylsulfate, SDS [16], and tetradecyltrimethylammonium bromide [17], 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 [18]. This leads to the close packing of the surfactants in the micelle, and the micellar growth [19,20]. 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 [21–23] and lyotropic nematic mesophases [24–26] 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 [8]. 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.

2 Experimental

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 25 °C under strong mixing by magnetic stirrer according to the procedure given in refs. [27,28]. 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.

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 ($1\,\mu$L per 1 g of the mixture) of water-based ferrofluid (Ferrotec) was added to the samples.

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, 0.1 °C) with water circulation (Polyscience SD07R with an accuracy of ±0.04 °C) to provide the homogenous heat distribution in the temperature control unit.

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 ±0.001 °C).

Electrical conductivity measurements were carried out in a Mettler Toledo S470 SevenExcellence at 40.0 °C. The dip-type conductivity cell was placed in a homemade aluminum sample holder in which water circulates for providing stable temperature (±0.1 °C). The cell constant was determined as $1.03\,\mathrm{cm}^{-1}$ 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.

Surface tension measurements were carried out in an Attension tensiometer (Model 701) by platinum ring detachment method at $40.0 \pm 0.1\,^\circ\mathrm{C}$. On the logarithm of surface tension ($\ln \gamma$) *versus* surfactant concentration (C) plot, a minimum was observed for each surfactant. This is a common situation for ionic surfactants [29], especially for SDS [30,31]. 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 [32]

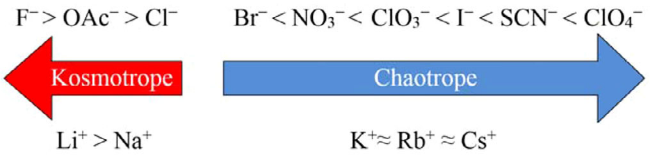
$$F = 2\pi(r_1 + r_2)\gamma,$$

where r_1 and r_2 are the radius of the inner 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}.

Ultrapure water was provided by Millipore Direct-Q3 UV, which produces a water having $18.2\,\mathrm{M\Omega\,cm}$ of resistivity at 25 °C.

3 Results and discussions

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 [16]. 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 [11,12], were used. Among the anions (cations), F^-, OAc^- and Cl^- (Li^+ and Na^+) are classified as kosmotrope, Br^-, $\mathrm{NO_3}^-$, $\mathrm{ClO_3}^-$, I^-, SCN^- and $\mathrm{ClO_4}^-$ (K^+, Rb^+ and Cs^+) are chaotrope [14,15]. The kosmotrope and chaotrope order of these Hofmeister ions are, in general, given as follows [14,33]



However, at this point, we would like to mention some controversies on the order of the Hofmeister anions in the literature. In some studies [34], Cl^- ion is reported as a chaotrope ion while others accept it as kosmotrope [35]. 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_0) of salt solutions, according to the relation: $\eta/\eta_0 = 1 + A\sqrt{c_{\mathrm{salt}}} + Bc_{\mathrm{salt}}$, where A is an "electrostatic" parameter [13]. 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 [34]. 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 [14].

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 [36] 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

Table 1. Critical micelle concentrations (cmc), degree of counterion bindings (β) and micellization Gibbs free energy ($\Delta_{\text{mic}}G$) obtained from the electrical conductivity measurements for the isotropic micellar solutions of KL/water/alkali sulfate and SDS/water/alkali sulfate at 40.0 °C. Errors are within ±2%, ±7% and ±2% in cmc, β and $\Delta_{\text{mic}}G$ for KL solutions, respectively; ±4%, ±3% and ±2% in cmc, β and $\Delta_{\text{mic}}G$ for SDS solutions.

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
	$\Delta_{\text{mic}}G$/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
	$\Delta_{\text{mic}}G$/kJ mol^{-1}	−34.80	−35.90	−37.92	−38.56	−38.58

pairings [37,38]. 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 [36,37], 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 [36]. 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.

3.1 Isotropic micellar solutions

Some experimental [39] and theoretical [11,18,40] 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 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 40.0 °C. 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 40.0 °C 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 figs. 1 and 2, respectively. The break point observed on the κ-C

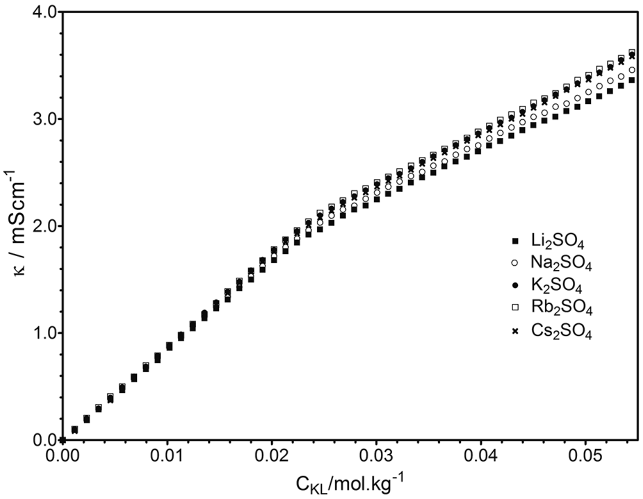


Fig. 1. Specific conductance as a function of the total surfactant concentration of alkali sulfate salts for the isotropic micellar solutions of KL/water/alkali salt at constant salt concentration and temperature of 40.0 °C. All curves, post- and pre-micellar regions, have regressions > 0.999.

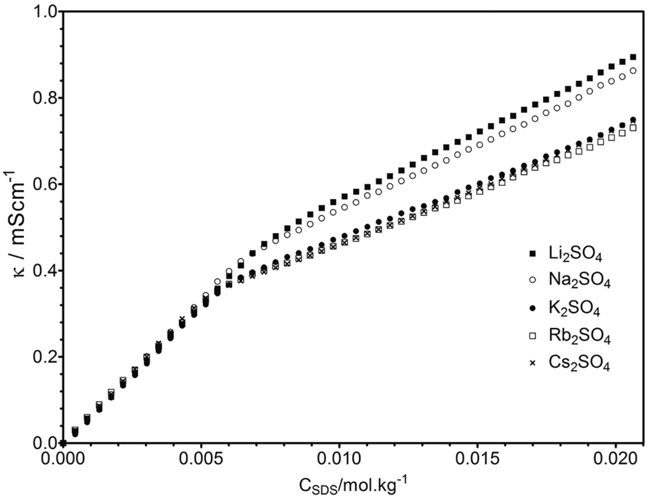


Fig. 2. Specific conductivity as a function of the total surfactant concentration of alkali sulfate salts for the isotropic micellar solutions of SDS/water/alkali salt at constant salt concentration and temperature of 40.0 °C. All curves, post- and pre-micellar regions, have regressions > 0.999.

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 ($\beta = 1 - \alpha$).

The micellization Gibbs free energies, $\Delta_{\text{mic}}G$, were calculated according to the following equation [41,42]:

$$\Delta_{\text{mic}}G = RT\left[\ln X_{\text{cmc}} + \beta \ln(X_{\text{cmc}} + X_{\text{salt}})\right], \qquad (1)$$

where R is the ideal gas constant ($8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$), 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 $\Delta_{\text{mic}}G$ values obtained for KL/water/alkali and SDS/water/alkali sulfate are given in table 1. The decrease in the cmc values from Li^+ to Cs^+ follows the order of the Hofmeister series, *i.e.* $\text{Li}^+ < \text{Na}^+ < \text{K}^+ \approx \text{Rb}^+ \approx \text{Cs}^+$ for KL/water/alkali sulfate and $\text{Li}^+ > \text{Na}^+ > \text{K}^+ \approx \text{Rb}^+ \approx \text{Cs}^+$ 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 $\Delta_{\text{mic}}G$. Higher β values of Li^+ indicate that it is efficiently bound to the micelle surface with respect to other cations, and the more negative $\Delta_{\text{mic}}G$ 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 $\Delta_{\text{mic}}G$ 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 [43], *i.e.* $\text{Li}^+ > \text{Na}^+ > \text{K}^+ \approx \text{Rb}^+ \approx \text{Cs}^+$. 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.

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,

Table 2. Maximum surface excess concentration ($\Gamma_{\max}$) 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 40.0 °C. Errors are within ±5% (±2%) and ±5% (±2%) in $\Gamma_{\max}$ and $A_{\min}$ for KL (SDS) solutions, respectively.

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

this assumption may help us to understand the relative effect of the ions in the micellar solutions and lyotropic liquid crystalline phases.

The amount of the surfactant adsorbed at the air-liquid surface is given by its surface excess concentration, Γ, defined as the maximum surface excess concentration at surface saturation, $\Gamma_{\max}$. The surface excess concentration can be evaluated from the surface tension measurements by the Gibbs equation (eq. (2)) [32,44], as

$$\Gamma_{\max} = -\frac{1}{nRT}\left(\frac{\partial\gamma}{\partial \ln C}\right)_T, \tag{2}$$

where $n = 2$ for a 1:1 ionic surfactant such as potassium laurate, sodium dodecylsulfate and tetradecyltrimethylammonium bromide in the absence of any additional electrolyte. In the case of ionic surfactants in the presence of strong electrolytes, n is taken 1 [44–46]. The linear part of γ-$\ln C$ plot was taken for the calculation of $\Gamma_{\max}$, [31]. The maximum surface excess concentration is related to the minimum area per surfactant head group at the interface according to eq. (3) [32]

$$A_{\min} = \frac{10^{16}}{N_A \Gamma_{\max}}, \tag{3}$$

where N_A is Avogadro's number. The evaluated $\Gamma_{\max}$ and $A_{\min}$ values are given in table 2 for KL/water/alkali salt and SDS/water/alkali sulfate isotropic solutions.

$\Gamma_{\max}$ is a measure of the adsorption of a surfactant molecule at the air-liquid interface and, hence, the higher $\Gamma_{\max}$ is attributed to the higher surface activity [32]. In other words, a higher $\Gamma_{\max}$ 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 $\Gamma_{\max}$ ($A_{\min}$) 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 $\Gamma_{\max}$ 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 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 [39,47,48]. 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 $ClO_4{}^-$.

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 $\Delta_{\mathrm{mic}}G$ 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 [15].

At this point, before passing on to 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

Table 3. Critical micelle concentration (cmc), degree of counterion binding (β) and micellization Gibbs free energy ($\Delta_{\mathrm{mic}}G$) from the electrical conductivity measurements and the maximum surface excess surfactant concentration ($\Gamma_{\max}$); 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 40.0 °C. Errors were within ±4%, ±2%, ±2%, ±3% and ±3% in cmc, β, $\Delta_{\mathrm{mic}}G$, $\Gamma_{\max}$ and $A_{\min}$ values, respectively.

	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
$\Delta_{\mathrm{mic}}G$/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

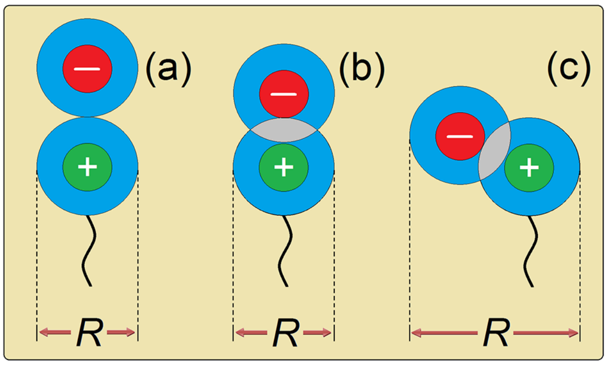


Fig. 3. Sketch of the formation of possible headgroup-counterion/ions pairing at the micelle surface. Here, for instance, the positively (negatively) charged headgroup (counterion/ion) is represented by green (red). Since blue regions show the hydration shell around the head groups, grey ones correspond to the region where two hydration shells overlap. R is total diameter of the cosphere. This figure is adapted from fig. 4 of ref. [36].

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.

If we compare the $A_{\min}$ values of KL and SDS systems (table 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, a completely 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 fig. 3c. However, for kosmotrope-chaotrope interactions, the ion pairing shown in fig. 3a or b is most likely to be formed [36]. If the opposite character between the ionic species is large, they may produce an ion pair as shown in fig. 3a. However, if they have a relatively less opposite character, their ion pairing may be as shown in fig. 3b. Consequently, taking into account the $A_{\min}$ values, KL head groups produce closer ion pair with kosmotrope ions, as shown in fig. 3c. In this way, the kosmotrope counterions/ions enter 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 $A_{\min}$) in both isotropic micellar solutions and lyotropic liquid crystalline phases (stabilization of N_B and/or N_D [8] and N_D and/or lamellar phases are favored [24,49]). 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 $A_{\min}$) 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 [8]. 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 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 [50], *i.e.* just head groups are important on those classifications. Then, in those three molecules, an additional –CH_3 group was shown as an alkyl chain length of each surfactant molecule, fig. 4.

Let us start the discussion by comparing the ions acetate and methylsulfate. Note that the π-electrons of

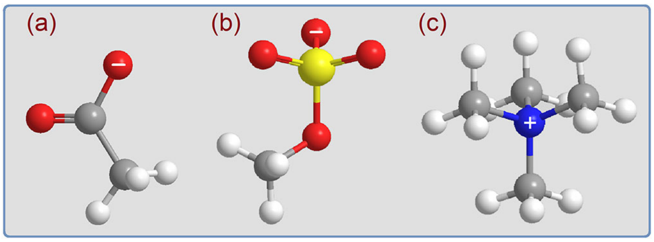


Fig. 4. Molecular structures of (a) acetate, (b) methylsulfate and (c) tetrametylammonium ions. Grey: carbon; white: hydrogen; red: oxygen; yellow: sulfur; blue: nitrogen.

a double bond –C=O in acetate, fig. 4a (two double bonds –S=O in sulfate, fig. 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 fig. 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, fig. 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. [51], 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 [14,52] 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 fig. 3c, which causes the higher packing of the surfactants in the micelles of both isotropic solutions and lyotropic nematic phases (*i.e.* the smaller $A_{\min}$). 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 $A_{\min}$, see table 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 (fig. 3c) and exhibit larger surfactant head group area (larger $A_{\min}$), table 3. As seen in table 3, from the highly kosmotrope one F^- to relatively highly chaotrope one ${ClO_3}^-$, $A_{\min}$ increases as 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 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 fig. 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 3.

3.2 Lyotropic liquid crystalline phases

Three series of lyotropic ternary mixtures were prepared. These mixtures were composed of KL/DeOH/water, SDS/DeOH/water, 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 tables 4, 5 and 6.

The lyotropic uniaxial-to-biaxial phase transitions were determined by laser conoscopy, which enables us

Table 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 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 the 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 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 the 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

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 [5]. Figures 5, 6 and 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.

Let us start the discussion of the laser conoscopy results for the kosmotrope surfactant KL mixture (fig. 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

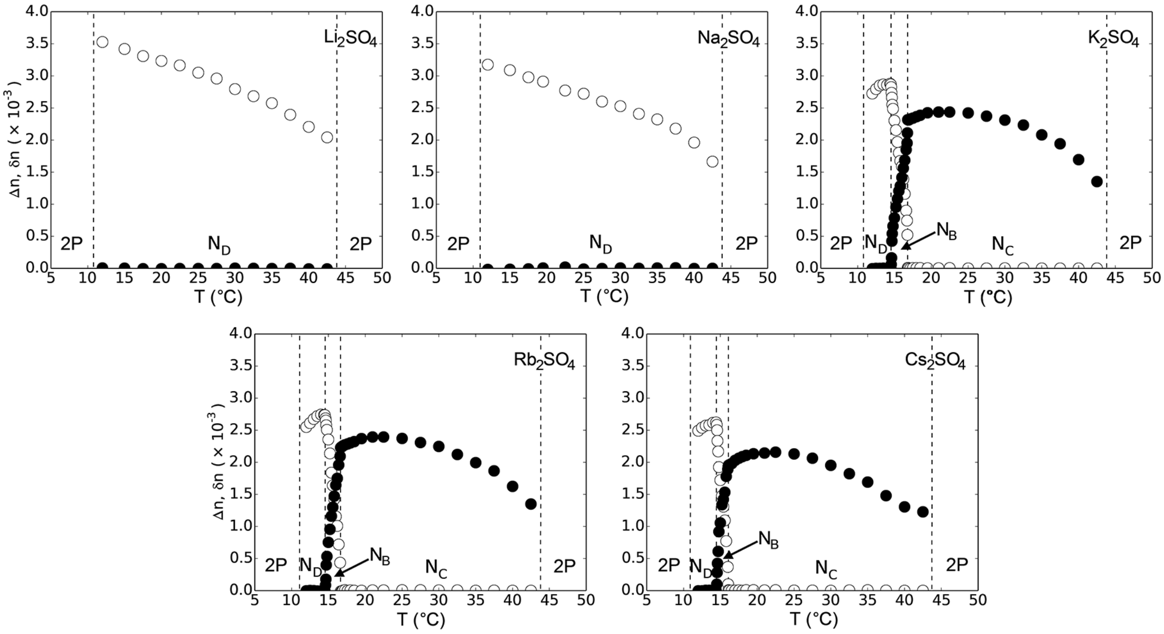


Fig. 5. Temperature dependence of the birefringences of the lyotropic mixture KL/DeOH/water/alkali sulfate. 2P: biphasic region. The biphasic regions are beyond the scope of this study.

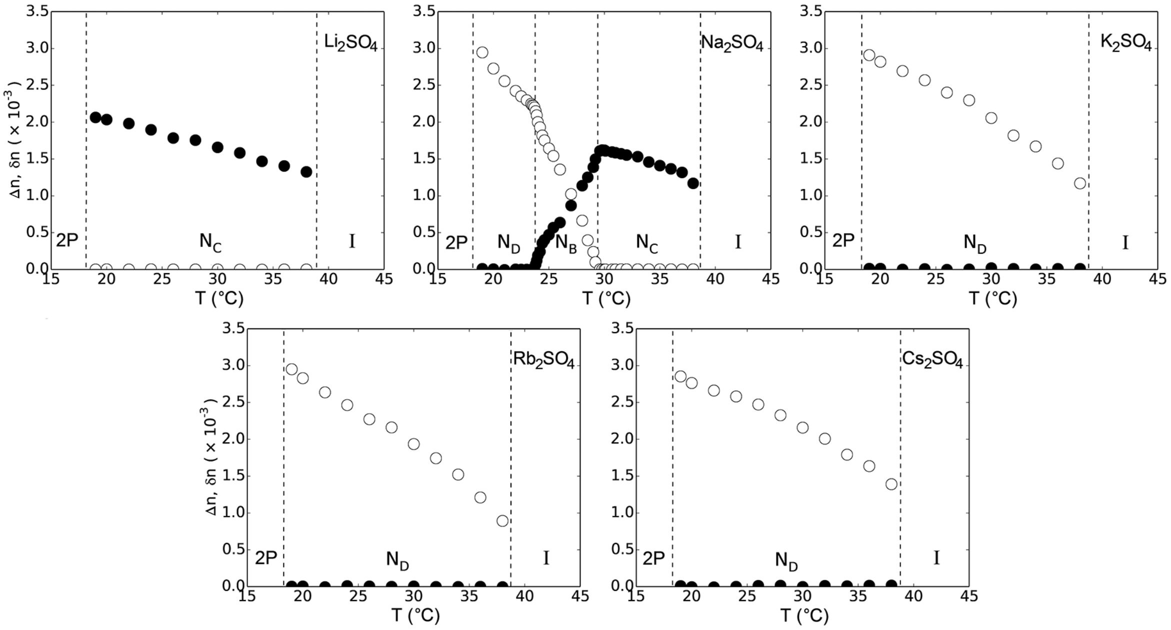


Fig. 6. Temperature dependence of the birefringences of the lyotropic mixture SDS/DeOH/water/alkali sulfate. 2P: biphasic region. The biphasic region is beyond the scope of this study. I: isotropic phase.

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 [33] and their adsorption on metal oxides [43]. 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 [53], see table 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 3.5×10^{-3} (Li^+ mixture) to 2.7×10^{-3} (K^+ mixture), and remained almost constant

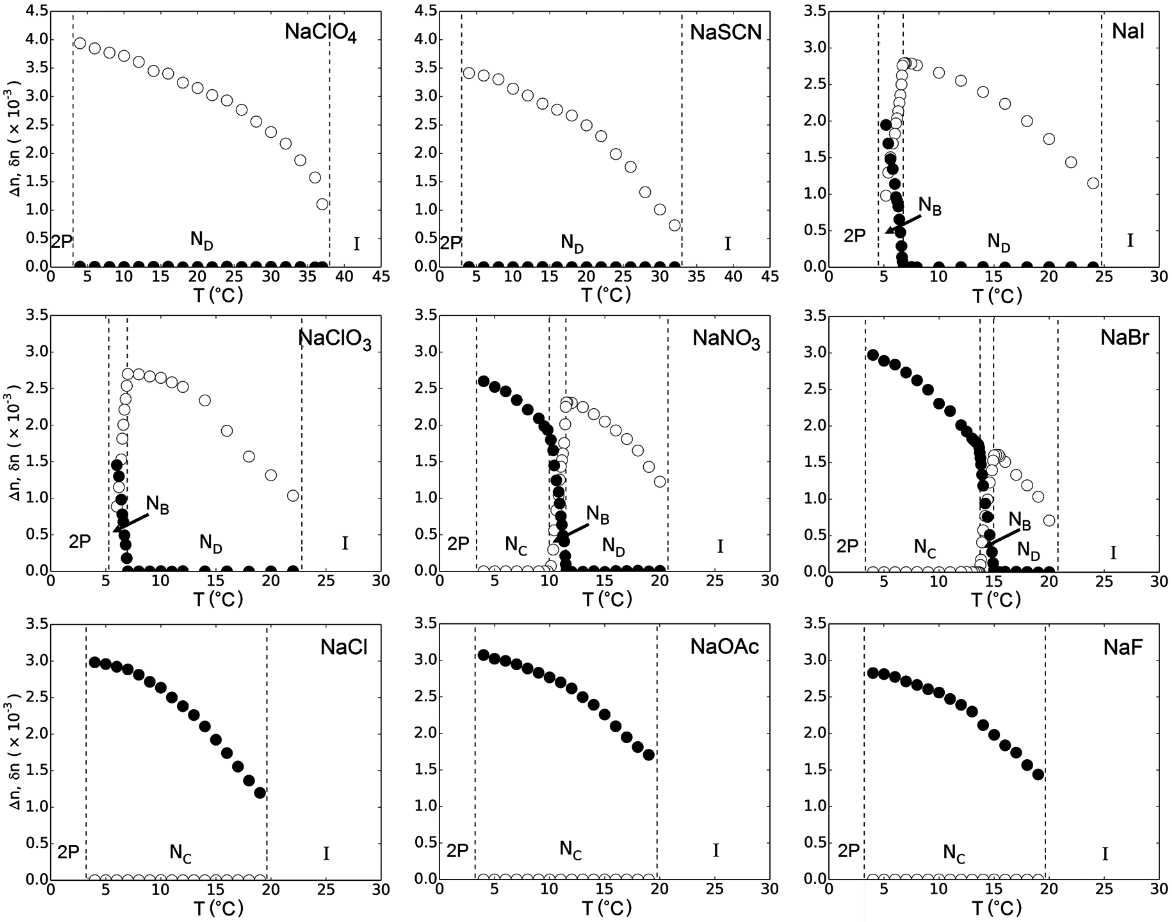


Fig. 7. Temperature dependence of the birefringences of the lyotropic mixture TDTMABr/DeOH/water/alkali sulfate. 2P: biphasic region. The biphasic region is beyond the scope of this study. I: isotropic phase.

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 fig. 6. As can be seen from fig. 6 and table 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 fig. 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 fig. 7. Among the chaotrope anions added to the

Table 7. Pauling radius, r_p, (anions from [54]; cations from [55]), hydrodynamic radius, r_h, (anions from [56]; cations from [55]) and surface charge density, σ, (anions from [14]) of the Hofmeister ions. The σ values of the alkali metal cations were calculated as given in ref. [14], according to the equation $\sigma = ze/4\pi(r_\mathrm{p})^2$, where $z = +1$ and e is 1.602×10^{-19} C.

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[(a)]	0.318
SCN^-	2.13	2.42	0.281
I^-	2.20	2.46	0.263
$ClO_4{}^-$	2.50	2.61	0.221

[(a)] From ref. [57].

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 fig. 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 ($\sim 4.0 \times 10^{-3}$). If the less chaotrope ions were replaced by the $ClO_4{}^-$, the maximum values of the birefringences in the N_D phase decreased to $\sim 1.6 \times 10^{-3}$. 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 $\sim 3.5 \times 10^{-3}$ in the N_D phase region whereas the doping with the less chaotrope ion Cs^+ ($\approx K^+$ and Rb^+) exhibits that of $\sim 2.5 \times 10^{-3}$. 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 bound to the micelle surfaces. In the case of the SDS mixtures (chaotrope head groups) a different behavior with respect to the KL mixtures is expected, 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 ($\sim 3.0 \times 10^{-3}$) 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 in-

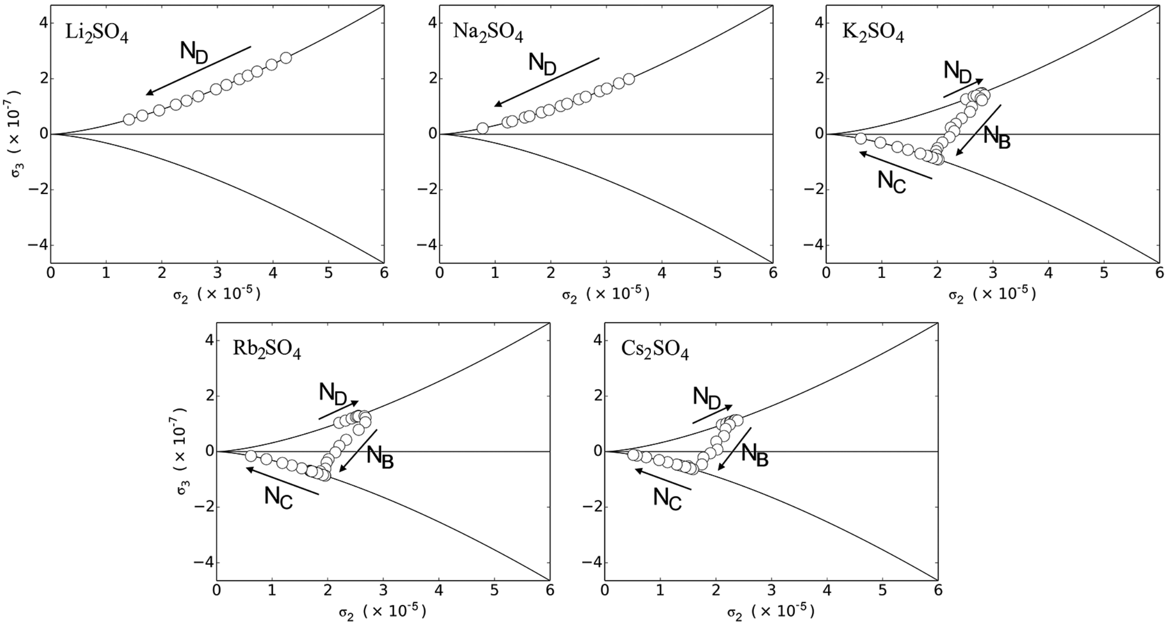


Fig. 8. The plot of σ_3 *versus* σ_2 of the lyotropic mixtures KL/alkali salt/DeOH/H_2O, with different alkali salts.

crease 2.5 times from Br^- to $ClO_4{}^-$ (fig. 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 1) and the N_D phase domain in fig. 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 [7,22] σ_2 and σ_3. 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" [22]. 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 [22].

The plot of σ_2 *versus* σ_3 for three quaternary lyotropic mixtures are given in figs. 8, 9 and 10.

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 [24]). 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 sur-

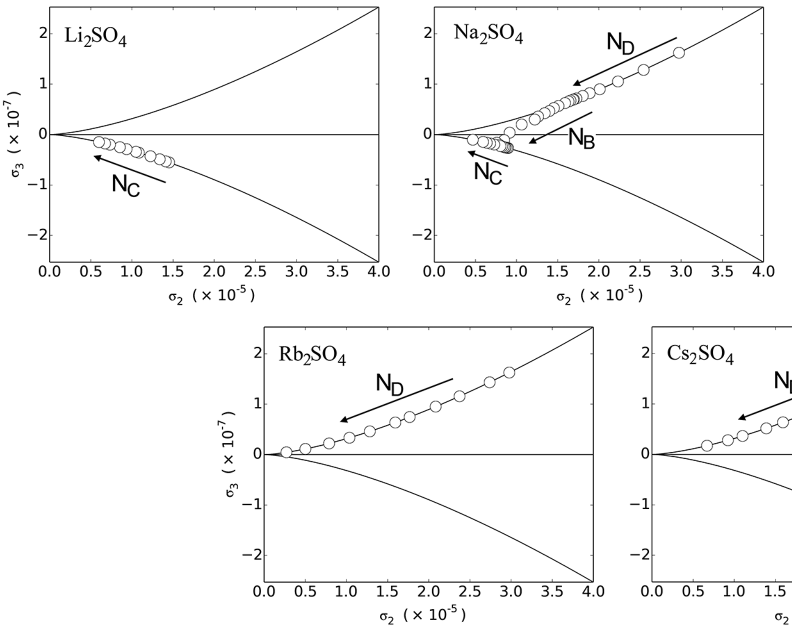


Fig. 9. The plot of σ_3 *versus* σ_2 of the lyotropic mixture SDS/alkali salt/DeOH/H$_2$O, with different alkali salts.

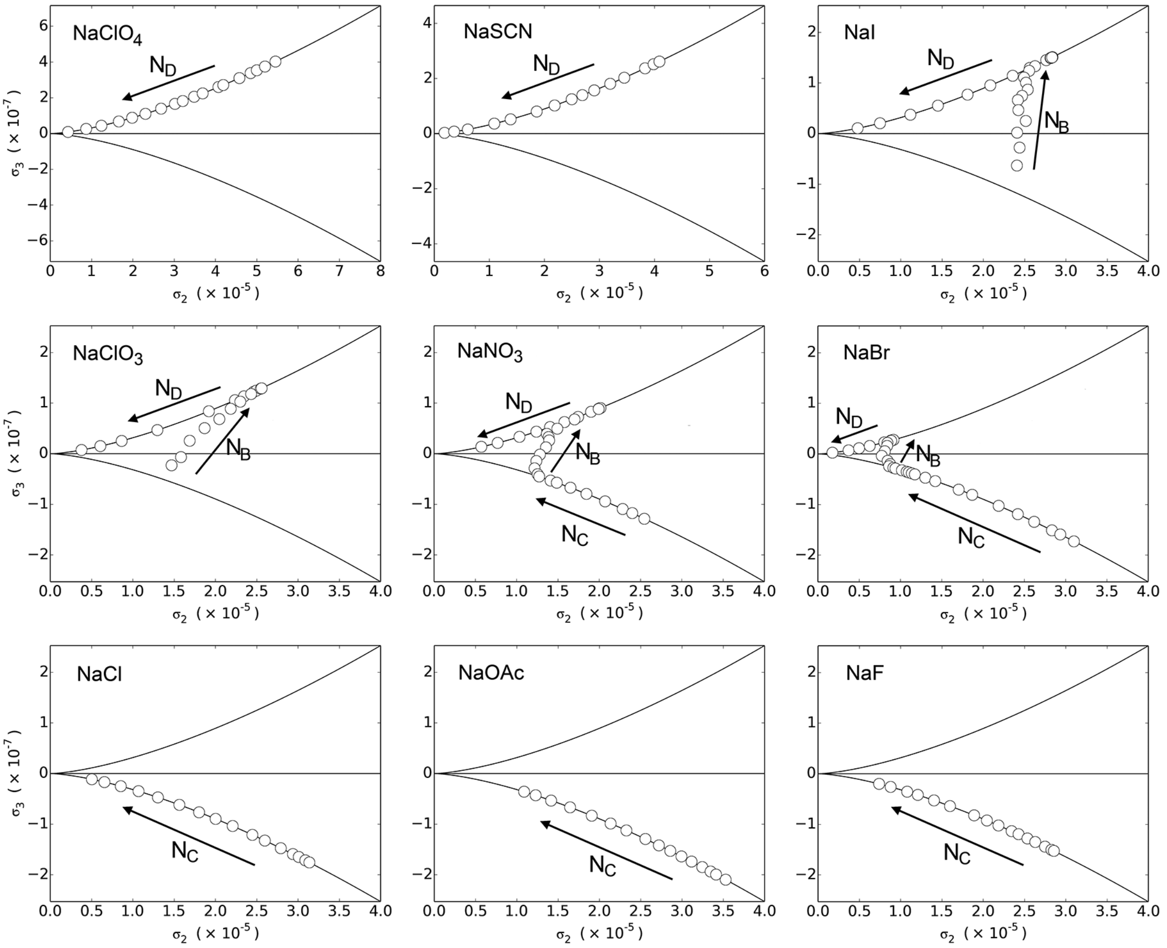


Fig. 10. The plot of σ_3 *versus* σ_2 of the lyotropic system TDTMABr/sodium salt/DeOH/H$_2$O, with different Hofmeister anions.

face 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 7.

4 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 $\mathrm{N_D}$ phase. Conversely, weak interactions between the ionic species (head groups and ions) are related to the stabilization of the $\mathrm{N_C}$ 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 $\mathrm{N_B}$ 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 $\mathrm{N_D}$ ($\mathrm{N_C}$) 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 $\mathrm{N_B}$ 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 $\mathrm{N_B}$ one.

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