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Investigation of the interaction of alkali ions with surfactant head groups for the formation of lyotropic biaxial nematic phase via optical birefringence measurements

Erol Akpınar^a, Dennys Reis^b and Antonio Martins Figueiredo Neto*^b

^a Abant İzzet Baysal University, Arts and Sciences Faculty, Department of Chemistry, Golkoy, Bolu, Turkey, 14280; ^b Instituto de Física, Universidade de São Paulo, São Paulo, SP, Brazil, 05314-970

ABSTRACT

Lyotropic liquid crystals exhibiting nematic phases were obtained from the mixtures potassium laurate/alkali sulfate salts (M_2SO_4)/1-undecanol (UndeOH)/water and sodium dodecyl sulfate (SDS)/ M_2SO_4 /1-dodecanol (DDeOH)/water, where M_2SO_4 represents the alkali sulfate salts being Li_2SO_4 , Na_2SO_4 , K_2SO_4 , Rb_2SO_4 or Cs_2SO_4 . The birefringences measurements were performed via laser conoscopy. Our results indicated that cosmotropic and chaotropic behaviors of both ions and head groups are very important to obtain lyotropic biaxial nematic phase. To obtain the biaxial nematic phase, surfactant head group and ion present in lyotropic mixture have relatively opposite behavior, e.g. one more cosmotropic (more chaotropic) other less cosmotropic (less chaotropic) or vice versa.

Keywords: intrinsically biaxial micelles model, orthorhombic micelle, cosmotropes, chaotropes, counterion, alkali ions, laser conoscopy

1. INTRODUCTION

After the discovery of the first lyotropic biaxial nematic phase N_B by Yu and Saupe in the mixture of potassium laurate (KL), decanol (DeOH), water¹, other research groups produced different lyotropic mixtures presenting the N_B phase aiming to understand the characteristics of this new remarkable phase.²⁻⁹ At the beginning, there were some controversies about the N_B in the literature. Initially, the N_B phase was thought to be made by a mixture of the two uniaxial nematic phases, discotic (N_D) and calamitic (N_C). In this picture, a mixture of disk-like and cylindrical-like micelles should exist in the N_B . This type of model will be named hereafter as “mixture of cylindrical and disc-like micelles model, MCD”.¹⁰ However, it was experimentally established that this type of mixture is not stable, i.e. demixing occurs.¹¹⁻¹³ So, nowadays, the existence of the biaxial nematic phase is fully accepted being physically and chemically a stable intermediate phase between the N_D and N_C phases.

Up to now, it is our belief that the intrinsically biaxial micelles model (IBM) explains the mechanism concerning the transitions between the different uniaxial and the biaxial phases.^{14,15} In the IBM model, the driving force for the existence of three nematic phases, the two uniaxial N_D and N_C and the biaxial N_B , is related to characteristic orientational fluctuations of the same type of (orthorhombic) micelles in these nematic phases. The investigation of the uniaxial-to-biaxial phase transition requires precise measurements of an order parameter in the vicinity of the transition temperature. For this purpose, a reliable experimental technique is the laser conoscopy.^{16,17} This technique is based on the determination of the birefringences of the nematic phases with good accuracy. The temperature dependence of the birefringences is usually employed for the construction of these phase diagrams.¹⁸

It is well known that in lyotropic liquid crystals the phase transitions between uniaxial nematics and biaxial nematic occur by changing the temperature and/or the relative concentrations of the mixture components. In a previous study,¹⁹ we showed that the alcohol-chain length (present as a co-surfactant in the lyotropic mixture) with respect to the main surfactant alkyl chain has an important effect on the topology of the phase diagram. In that study, it was observed that, at a given temperature, an increase in the alkyl chain length of the alcohol causes the transition from the N_D phase to first N_B and then N_C phase.

To the best of our knowledge, there is no systematic investigation of the effect of alkali metal salts on the birefringences of the nematic phases, on the range of the biaxial nematic phases and on the behavior of the uniaxial-to-biaxial nematic phase transitions in lyotropic mixtures with salt. For this purpose, we used the mixture of KL/alkali sulfate (M_2SO_4)/1-undecanol (UndeOH)/water, (with $M = Li, Na, K, Rb$ or Cs), where the salts are lithium sulfate

(Li₂SO₄), sodium sulfate (Na₂SO₄), potassium sulfate (K₂SO₄), rubidium sulfate (Rb₂SO₄) and cesium sulfate (Cs₂SO₄), keeping the molar concentration of all constituents constants. Moreover, we investigated the mixtures of sodium dodecylsulfate (SDS)/alkali sulfate (M₂SO₄)/1-dodecanol (DDeOH)/water.

2. EXPERIMENTAL

All chemicals used in this study, except KL, were commercially available from Merck and Sigma with purity >99%. KL was synthesized in our laboratory from the neutralization of lauric acid with potassium hydroxide in ethanol. A small quantity (1 μL per 1 g of sample) of water-based ferrofluid from Ferrotec was added to the mixtures to help the magnetic field alignment of the samples.²⁰

Lyotropic liquid crystalline mixtures of KL/M₂SO₄/UndeOH/water were prepared as discussed in Refs. [18,19]. SDS/M₂SO₄/DDeOH/water mixtures were similarly produced. The mixtures compositions of these two systems were given in Table 1.

For laser conoscopy measurements, each mixture was transferred into a sample cell that consisted of two circular optical glasses and a 1.0 mm glass O-ring. By this way, 1.0 mm thick sample was obtained. This sample cell was put in a special experimental set-up having a HeNe laser (λ=632 nm), a Neocera LTC-21 temperature controller which controls temperature with an accuracy of 0.01°C and a Walker Sci. Electromagnet to apply a static magnetic field ($H = 2.04 \text{ kG}$) to obtain well-oriented samples.

In the sample's birefringences measurements with the laser conoscopy, the laboratory frame axes were defined as follows: the horizontal plane is formed by the two orthogonal axes 1 and 2; the magnetic field is aligned along the axis 1; axis 3 is vertical and parallel to the laser beam propagation direction. Two main optical birefringences, $\Delta n = n_2 - n_1$ and $\delta n = n_3 - n_2$, were measured as a function of temperature, starting from the N_D phase.

Table 1. Compositions of each constituent in the lyotropic mixtures of (a) KL/salt/UndeOH/water and (b) SDS/salt/DDeOH/water. X_s , X_{salt} , X_{UndeOH} , X_{DDeOH} , X_{H_2O} are the concentrations of amphiphiles KL and SDS, salts, UndeOH, DDeOH and water in mole fractions, respectively. δn is the birefringence of the N_D phase at 45°C and ΔT_{N_B} is the temperature range of the biaxial domain.

(a)	Salt	X_s	X_{salt}	X_{UndeOH}	X_{H_2O}	Phase type	$\delta n \times 10^{-3}$	$\Delta T_{N_B} / ^\circ C$
KL	Na ₂ SO ₄	0.0383	0.0060	0.0114	0.9443	N _D	5.95	---
	K ₂ SO ₄ *	0.0383	0.0060	0.0114	0.9443	N _C , N _B , N _D	3.44	5.55
	Rb ₂ SO ₄	0.0383	0.0060	0.0114	0.9443	N _C , N _B , N _D	3.67	6.30
	Cs ₂ SO ₄	0.0383	0.0060	0.0114	0.9443	N _C , N _B , N _D	3.16	5.20
(b)	Salt	X_s	X_{salt}	X_{DDeOH}	X_{H_2O}	Phase type	$\delta n \times 10^{-3}$	$\Delta T_{N_B} / ^\circ C$
SDS	Li ₂ SO ₄	0.0301	0.0029	0.0093	0.9577	N _D	3.09	---
	Na ₂ SO ₄	0.0301	0.0029	0.0093	0.9577	N _D	3.78	---
	K ₂ SO ₄	0.0301	0.0029	0.0093	0.9577	N _D	4.37	---
	Rb ₂ SO ₄	0.0301	0.0029	0.0093	0.9577	N _D	4.43	---
	Cs ₂ SO ₄	0.0301	0.0029	0.0093	0.9577	N _D	4.44	---

*From Ref. [18,19]

3. RESULTS AND DISCUSSIONS

At the relative concentrations investigated, we did not get lyotropic mixture with KL and Li_2SO_4 . The apparent reason for this will be discussed in the following. In order to get some hints about the behavior of Li_2SO_4 in the mesophase, we measured the birefringences of SDS/salt/dodecanol (DDeOH)/water in the N_D phase, where the salts are from Li_2SO_4 to Cs_2SO_4 .

The birefringences of the nematic phases were measured by laser conoscopy. This technique is very useful to precisely determine the uniaxial-to-biaxial phase transitions. In the KL/alkali sulfate/UndeOH/water lyotropic mixture, the birefringences were measured starting from the magnetically well-aligned N_D phase (homeotropic alignment) and, by decreasing the temperature, the phase transition temperatures were determined. However, in the mixture with Na_2SO_4 , only the discotic nematic phase was observed (Figure 1a). As can be seen from the Figure 1b-d, the uniaxial-to-biaxial phase transitions are of second order, as predicted by the mean-field theory.¹⁷ The mixtures with K, Rb and Cs salts presented a biaxial temperature domain of about 6°C (Figure 1 and Table 1).

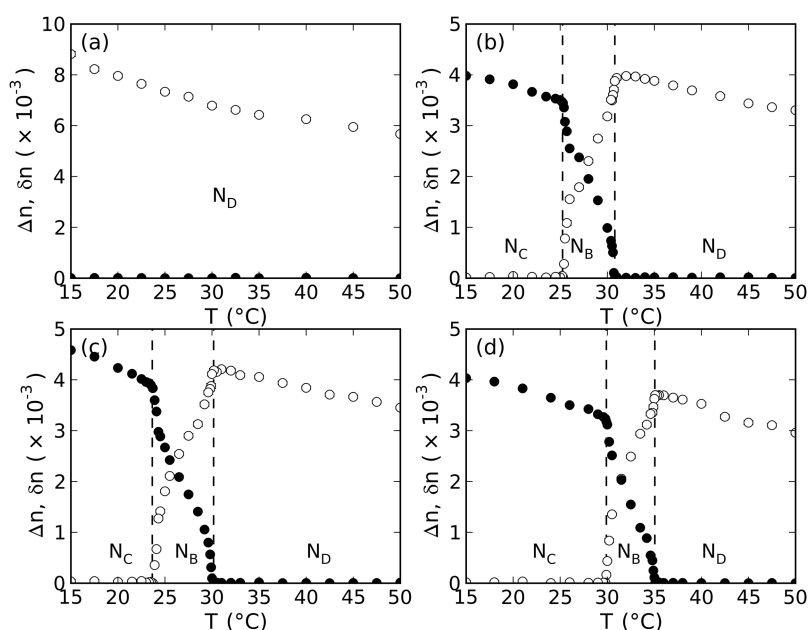


Figure 1. Birefringences as a function of temperature of the mixtures KL/ $M_2\text{SO}_4$ /UndeOH/water with (a) Na_2SO_4 , (b) K_2SO_4 , (c) Rb_2SO_4 and (d) Cs_2SO_4 . (o) and (•) represent δn and Δn , respectively.

The mixtures of SDS/alkali sulfate/DDeOH/water with five different salts presented only the N_D phase. Note that we selected UndeOH and DDeOH as co-surfactant for KL and SDS mixtures, respectively. By this way we kept the ratio of the carbon numbers in the alkyl chain of the surfactants, n_s , to that of the alcohols, n_a , as 1:1 (since KL and UndeOH have 11 carbon atoms in their alkyl chains, SDS and DDeOH have 12 carbon atoms). As reported before, the relation between n_s and n_a is important to have different types of nematic phases.¹⁹ For instance, if a lyotropic mixture presents a nematic phase, in the case of $n_s > n_a$ a N_D phase is most likely to be observed and in the reverse situation, $n_s < n_a$, a N_C phase is more probable.

The ionic radii of the cations from Li^+ to Cs^+ in crystal structure and in the hydrated state are given in Table 2.²¹ Li^+ (Cs^+) has the smallest (biggest) ionic radius in the crystal structure, so, as it is expected, the charge-density of the cations increases following the sequence Cs^+ , Rb^+ , K^+ , Na^+ , Li^+ .²² As is known that a smaller (bigger) cation is surrounded by large (small) number of water molecules, this leads to bigger (smaller) hydration sphere.²³ At this point, it is important to remark that Cs^+ , Rb^+ , and K^+ have about the same hydrated ionic radius.

Table 2. The ionic radius of alkali ions in crystal, r_{cry} , and in the hydrated state, r_{hyd} . (From Ref. [21])

	Li^+	Na^+	K^+	Rb^+	Cs^+
$r_{\text{cry}} / \text{\AA}$	0.59	0.99	1.37	1.52	1.67
$r_{\text{hyd}} / \text{\AA}$	3.40	2.76	2.32	2.28	2.28

In order to understand the role of the cations of the alkali salts it is interesting to consider also the head groups of the main surfactant present in the micelles (in our case, the KL and SDS). In SDS and KL, the head groups are sulfate and carboxylate groups, respectively. For the sake of comparison, if we choose methyl sulfate and acetate to represent the head groups of SDS and KL, ²⁴ respectively (Figure 2), it can be easily seen that the size of sulfate group is larger than that of the acetate group. Since both sulfate and acetate have the same net charge (-1) on their head groups, SDS molecule exhibits lower charge-density on its head group than that of the KL molecule.²⁴ By this way, SDS head group has to be surrounded by less water molecules than KL head group, as a result of different ion-dipole interactions between SDS and water and between KL and water. This situation may be explained via Collins' concept, so-called "matching water affinities". In this framework, ions are classified according to their relative competence to change the structure of surrounding water molecules around them, being (a) cosmotropes (structure makers) and (b) chaotropes (structure breakers).²⁵⁻²⁷ In our case, Li^+ and Na^+ are cosmotropic, and K^+ , Rb^+ and Cs^+ are chaotropic.²⁸ Vlachy et. al. proposed that an alkyl carboxylate and an alkyl sulfate head groups can be classified as a cosmotrope and chaotrope, respectively, similar to the classification of ions.²⁴ In addition, it was stated that there is no effect on the cosmotropic or chaotropic behavior of the head groups if short or long chain alkyl groups are bounded to the head groups.²⁹ This means that both methyl carboxylate (methyl sulfate) and KL (SDS) are cosmotropic (chaotropic).

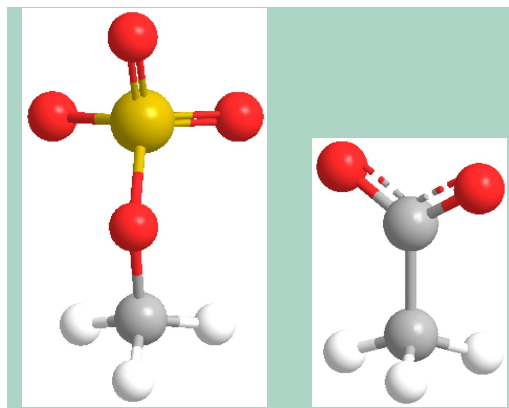


Figure 2. Structures of methyl sulfate (left) and carboxylate (right). The C=O double bond in carboxylate group was shown with dashed line because the bond is delocalized between two oxygen atoms.

As it was reported in the literature, a cosmotropic (chaotropic) ion prefers to be bound to the head group of a cosmotropic (chaotropic) surfactant.²⁴ This implies that cosmotropes (chaotropes) form direct ion pairs with other cosmotropes (chaotropes).^{24, 28} Then, in our case, while Cs^+ is in the closest (farthest) contact with the head group of SDS (KL), Li^+ is highly (loosely) bounded to the head group of KL (SDS).^{24,28,30,31} If we compare the strength of the counterion binding of alkali cations to the carboxylate (i.e. KL) micelles, it decreases following the sequence $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ and, for SDS micelles, the reversed order is observed.^{32,33} The free-energy change upon replacing K^+ ion by Na^+ in a contact ion pair with acetate (-2.50 kcal/mol) and methyl sulfate (+0.37 kcal/mol) revealed that, while acetate ion strongly prefers sodium ion instead the potassium ion, methyl sulfate prefers potassium ion instead the sodium ion.^{24,34,35} Moreover, if two ions, one from the counterion and the other from the head group of surfactant, constitute the closest ion pair, they are less hydrated than their free forms. This situation gives rise to a smaller effective head group area, leading to higher packing parameter and larger object.²⁴ This is, of course, related to the decrease in the repulsion forces between the head groups of the surfactant molecules at the micelle surfaces, as a result of the effect of the closer contact of the cations with the head groups.

Now we may come back to our results. In the KL/alkali salt/UndeOH/water lyotropic mixture, with Cs⁺, Rb⁺ and K⁺, no significant difference on the biaxial phase domain and nematic phase sequence was observed. However, with Na⁺, there was a significant change in the topology of the phase diagram and birefringence of the N_D phase (Figure 1). The mixtures with Cs⁺, Rb⁺ and K⁺ exhibited the three nematic phases, while that with Na⁺ presented only the N_D phase with birefringence values, about ~2 times higher than those with the other cations. This result seems to indicate that Na⁺ ions of Na₂SO₄ were replaced by some amount of K⁺ from the KL. As discussed above, since both Na⁺ and laurate (carboxylate) are cosmotropes, they are in closer contact than K⁺ and laurate, decreasing the repulsion between the head groups of KL at the micelle surface more efficiently than K⁺ (and, of course, Rb⁺ and Cs⁺). Then, it is expected that in KL/Na₂SO₄/UndeOH/water lyotropic mixture the micelles should be more anisometric (or even favor a larger molecular segregation) than in the mixtures with K₂SO₄, Rb₂SO₄ or Cs₂SO₄. This is in accordance with our birefringence results obtained by laser conoscopy. The large value of the birefringence in the N_D phase of the Na₂SO₄ mixture ($\sim 8 \times 10^{-3}$ at 25°C) indicates the existence of more anisometric micelles (or reveals a larger molecular segregation in the micelle).^{15, 18, 19, 36} The reason why we could not obtain nematic phases with Li₂SO₄ may be related to the crystallization process, since Li⁺ highly binds to the head group of KL. This situation was also reported for LiBr in the mixture KL/dodecyltrimethylammonium bromide/alkali bromide/water.³⁷

In order to compare the effect of the Li⁺ ion with respect to other cations, we investigate the SDS/alkali salt/DDeOH/water lyotropic mixtures with all alkali salts from Li₂SO₄ to Cs₂SO₄. All the mixtures of SDS exhibited only N_D phase. The birefringences of these mixtures are shown in Figure 3. As discussed before, the head group of SDS molecule is chaotropic and it forms the closest ion pairs with Cs⁺ (the most chaotropic and the least cosmotropic ion) and the farthest ion pairs with Li⁺ (the least chaotropic and the most cosmotropic ion). Since, SDS prefers K⁺ ion (and of course Rb⁺ and Cs⁺) instead of Na⁺, we could expect that the micelles with K⁺ should be more anisometric (or present a bigger molecular segregation) than those with Na⁺ and Li⁺. This situation may be qualitatively verified analyzing the results on Figure 3. The mixture with Cs₂SO₄ showed the higher birefringence than those with Na₂SO₄ and Li₂SO₄. The mixture with Cs₂SO₄ showed the same effect on the birefringence observed on the N_D phase of the mixtures with Rb₂SO₄ and K₂SO₄. Hendrikx and co-workers³⁸ investigated by using NMR the interactions of alkali metal ions in lyotropic nematic phases, and concluded that (a) Li⁺ behaves differently from Na⁺, K⁺, Rb⁺ and Cs⁺, (b) Na⁺ behaves differently from K⁺, Rb⁺ and Cs⁺, (c) K⁺, Rb⁺ and Cs⁺ behave similarly. Their results fully agree with ours obtained with the laser conoscopy.

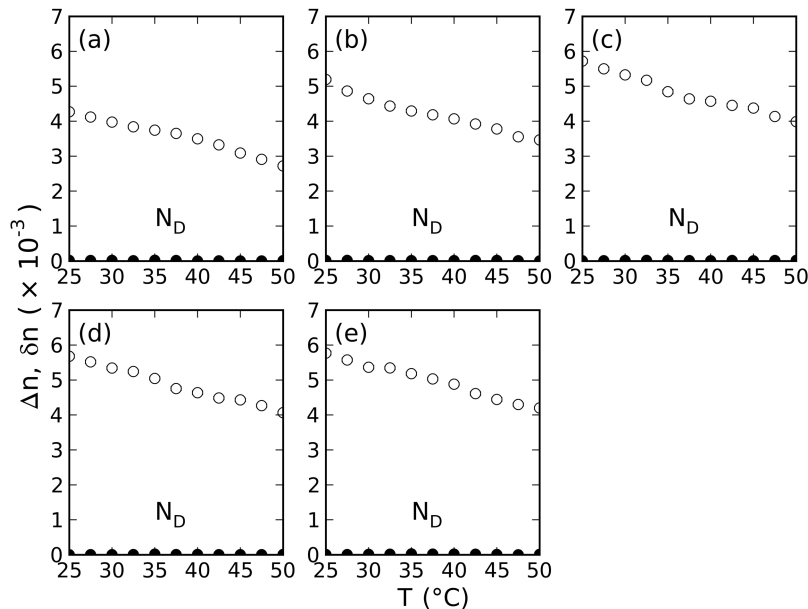


Figure 3. Birefringences as a function of temperature of the mixtures SDS/M₂SO₄/DDeOH/water with (a) Li₂SO₄, (b) Na₂SO₄, (c) K₂SO₄, (d) Rb₂SO₄ and (e) Cs₂SO₄. (○) and (●) represent δn and Δn, respectively.

Figure 4 shows the birefringences of the N_D phases of both KL and SDS mixtures at 45°C (Table 1) and the hydrated radius of alkali salts (Table 2). In the case of the KL mixtures, while the birefringence decreases on going from Na_2SO_4 to Cs_2SO_4 , the reverse situation was observed for SDS system from Li_2SO_4 to Cs_2SO_4 , i.e. the micellar shape anisotropy decreases (increases) in the KL (SDS) system. Going from K_2SO_4 to Cs_2SO_4 , in the KL system, if we compare the birefringences just before the N_C -to- N_B and just after N_B -to- N_D , the N_D phases always have higher birefringences than the N_C phases, Figures 1b-d. In addition, the mixture with Na_2SO_4 exhibited N_D phase having ~ 2 times higher birefringence than others mixtures. These results are in good agreement with those reported before.³⁸ Hendrikx et.al. calculated the axial ratios, $q = b/a$, where b and a are the longest and shortest dimensions of a micelle in the nematic phase, for sodium decyl sulfate (SDS)/1-decanol (DeOH)/water and in KL/DeOH/water lyotropic mixtures, from X-ray and neutron scatterings. They assumed the hypothesis that the micelles in the N_D and N_C phases are discs and cylinders, respectively. Despite the fact that these assumptions are not true, in the framework of the IBM model^{14, 15, 20}, their results of typical dimensions may give a reasonable approximation for the micellar anisotropy. They reported that, in SDS (KL) system, the axial ratios were calculated as 2.8 (2.8) in N_D phase and > 2.3 (1.75) in N_C phase. Consequently, as observed for these two systems, the micellar shape anisotropy in N_C phase should be smaller than that in the N_D phase, similarly to our results obtained from the birefringence measurements.

All our results and the results reported in the literature indicate that, to obtain the biaxial nematic phase, we have to choose a surfactant and electrolyte or counterion of surfactant as follows: (a) if we use a cosmotropic surfactant, the electrolyte or counterion has to have less cosmotope (more chaotrope) behavior, or (b) if we use a chaotropic surfactant, we should prefer the use of less chaotropic (cosmotropic) electrolyte or counterion. Note that these selections are correlated with relatively different interaction between ions and the head groups as pointed out before.

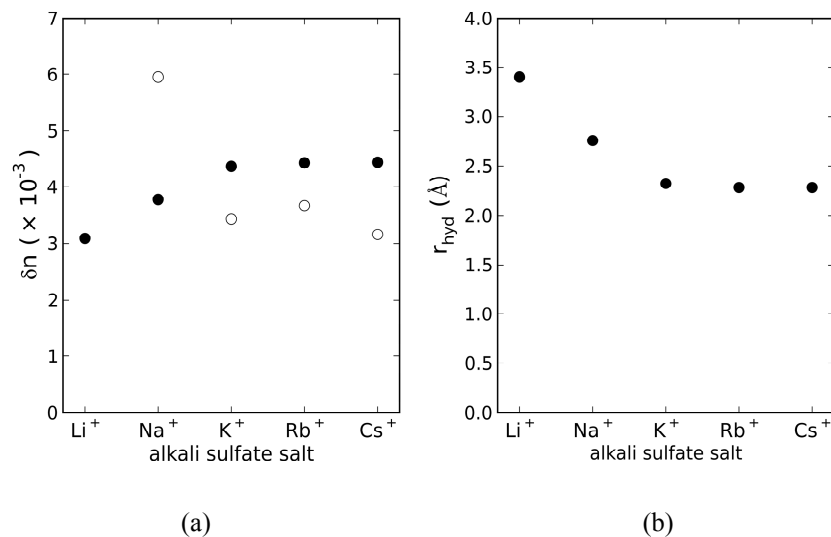


Figure 4. (a) Birefringence δn of the KL/ M_2SO_4 /UndeOH/water mixtures (o) and of the SDS/ M_2SO_4 /DDeOH/water mixtures (●). The birefringences were measured at 45°C (N_D phase); (b) hydrated radius of the cations of the alkali sulfates (●).

Assuming the IBM model, as pointed out before, different orientational fluctuations of the same type (orthorhombic) of micelles in these nematic phases (mixtures with, at least, a surfactant and a co-surfactant) are the driving mechanism for the formation of three nematic phases, two uniaxial N_D and N_C and biaxial N_B . In the case of KL (cosmotropic surfactant), since Na_2SO_4 (more cosmotropic) favors the orientational fluctuations around axis perpendicular to the surfactant double-layer (N_D phase), and K_2SO_4 , Rb_2SO_4 and Cs_2SO_4 (chaotropics) favor the orientational fluctuations along the largest micellar dimension (N_C phase).

4. CONCLUSIONS

The birefringences measurements were performed on two different lyotropic mixtures: (a) KL/alkali sulfate/UndeOH/water and (b) SDS/alkali sulfate/DDeOH/water, with different salts. The former presented, as a function of the temperature, three nematic phases (two uniaxial N_D and N_C and biaxial N_B), with different alkali sulfate salts. The latter presented only the N_D phase with all alkali sulfate salts. According to our results and the results reported in the literature, we concluded that cosmotropic and chaotropic behaviors of both ions and head groups are very important to obtain lyotropic biaxial nematic phase. It was observed that to obtain the biaxial nematic phase, surfactant head group and ion present in lyotropic mixture, have relatively opposite behavior, e.g. one more cosmotropic (more chaotropic) other less cosmotropic (less chaotropic) or vice versa.

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