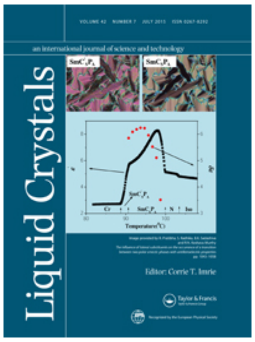

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Effect of Hofmeister anions on the existence of the biaxial nematic phase in lyotropic mixtures of dodecyltrimethylammonium bromide/sodium salt/1-dodecanol/water

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Lyotropic mixtures including different sodium salts of Hofmeister anions were studied in order to investigate the effect of these anions on the existence of biaxial nematic phase and on the uniaxial to biaxial phase transitions. For this purpose, these sodium salts were added singly into different mixtures of dodecyltrimethylammonium bromide (DDTMABr)/1-dodecanol/water, keeping the relative molar concentration of all the constituents constant. The uniaxial to biaxial phase transitions were determined from the temperature dependence of the birefringences by laser conoscopy. Micellar shape anisometry and average micellar volume were evaluated from small-angle X-ray scattering measurements. The results indicated that the Hofmeister anions were bounded to the head groups of DDTMABr molecules at the micelles' surfaces, which significantly affect the different orientational fluctuations responsible for the formation of different nematic phases, biaxial phase domains and uniaxial to biaxial phase transition temperatures.

Keywords: lyotropic liquid crystal; biaxial nematic phase; uniaxial to biaxial nematic phase transition; Hofmeister series; laser conoscopy; small-angle X-ray scattering

Introduction

The biaxial nematic (N_B) phase is a thermodynamically stable phase, identified in lyotropic liquid crystalline mixtures.[1] In phase diagrams its location is mainly between the uniaxial discotic (N_D) and uniaxial calamitic (N_C) nematic phases.[1] Experimental [2] studies have showed that the uniaxial to biaxial phase transitions are of second order, well described by a mean-field Landau-type theory.[3, 4] Furthermore, in the case of a lyotropic mixture with only one surfactant, without a co-surfactant, only uniaxial N_D or uniaxial N_C phases are observed.[5] If there is a co-surfactant in the mixture, there is a possibility to obtain the biaxial nematic phase in addition to other two uniaxial ones,[5–9] depending on the temperature and relative concentrations of the constituents of the lyotropic mixture.

The uniaxial (biaxial) phase present two (three) different values of the principal refractive indices,[5] which are used to define the birefringences $\Delta n = n_y - n_x$ and $\delta n = n_z - n_y$, where x, y and z represent the three orthogonal axes of the reference frame when the phases are aligned (details in the Experimental section). In the case of uniaxial N_D phase, $n_z > n_y = n_x$, leading to $\Delta n = 0$ and $\delta n \neq 0$, respectively.[2] In the uniaxial N_C phase, $n_z = n_y > n_x$, which result that $\delta n = 0$ and $\Delta n \neq 0$.[2] In the biaxial phase domain $\Delta n \neq 0$ and $\delta n \neq 0$.

Recent studies have shown that the choice of components of lyotropic mixtures is a key issue for the stabilisation of both uniaxial and biaxial nematic phases [10,11] and also cholesteric [12] phases. For instance, alcohols having long and straight alkyl chain were used as co-surfactants, and their alkyl chain lengths, n_a, play an important role on the preparation of mixtures that give the nematic phases.[10] Depending on the alkyl chain length of the main surfactant molecule, n_s, present in the lyotropic mixture, if n_a is greater (smaller) than n_s, the N_C (N_D) phase is most probably stabilised.

However, in the literature there is no systematic investigation about the effect of the electrolytes or salts on the formation of the biaxial nematic phase. In this work, we studied the effect of sodium salts with Hofmeister series of anions in the mixture of dodecyltrimethylammonium bromide (DDTMABr)/salt/1-dodecanol/water. The chosen salts were Na_2SO_4, NaF, NaCl, NaBr, $NaNO_3$, NaI and $NaClO_4$. Hofmeister anions of these salts are,

$$SO_4^{2-} > F^- > Cl^- > Br^- \approx NO_3^- > I^- > ClO_4^-,$$

ordered according to their *effective size*, which is defined as a typical dimension of the ion surrounded by a hydration shell.[13]

Using laser conoscopy, small-angle X-ray scattering (SAXS) and polarised light microscopy, the

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*Corresponding author. Email: akpinar_e@ibu.edu.tr different nematic phases and ranges of temperature of phase domains were identified.

Experimental section

Samples

DDTMABr (Sigma, St Louis, MO, USA), 1-dodecanol (Fluka, St Louis, MO, USA), $NaClO_4$ (Sigma), NaI (JT Baker, Deventer, Netherlands), NaBr (Carlo Erba, Milan, Italy), $NaNO_3$ (Merck, Darmstadt, Germany), NaCl (Merck), NaF (Merck) and Na_2SO_4 (Merck) were purchased with purities higher than 99%. DDTMABr was used without further purification. Ultrapure water from a Millipore Direct-Q_3 water purification system was used.

Sample preparation procedure is as follows. Each chemical substance was carefully weighed in glass test tubes. Then, mixing with vortex and centrifuging occasionally at room temperature, without heating, we finely homogenised them. After homogenisation, a small amount of water-based ferrofluid (EMG 605, Ferrotec Corp., Bedford, NH, USA) was added as 1 μL of ferrofluid per 1 g of mixture to improve and speed the alignment of the phases in external magnetic field. Experimental studies [5] proved that this amount of ferrofluid does not modify the topology of the phase diagrams. The compositions of the mixtures are given in Table 1.

Polarised light microscopy

Textures were observed under a Leitz Orthoplan-Pol polarised light microscope, after the samples were transferred into rectangular glass capillary 0.3 μm thick (thickness of the sample). Capillary was sealed after filling. Samples were placed in an INSTEC HS1 device. The sample alignment was achieved by applying a magnetic field of about 300 G in the plane of the microscope stage, perpendicular to the light propagation direction. In the case of samples presenting the anomalous behaviour (see, e.g. [14]), the birefringence was evaluated using the Berek compensator and monochromatic light ($\lambda = 546$ nm).

Laser conoscopy

Laser conoscopy [2] is a reliable technique to measure both birefringences Δn and δn in the three nematic phases N_D, N_B and N_C as a function of temperature. It allows the measurement of birefringence values of about 10^{-4} from the interference fringes formed when a convergent laser beam (linearly polarised) interacts with the sample. For this purpose, lyotropic samples were transferred into a cell made of two optical circular glass plates, separated by a glass O-ring 2.50 mm thick. The cell was placed in a homemade sample holder, which allows precise control of the temperature. It has two stages and is coupled to a Neocera LTC-21 temperature controller, with a precision of 0.01°C and a JulaboF12-MA water circulator (precision of 0.01°C). An expanded and linearly polarised laser beam (HeNe, $\lambda = 632.8$ nm) was used. The laboratory frame of reference axes was chosen as follows: two orthogonal axes x and y define the horizontal plane; z-axis is perpendicular to this plane and parallel to the laser beam propagation direction. A static magnetic field of $H = 3.05$ kG (Walker Sci. electromagnet), parallel to x-axis, aligns the samples. The resulting interference pattern is projected on a screen in the horizontal plane, after the transmitted light interfere in a linear analyser.

The key point in the laser conoscopy technique is to get high-quality interference patterns, which are obtained with well-aligned samples. In the case of the N_C phase, as the director orients parallel to the applied magnetic field, well-aligned samples are easily

Table 1. Compositions of the mixtures DDTMABr/sodium salt/1-dodecanol/water.

Salt	$X_{DDTMABr}$	X_{salt}	X_{DDeOH}	X_{H_2O}	Phase sequence	$T_{N_D-N_B}$ (°C)	$T_{N_B-N_C}$ (°C)	ΔT_{N_B} (°C)
$NaClO_4$	0.0497	0.0032	0.0185	0.9286	N_D	–	–	–
NaI	0.0497	0.0031	0.0185	0.9287	N_B, N_D	14.75	–[a]	2.75
NaBr[b]	0.0497	0.0032	0.0185	0.9286	N_C, N_B, N_D	19.85	13.45	6.40
$NaNO_3$	0.0497	0.0032	0.0185	0.9286	N_C, N_B, N_D	19.95	14.75	5.20
NaCl	0.0497	0.0032	0.0185	0.9286	N_C, N_B, N_D	25.85	23.60	2.25
NaF	0.0497	0.0032	0.0185	0.9286	N_C, N_B, N_D	29.55	27.20	2.35
Na_2SO_4[c]	0.0497	0.0032	0.0185	0.9286	N_C, N_B, N_D	31.15	28.60	2.55
–	0.0498	–	0.0186	0.9316	N_C	–	–	–

Notes: Phase sequences correspond to the observed phases (from left to right, the temperature was increased), X is the mole fraction of each constituent and ΔT_{N_B} represents the temperature range of the biaxial nematic phase domain.

[a] Below 12°C, the sample started to freeze.

[b] From [14].

[c] Since this salt consists of two Na^+ ions and its anion has the charge 2^-, its mole number was multiplied by the factor 2 in the calculations.

obtained. The alignment process in both N_D and N_B phases is a crucial aspect. For this purpose, the samples were rotated about an angle of ±30° several times around the *z*-axis in the N_D and N_B phases, in the presence of the magnetic field (see [5] for details). Then, when going from N_D to N_C phase, the measurement of the birefringences was performed as a function of temperature.

Small-angle X-ray scattering

These experiments were made in a Xenocs Xeuss apparatus, with a GeniX X-ray beam delivery system, with Cu anode microfocus X-ray source ($\lambda = 0.15411$nm). The collimation system, made by two scatterless slits, delivers a beam of square cross-section (0.8×0.8 mm^2) at the sample position. A Pilatus 300 K 20 Hz detector from Dectris registers the two-dimensional patterns. The lyotropic samples were placed in cylindrical glass capillaries (1.5 mm diameter). The capillaries are sealed and placed in homemade sample holders coupled to a water circulation system, which is used to control the temperature of the samples (precision 0.1°C). A magnetic field of about 1 kG (perpendicular to the X-ray beam, from permanent magnets) is applied in the sample illuminated by the X-ray beam. Each nematic phase was aligned according to the same procedure described in the conoscopy experiment. The laboratory frame is defined with axis 3 parallel to the capillary long axis, along the vertical direction; axis 1 is parallel to the magnetic field direction, and axis 2 is perpendicular to both (along the X-ray beam). In the case of the N_B phase, two patterns in different orientations of the capillary (rotation of the capillary around its principal axis by 90°) were obtained, one with the field applied and other without the field (since one of the directors aligns parallel to the field). The typical exposure time was 1200s. Ultrapure water (Millipore Direct-Q_3 system) was used as background for subtraction.

Results and discussion

Hofmeister anions in micellar systems

Let us first discuss the role of electrolytes or salts in micellar systems. Israelachvili [15] proposed that if an electrolyte is added to isotropic micellar solutions, the micelles grow as a result of screening of the repulsions between the head groups at the micelle surface. Similar results were reported by Holmes et al. [16] and Leaver et al. [17] for cesium perfluorooctanote (CsPFO)/water system, which exhibited a lyotropic nematic phase at certain temperature range. They showed that the micelles of the nematic phase of CsPFO/water mixture grow by the addition of cesium chloride (CsCl) into this mixture.

Micellar systems consist of micelles in thermodynamical equilibrium with an ionic bath.[18] The characteristic intermicellar distance is achieved by the competition between the different forces acting on micelles. Since the polar heads of the main amphiphile of the micelle are ionised, an electrical layer formed by counterions exists around the micelles. This fact gives rise to a Coulombian interaction between micelles, mediated by the overlap of the electrical double layers of them. When ions are added to a micellar solution, their role may be explained by two mechanisms, which were stated by Sein et al. [19]: (1) dehydration of the head groups of the amphiphiles and (2) reduction of the repulsive interactions between the head groups at the micelle surfaces and, consequently, between the charged micelles.

In the case of mechanism (1), since the added ions have high tendency of hydration by the free water, this results in the lower hydration of the head groups of the surfactant molecules.[20] Smaller hydration layers lead to, as expected, a decrease of the Debye length at the surface of the micelles.[21] This effect may be understood inspecting the values of the hydration enthalpy, $\Delta_{\text{hyd}}H°$ [22], and Gibbs free energy of hydration, $\Delta_{\text{hyd}}G°$ [23], given in the literature, and reproduced in Table 2.

The thermodynamic functions of hydration of Hofmeister anions indicate that, from SO_4^{2-} to ClO_4^-, the hydration of these anions by free water molecules decreases. This phenomenon leads to the classification of ions and surfactant head groups as being kosmotrope or chaotrope, which informs about their water-matching affinities.[25,26] Small ions have relatively high surface-charge density, which implies in the existence of high local electric field in their surroundings.[27] Therefore, as expected, small ions with high surface-charge density exhibit high tendency to be hydrated by a large amount of free water molecules (water-structuring ions [28]). These ions are named kosmotropes. On the other hands, large ions show opposite behaviour with respect to small ions, that is, they are less hydrated (water-destructuring or breaking ions) and are named chaotropes.[28]

Experimental studies obtained from SAXS [29] indicated that these kosmotrope and chaotrope properties of ions or surfactant head groups are very important on the different packing of surfactant head groups at the micelle surfaces, which affects the micellar shape and shape anisotropy. In addition, it was reported that the kosmotrope (chaotrope) head groups from amphiphiles present higher affinity with kosmotrope (chaotrope) counterions at the micelle

Table 2. Thermodynamic functions of hydration of Hofmeister anions reproduced from the literature.

	SO_4^{2-}	F^-	Cl^-	NO_3^-	Br^-	I^-	CIO_4^-
$\Delta_{hyd}H^o$ (kJmol^{-1})	−1035	−510	−367	−312	−336	−291	−246
$\Delta_{hyd}G^o$ (kJmol^{-1})	−1145	−345	−270	−275	−250	−220	−180
r_{hyd} (nm)	0.273	0.212	0.224	0.223	0.231	0.246	0.261
ρ (mCm^{-2})	481.62	720.16	388.84	397.58	331.60	263.20	203.82

Notes: $\Delta_{hyd}H^o$is the hydration enthalpy,[22] $\Delta_{hyd}G^o$ is the Gibbs free energy of hydration,[23] r_{hyd} is the hydrodynamic radius,[24] ρ is the surface charge density.[24]

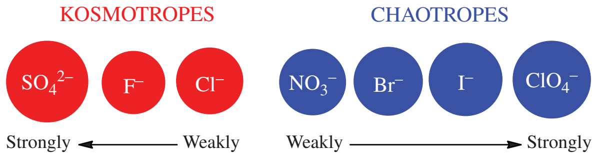

Figure 1. (colour online) The schematic representation of the relative sizes of hydrated ions, taking into account the hydrodynamic radius from Table 2. Arrows indicate the increase in the kosmotrope (chaotrope) nature of the ions from weak to strong.[31]

surfaces.[30] Taking into account the hydrodynamic radius (r_{hyd}) and the sequence of the Hofmeister anions, their relative kosmotrope and chaotrope natures are summarised in Figure 1.

In the case of mechanism (2), the counterions and/or ions from the salt added to the mixture are located in the region between the charged head groups, decreasing the electrostatic repulsions between the head groups. This causes the decrease in the effective head group size.[20] In other words, the salt added imposes a screening effect in the intramicellar interaction at the micelle surfaces, which favours the micellar growth [15] similar to the mechanism described in case (1).

From the intermicellar interactions point of view, the added salt affects the intermicellar interactions by screening the Coulombian repulsions existing between the micelles,[32,33] leading to micellar growth.[15,20] This screening behaviour was also observed in lyotropic chromonic liquid crystals. For instance, Park et al. [34] reported that mono- and divalent salts had significant effect on screening the repulsions within and between the aggregates in a lyotropic chromonic nematic phase.

In our present study we kept the molar concentrations of all the components of the lyotropic mixtures constant and studied different Hofmeister anions on the uniaxial-to-biaxial phase transitions. DDTMABr was chosen as a chaotropic surfactant [35] due to its large trimethylammonium head group. Among the selected Hofmeister anions (Table 2), when going from the less chaotropic (the more kosmotropic, SO_4^{2-}) to the more chaotropic (the less kosmotropic CIO_4^-), the SO_4^{2-} ion tends to remain, mainly, in the intermicellar aqueous region with respect to the micellar surface region. This means that the SO_4^{2-} ion is weakly bounded to the surfactant head groups at the micelle surface compared to other ions of the series.

Figure 2 shows the measurements of the optical birefringences as a function of temperature for different quaternary mixtures, from the more chaotropic ion CIO_4^-, to the less chaotropic one SO_4^{2-} (i.e. more kosmotrope) of the Hofmeister series and also for ternary mixture without any salt. The ternary mixture of DDTMABr/1-dodecanol/water exhibited only calamitic nematic phase in the temperature range from 15 to 42°C. Two biphasic regions were observed below 15°C (N_C and crystalline phase) and above 42°C (N_C and isotropic phase) (see Figure 2h). Let us investigate now the effect of adding a salt from the Hofmeister series to the ternary mixture. Chaotrope anions are mainly located at the micelle surface, leading to the micelle growth more efficiently than the kosmotrope ones. On the other hand, kosmotrope anions are located, mainly, in the intermicellar region, decreasing the Debye length of the system. The role of Hofmeister anions can be understood inspecting the salting-in/salting-out behaviour of electrolytes, since there is a direct relation between salting-in (salting-out) and the chaotropic (kosmotropic) behaviour.[36–39] Salting-in electrolytes tend to be less hydrated by free water existing in the intermicellar region. They are adsorbed at the micelle surfaces (interfacial region) instead of being in the intermicellar region. Salting-in electrolytes screen the Coulombic repulsions between the head groups of the surfactant molecules [40,41], giving rise to the closer packing of these molecules.[19,42] Then, the surface area per surfactant molecule head decreases and the local micellar curvature also decreases. This effect increases the micellar surface, which leads to the formation of discotic nematic phases, as we observed in this study. This situation was also reported for isotropic micellar solutions [42]: the addition of salting-in electrolytes in isotropic solutions composed of spherical micelles induces the transformation of spherical micelles to cylindrical

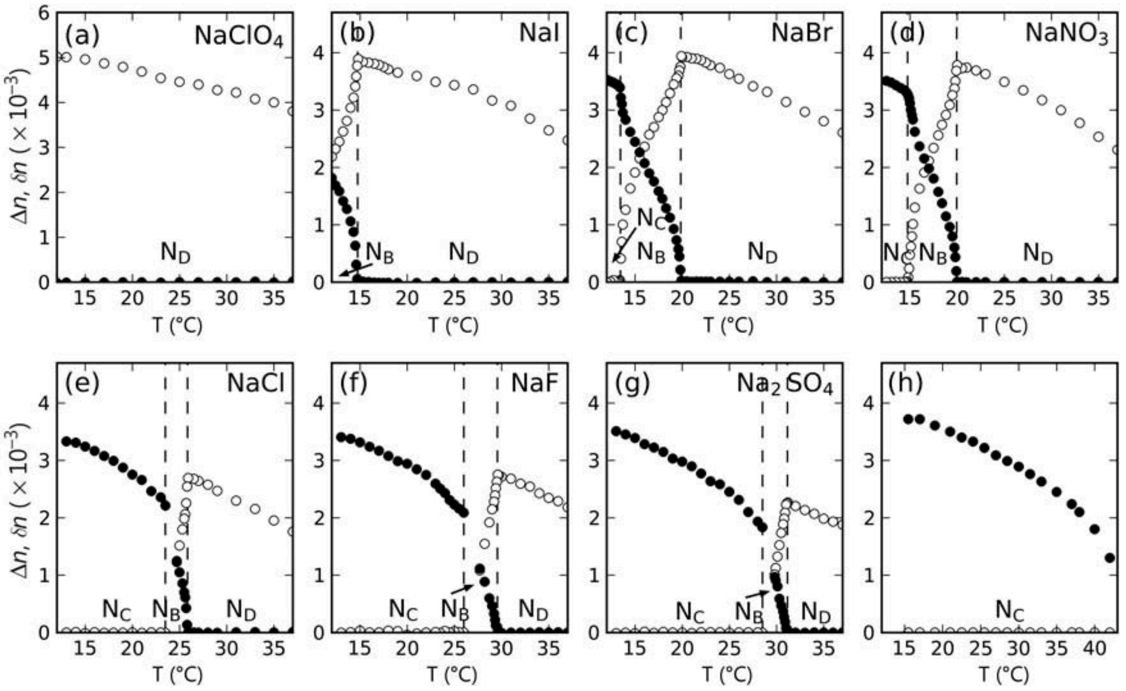

Figure 2. Birefringences Δn (•) and δn (◦) as a function of temperature in the nematic phases of (a–g) quaternary mixtures of DDTMABr/sodium salt/1-dodecanol/water with different anions of the Hofmeister series; and of (h) ternary mixture of DDTMABr/1-dodecanol/water.

micelles. The opposite behaviour is observed for salting-out electrolytes. These ions tend to be located, mainly, in the intermicellar region, decreasing the electrostatic interactions between neighbouring micelles. This effect also decreases the Debye length of the system.[43–45] The charged head groups of the surfactant molecules at the micelle surface are not fully screened, leading to an increase of the local curvature of the micellar surface. This effect gives rise to the appearance of the calamitic and biaxial nematic phases.

Let us now investigate the effect of all Hofmeister anions, comparing the birefringences at the N_D–N_B phase transitions. The maximum value of the birefringence in the N_D phase decreased to ~2.5 × 10^{-3} for the kosmotrope ions Cl^-, F^- and SO_4^{2-} with respect to those values for the chaotropic ions Br^-, I^-, NO_3^- and ClO_4^-,, whose values were about 4 × 10^{-3} and 5 × 10^{-3}. As previously reported,[9,10] the higher (smaller) the birefringence the higher (smaller) micellar shape anisotropy. In this framework chaotropic ions (Figure 2(a)–(d)) lead to the formation of micelles with bigger shape anisotropy compared with those from kosmotrope ions (Figure 2(e)–(g)).

Let us focus now on the biaxial phase domain for the different mixtures. In the case of chaotropic ions Br^-, NO_3^-, I^- and ClO_4^-,, both birefringences were measured in the N_B phase, indicating that the alignment process to get a well-oriented nematic sample worked perfectly (2(a)–(d)). However, in the case of the mixtures with Cl^-, F^- and SO_4^{2-} ions, Figure 2(e)–(g), the samples completely lost the alignment in the N_B^- to N_B^+ crossover. A similar behaviour was observed before in mixtures of DDTMABr/sodium bromide/1-dodecanol/water.[14] There, we attributed this phenomenon, named *anomalous behaviour*, to the presence of micelles with small shape anisotropy, fact that leads to smaller values of the anisotropy of diamagnetic susceptibility of the phase. Present results clearly show that the *anomalous behaviour* depends not only on the main amphiphilic molecule concentration [14] but also on the type of the salt present in the lyotropic mixture. We may argue that kosmotropic ions weakly bounded to the surfactant head group cause the decrease in the micellar shape anisotropy. To check this hypothesis SAXS experiments were performed in aligned nematic phases of the different mixtures.

The SAXS measurements with well-aligned samples in the nematic phases (for details about the data treatment, see [46]) allowed the determination of the characteristic distances s_i^{-1}, i = 1, 2 and 3 along the three orthogonal axis of the laboratory frame, where $s = (2\sin\theta)/\lambda$ is the scattering vector modulus, 2θ is the scattering angle and λ the X-ray wavelength. Assuming the Intrinsic Biaxial Micelle (IBM) model

Table 3. The small-angle X-ray scattering data: repeating distances along the three orthogonal laboratory frame axis (1, 2, 3), available micellar volume and anisotropy parameters for the lyotropic mixtures with different Hofmeister ions.

Hofmeister ion	s_1^{-1} (Å)	s_2^{-1} (Å)	s_3^{-1} (Å)	s_1^{-1}/s_3^{-1}	s_2^{-1}/s_3^{-1}	V (nm^3)
ClO_4^-	74.8 ± 3.6	64.8 ± 2.7	43.6 ± 0.6	1.71 ± 0.09	1.48 ± 0.06	211 ± 14
I^-	69.0 ± 2.3	58.7 ± 2.7	43.6 ± 0.6	1.58 ± 0.06	1.35 ± 0.07	177 ± 10
Br^-	66.5 ± 3.5	56.1 ± 5.0	43.6 ± 1.2	1.52 ± 0.09	1.29 ± 0.12	163 ± 17
NO_3^-	69.8 ± 3.9	53.5 ± 2.3	43.6 ± 0.9	1.60 ± 0.09	1.23 ± 0.06	163 ± 12
Cl^-	62.8 ± 3.8	49.5 ± 2.3	43.3 ± 0.6	1.45 ± 0.09	1.14 ± 0.06	135 ± 10
F^-	67.6 ± 3.6	47.9 ± 1.5	43.3 ± 0.6	1.56 ± 0.09	1.11 ± 0.04	140 ± 9
SO_4^{2-}	61.6 ± 4.2	45.1 ± 1.6	43.0 ± 0.9	1.43 ± 0.10	1.05 ± 0.04	120 ± 10

[5], micelles have an orthorhombic symmetry in the three nematic phases. The alignment procedure of the N_B phase in the presence of the external magnetic field is such that the plane of the main amphiphilic bilayer of the micelles lays perpendicular to 3-axis. As discussed in the experimental section, X-ray beam may be aligned parallel to axis 1 or 2. The available volume per micelle $V = s_1^{-1}s_2^{-1}s_3^{-1}$ [46], and anisometry (i.e., shape anisotropy) parameters (s_1^{-1}/s_3^{-1}) and (s_1^{-1}/s_3^{-1}) are given in Table 3. The Hofmeister ion sequence shows an interesting effect in the available volume per micelle: it decreases when going from ClO_4^-, to NO_3^- in the chaotrope series and remains almost constant in the kosmotrope series (Figure 3). Moreover, the anisometry parameters follow the same behaviour of the available volume with respect to the Hofmeister ion series (see Figure 4). In particular, the anisometry parameters reach the smallest values in the kosmotrope series, supporting the hypothesis that in the case of micelles with small anisometries the *anomalous behaviour* would be expected. As expected, the values of s_3^{-1} are constant for all the mixtures, within the experimental error, since the main amphiphile bilayer dimension determines it. It is reasonable to assume that water covers equally the micelles, and under this assumption, the analysis of the dimensions and symmetry of the available

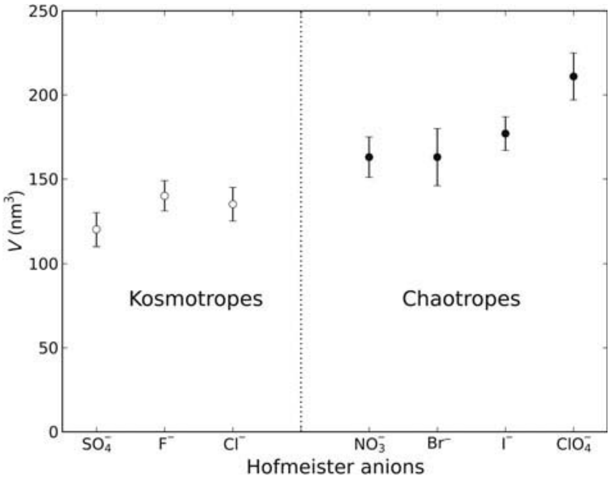

Figure 3. Available volume per micelle for the samples described in Table 1.

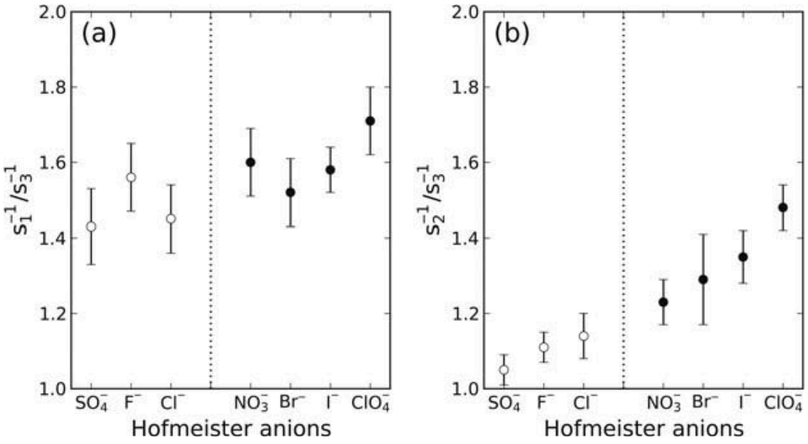

Figure 4. Anisotropies for the samples described in Table 1. (a) s_1^{-1}/s_3^{-1}; (b) s_2^{-1}/s_3^{-1}.

volume per micelle gives a good picture of the micelle itself.

For the mixture with ion ClO_4^-, , highly bound to the DDTMABr head group, $s_1^{-1} \sim s_2^{-1} > s_3^{-1}$ and, according to the IBM model, this micellar anisometry favours the orientational fluctuations responsible for the formation of the N_D phase. In particular, in this mixture we obtained the largest values of $s_{1,2}^{-1}$ with respect to s_3^{-1}, , which is consistent with the highest values of the birefringence in the N_D phase ~ 5×10^{-3}. In the chaotrope series, Br^- and NO_3^- presented similar behaviours with respect to the birefringences, range of temperature of the biaxial phase, uniaxial-to-biaxial phase transition temperatures and structural parameters. These results are consistent with the fact that these ions present similar chaotropic properties.[13] The effect of the salt addition when going from ClO_4^-, to NO_3^- ions is to increase the temperature domains of the N_C and N_B phases. The effect of the ClO_4^-, ions, tightly bounded to the main amphiphile head group, tends to increase the micellar dimensions in the plane perpendicular to the bilayer thickness, favouring the orientational fluctuations that give rise to the N_D phase. The higher chaotropic behaviour of the ion in the Hofmeister series leads to larger N_D phase temperature domain.

In the kosmotrope series, all the ions show similar effects on the phase sequence and temperature range of the nematic biaxial phase. The higher the kosmotropic behaviour of the ion results in larger temperature domains of the N_C and N_B phases.

Comparing the phase sequence and temperature phase domains of mixtures with ions in the chaotrope and kosmotrope series, we see that, if the ions are strongly bounded to the micelle surfaces, the N_D phase domain is favoured. On the other hand, if they are weakly bounded to the micelle surfaces, the N_B and/or N_C phases tend to be stabilised. This result suggests that not only the ions and counterions located in the intermicellar medium but also those bounded to the micelle surfaces play important role in the stabilisation of the nematic phases.

Now we can summarise the role of Hofmeister anions on the nematic phase sequence of the DDTMABr/salt/1-dodecanol/water mixture. When going from ClO_4^-, (Figure 2(a)) to SO_4^{2-} (Figure 2(g)): since ClO_4^-, is the most chaotropic ion, it is more efficiently bounded to micelle surfaces with respect to the other ions of the series. This leads to a decrease of the repulsions between the head groups, which favour the micelles growth in the plane perpendicular to the main amphiphilic bilayer, which is kept with a fixed thickness. This growth will favour the orientational fluctuations of the micelles that give rise to the N_D phase. The mixture with ClO_4^-, exhibited the biggest birefringence value (~5×10^{-3} in N_D phase), which reveals the presence of micelles with large anisometry. Replacing the ClO_4^-, ion with I^- ion, a biaxial phase region appeared and the maximum birefringences value in the N_D phase decreased from 5×10^{-3} to ~4×10^{-3}. The I^- ions are less chaotropic than ClO_4^-, and I^- ions cannot be bounded to the highly chaotropic trimethylammonium head groups at the micelles surfaces as efficiently as ClO_4^- ions. In the cases of the Br^- and NO_3^-, ions, the mixtures investigated exhibited three nematic phases, and their maximum birefringences values were similar to that of I^- ion. Moving now from the Br^- to Cl^- (the weakly kosmotropic anion), the maximum birefringence value in the N_D phase decreases to ~2.5×10^{-3}. This means that Cl^- ions cannot be strongly bounded to the chaotropic trimethylammonium head groups like Br^-, and will be preferentially placed in the intermicellar medium. The other kosmotropic ions, F^- and SO_4^{2-}, also exhibited similar behaviour in terms of the birefringences and temperature range of the biaxial phase. The anisometry of the micelles is smaller in these mixtures, leading to the appearance of the *anomalous behaviour* in the biaxial phase.

Conclusions

We studied the effect of some Hofmeister series anions on the existence of the lyotropic biaxial nematic phase, biaxial nematic phase domains and uniaxial-to-biaxial nematic phase domains in the mixture of DDTMABr/sodium salt/1-dodecanol/water. In this series studied, from the highest chaotrope (ClO_4^-,) to the least chaotrope (i.e. the highest kosmotrope, SO_4^{2-}), it was observed that these anions have significant impacts as follows: (1) the orientational fluctuations that favour the formation of N_C (N_D) phase were more (less) dominant, (2) the uniaxial-to-biaxial phase transitions shifted to the higher temperatures, (3) the biaxial phase domain got, in general manner, smaller, (4) the birefringence values decreased, which was supported by the SAXS data (micellar shape anisometry and the average micelle volumes). In addition, we observed that some mixtures gave the anomalous behaviour in the crossover N_{B+}–N_{B-} as it was reported in our previous study. This indicated that the appearance of the *anomalous behaviour* in the biaxial phase domain is related not only to the main amphiphilic molecule concentration but also to the type of the salt present in the lyotropic mixture.

All results were interpreted as a result of the importance of the location of the ions bounded to the head groups of the amphiphilic molecules at the micelle surfaces. If any counterion (here, Hofmeister anions) is tightly (weakly) bounded to the amphiphile head groups (here, TMA^+), it gives rise to the formation of the N_D (N_C) phase.

Disclosure statement

No potential conflict of interest was reported by the authors.

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