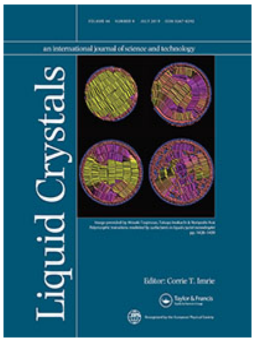

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Re-entrant direct hexagonal phases in a lyotropic system of surfactant induced by an ionic liquid

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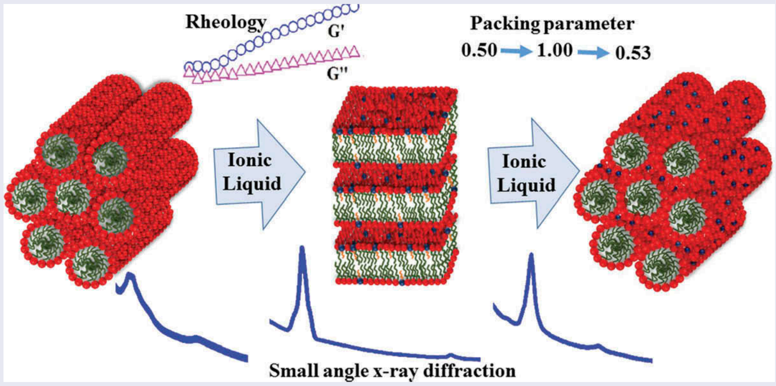
ABSTRACT

In the present study, an ionic liquid (IL), known as green solvent, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF_4) with four carbons in the hydrophobic chain (C-4) has been used as an additive to modify the self-assembled aggregates of an anionic surfactant sodium dodecyl sulfate (SDS) and then the evolution of the liquid crystalline phases has been investigated. Small angle synchrotron x-ray diffraction study has revealed an unprecedented phase sequence where a hexagonal phase (H_I) of direct cylindrical micelles is observed to evolve to another hexagonal phase (H_{II}) of, again, direct cylindrical micelles with a lamellar phase (L_α) as the intermediate. The rheological data and the theoretical calculations have confirmed the phases. To understand such a phase behaviour of the system, the work is extended by considering the ionic liquids with the same head group but of shorter (C-2) and longer (C-10) hydrocarbon chains compared to BMIM-BF4. While the shorter chain IL causes the hexagonal phase to form rectangular (R) phase, the longer chain is observed to induce the lamellar phase (L_α). The molecular mechanism of appearance of such different phases has been discussed.



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Introduction

Surfactants are the major ingredients of laundry and cleaning products and, thus, these are used in the household. They are also used in pharmaceutical, cosmetic and food industry as emulsifiers, in the plastic industry as wetting agents, plasticizers, and foaming agents [1,2]. Because of the vast applications along with their interesting physiochemical behaviour in solutions, both the academic and industrial research communities have paid considerable attention to these systems over decades. In addition, surfactants have significant importance in biological research as they are extensively used in mimicking the cellular membrane, protein crystallization and protein preservation [3,4]. They are also used as nano-reactors for enzymatic reaction and synthesizing of nanoparticles [5,6]. The extensive applications of surfactants in various fields are mainly due to their unique properties in aqueous solution. These molecules usually form various mesoscopic structures in the solution including spherical and cylindrical micelles. They also form vesicles depending on the shape and size of the molecules and the interactions among themselves. Moreover, depending upon a specific application, the

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property of a surfactant in solution can be altered by controlling the physical conditions, such as temperature, or by adding suitable chemical reagents into the solution [7,8]. Various co-surfactants, organic solvents and electrolytes have been employed to tune the inter-surfactant interactions to form desirable mesoscopic structures towards achieving the intended properties of the system [9,10].

Recently, ionic liquids (ILs) are considered as better additives over the conventional organic solvents because of their various striking features. These IL molecules are nonexplosive, nonflammable and have high thermal stability and good ionic conductivity. More importantly, they are environmentlly benign [11]. In addition, ILs are in a liquid state [12,13] and have a negligible vapour pressure at room temperature which inhibits evaporation into the open atmosphere and allows simple recycling and reuses [14]. Miskolczy et al. have shown in their pioneer work that the imidazole-based ionic liquids possessing n-octyl moiety in the anion and 1-butyl-3-methylimidazolium octyl sulfate behave as a surfactant and form micelle above the critical micellar concentration (CMC). Whereas, 1-methyl-3-octylimidazolium chloride produced an inhomogeneous solution of larger aggregates in aqueous solution through self-assembly [15]. Moreover, they demonstrated that these ionic liquids can be used to modify the properties of the conventional micelles, in a controlled fashion. The small amount (<10 mM) of ionic liquids could markedly reduce the polarity of the Stern layer of sodium dodecyl sulfate (SDS) micelle. Addition of low concentration of an ionic liquid 1-butyl-3-methylimidazolium tetra fluoroborate (BMIM-BF_4) into the aqueous solution of SDS has shown to decrease the critical micellar concentration (CMC) of SDS while it increases the aggregation number and micellar size [16]. The long-chain imidazolium IL, 1-dodecyl-3-methylimidazolium bromide, is reported to alter the geometric packing and charge density of SDS in an aqueous aggregate [17]. In contrast, Pal et al. have shown the increase of CMC upon addition of 3-methyl-1-pentylimidazolium hexafluorophosphate in an aqueous solution of SDS [18]. Formation of thermodynamically stable vesicles in the solution of a pure cationic double tail surfactant (didodecyldimethylammonium bromide) in a protic IL (ethyl ammonium nitrate) has also been reported in the literature [19]. However, all these previous investigations, mentioned above, are confined to a low concentration of surfactant in water (≤5 weight %), in which the individual self-assembled aggregates are distributed isotropically. There are very few reports on the effects of ILs on the hierarchical lyotropic liquid crystalline (LLC) phases formed by these surfactant aggregates [20]. Understanding the structural evolution in LLC system is extremely important as it decides the complex rheological behaviour of the system, which is one of the main interests of the soft matter industry. Along with the effect of intermolecular interactions, ILs can influence the interaction among the self-assembled aggregates and can exhibit modified LLC structures formed by these surfactant aggregates.

Among others, the most known structures of lyotropic liquid crystalline phases are the hexagonal phase formed by cylindrical micelles with positive interfacial curvature and the lamellar phase of flat bilayers with zero interfacial curvature [21,22]. In aqueous solutions of surfactants, the transition among these phases is reported as a function of surfactant concentrations [23,24]. In these cases, the interfacial curvatures are modified by adding more surfactants in the binary mixtures of surfactant and water. Instead of changing the surfactant concentrations, the local curvature of an aggregate can be changed by tuning the electrostatic interactions among the surfactant molecules. In the present study, imidazolium-based ionic liquids with a different number of carbon atoms in their single hydrocarbon chains were used as the third component in the solution of water and the anionic surfactant SDS. At a fixed concentration of total non-aqueous components (SDS and IL) in water, the molar ratio of these components was changed which, effectively, altered the electrostatic interactions between the surfactant aggregates. As a result, the local curvature is expected to be modified, and correspondingly, the structure of the lyotropic hexagonal liquid crystalline phases are likely to be altered.

The small angle synchrotron x-ray diffraction study has indicated the changes in the pristine hexagonal phase, formed by cylindrical micelles of SDS in aqueous solution, due to the addition of the ILs. The rheological studies have shed lights on how these phases differ in their viscoelastic behaviour. Finally, the packing parameters, calculated for these phases, have explained the structure of self-assembled aggregates that formed these phases.

Experiment

Materials

The surfactant sodium dodecyl sulfate (SDS) (purity 99%), and the ionic liquids (ILs) 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF4), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF_4) and 1-decyl-3-methylimidazolium tetrafluoroborate (DMIM-BF_4) (purity 98%) were purchased from Sigma-Aldrich (USA) and were used without any purification. The molecular structures of all these chemicals are shown in Figure 1. To prepare solutions, an appropriate amount of de-ionized water (Millipore, 18 MΩ cm) was added to the mixture of an ionic liquid (IL) and SDS was taken in a glass vial. The total surfactant weight fraction (φ = (SDS + IL)/(SDS + IL + water) was kept

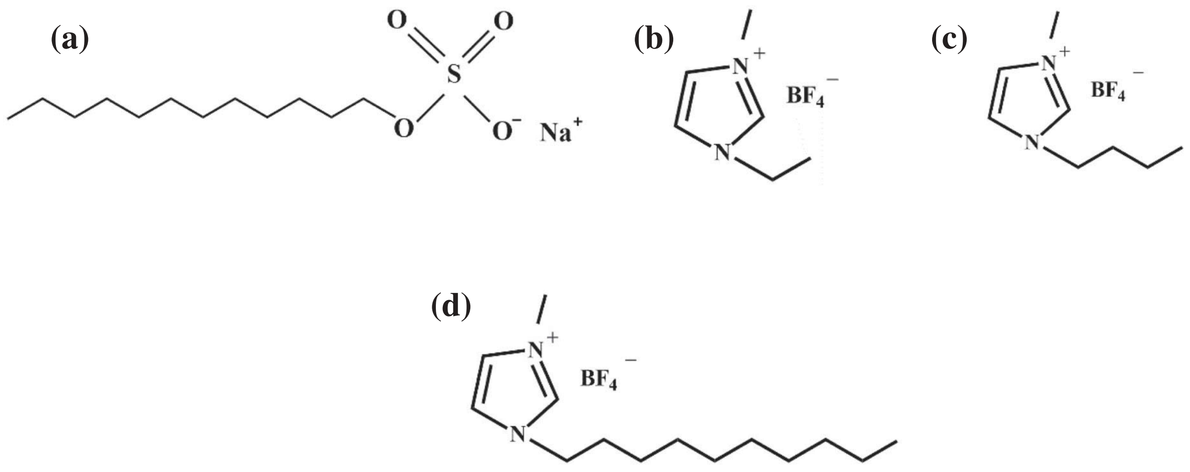

Figure 1. Chemical structure of (a) sodium dodecyl sulfate (SDS), (b) 1-ethyl-3-methylimidazolium tetrafluroborate (EMIM-BF4), (c) 1-butyl-3-methylimidazolium tetrafluroborate (BMIM-BF4) and (d) 1-decyl-3-methylimidazolium tetrafluroborate (DMIM-BF4).

constant (0.4) and IL to SDS molar ratio (α = [IL]/[SDS]) was varied. To attain equilibrium, the prepared solution was kept in an oven at 50°C for one week. For the production of uniform and homogeneous mixture, the solution was then vortexed and stored at the same temperature for another week.

Polarizing optical microscopy

For the microscopy, samples were placed in between a glass slide and a coverslip. To achieve a constant temperature of 30°C, these samples were placed in a hot-stage (Linkam, LTS120, UK) attached to a polarizing microscope (Nikon H 600L, Japan).

Small angle X-ray diffraction

Small angle x-ray diffraction measurements were performed at the Indian Beamline (BL-18B), Photon Factory, Tsukuba, Japan with the x-ray photons of wavelength 0.855Å. For these measurements, the samples were filled in glass capillaries (Hampton Research, USA, 1.5 mm diameter) and further flame sealed. The scattered photons from the sample solutions were collected at a fixed temperature of 30°C by a 100K Pilatus detector placed at 350 mm away from the sample cell. The typical exposure time was 100 s. DPDAK software was used to extract the diffraction data.

Rheology

A stress-controlled rheometer (MCR 501, Anton Paar) was used for rheological measurements with a sample cell of cone-plate geometry (cone diameter 50 mm, cone angle 0.5° and true gap 49 μm). To obtain the linear viscoelastic regime, the storage (G') and loss (G'') moduli were measured as a function of strain amplitude. After establishing the linear viscoelastic regime, the frequency sweep measurements were performed over four orders of magnitude of angular frequency (ω) (0.05–500 s^{-1}). The sample temperature was maintained at 30°C by a constant flow of water from a bath (JULABO GmbH, Germany).

Results

Polarizing optical microscopy

The polarizing optical microscope is the fundamental tool used to check the existence of crystalline phases in the sample of birefringent materials. The different textures in the surfactant solution in the presence of the medium chain length IL (C-4) BMIM-BF4 were investigated at a fixed value of φ = 0.4 and T = 30°C with varying values of α. For α = 0, the characteristic texture of the hexagonal phase is observed [24,25]. For intermediate values of α (0.05–0.1), the oily streak textures are seen [25], which indicates the presence of lamellar phase in the sample. For higher values of α, the texture is found to be different from that of low and intermediate values of α. In the case of low chain length IL (C-2) EMIM-BF4, at low values of α, the texture of the hexagonal phase was observed, while at higher values of α, a distinct texture was observed. For the long chain IL (C-10) DMIM-BF4, the textures of hexagonal and lamellar phases were seen at low and high values of α, respectively. The representative textures of different phases observed in these systems are shown in Figure 2. It is quite hard to conclude the exact structures of the phases from

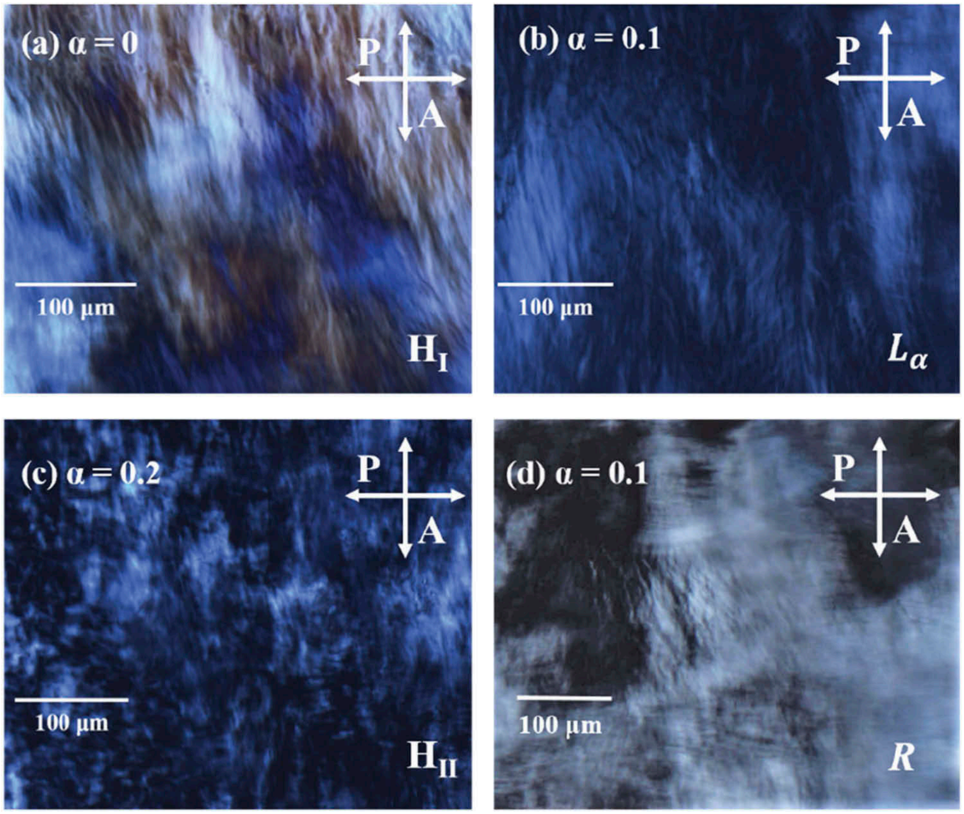

Figure 2. (Colour online) Textures of lyotropic liquid crystalline phases in ternary mixtures of surfactant SDS, ionic liquids and water, observed under crossed polarisers in an optical microscope. (a) α = 0 (pure SDS solution), corresponds to hexagonal phase (H_I), (b) α = 0.1 (added BMIM-BF_4), corresponds to lamellar phase (L_α), (c) α = 0.2 (added BMIM-BF_4) corresponds to hexagonal phase (H_{II}) and (d) α = 0.1 (added EMIM-BF_4) corresponds to rectangular phase (R). All the images were captured at 30°C.

these micrographs; hence, small angle x-ray diffraction experiments were performed.

Structural evolution of hexagonal phase

The microstructures of lyotropic liquid crystalline samples of SDS and the IL with four carbon atoms (C-4) in chain (BMIM-BF4), were investigated by small angle x-ray diffraction. Figure 3 shows the diffraction patterns obtained from the samples at various compositions. At φ = 0.4 and α = 0, two Bragg peaks are observed with the corresponding wave vector transfer (q) in the ratio $1{:}\sqrt{3}$ (Figure 3(a)). It confirms the existence of a two-dimensional hexagonal phase (H_I) of cylindrical micelles which has been reported in the study of the phase diagram of the SDS/water system by Kekicheff et al. [26]. The lattice constant (a) of the hexagonal phase can be calculated from, $a = \frac{2}{\sqrt{3}} d_{10}$, where $d_{10} = \frac{2\pi}{q_{10}}$, q_{10} being the position of first Bragg peak. The value of the lattice constant at this concentration is 54.4 ± 1.5Å. Such a cylindrical aggregate is expected by the self-assembly of a truncated cone-shaped molecule in an aqueous solution [27]. This is decided by the packing parameter, $p = \frac{v}{a_0 l}$, where v, a_0 and l are the volume, effective cross-sectional surface area of the head group and the length of the molecule, respectively [27]. At this concentration of φ = 0.4, the effective shape of the SDS molecule becomes a truncated cone with the value of p in the range of 1/3 to 1/2. As a result, the molecules form the cylindrical micelles. However, keeping the surfactant concentration fixed, the interfacial curvature of the cylindrical surface can be altered by changing the interactions between the molecules. Here, at a fixed value of φ = 0.4, the ionic liquid BMIM-BF_4 was added gradually. At α = 0.1, the diffraction pattern shows, again, two peaks but the q values are in the ratio of 1:2 (Figure 3(c)). It confirms the presence of lamellar phase (L_α) in the sample with a periodicity of 34.69 ± 0.38 Å. The first order phase transition from the hexagonal (H_I) to lamellar is evident from the diffraction pattern shown in Figure 3(b). At this intermediate value of α = 0.025, the co-existence of hexagonal (H_I) and lamellar (L_α) phases with the respective lattice constants 54.4 ± 1.5 Å and 34.7 ± 0.4 Å are observed. On further increasing of the IL concentration, the

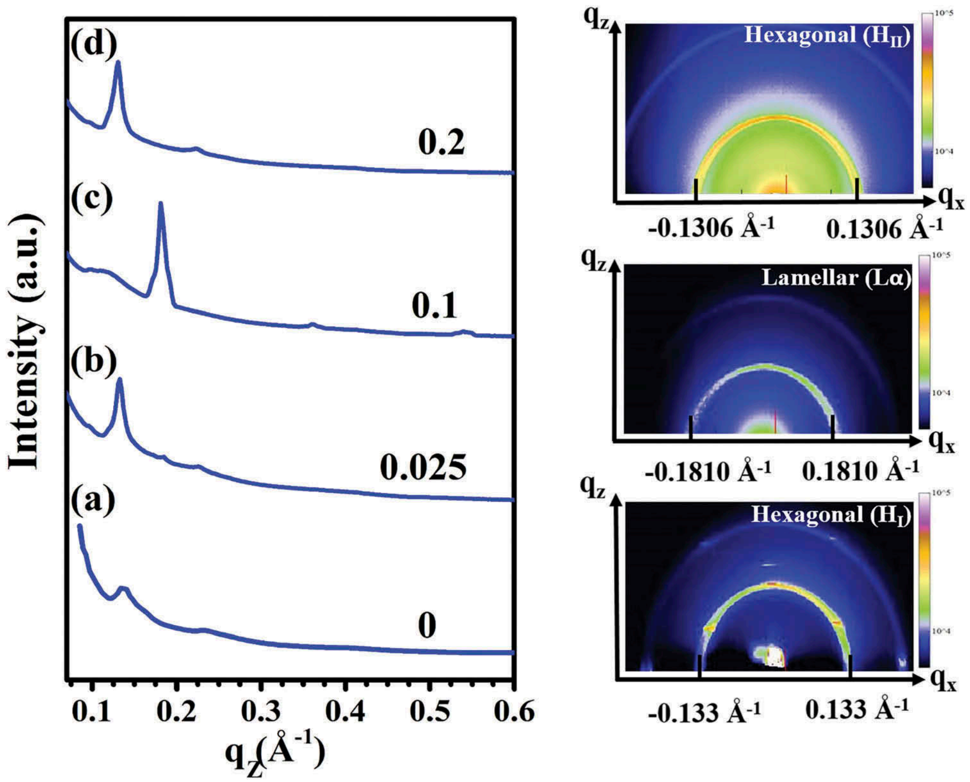

Figure 3. (Colour online) Small angle x-ray diffraction pattern of the different phases at φ = 0.4 at different values of α: (a) 0, (b) 0.025, (c) 0.1 and (d) 0.2, exhibiting the hexagonal (H_I), coexistence of hexagonal and lamellar (($H_I + L_\alpha$), lamellar (L_α) and second hexagonal (H_{II}) phases, respectively. The two-dimensional (2-D) images of the diffraction patterns are shown on the right panel of the figure.

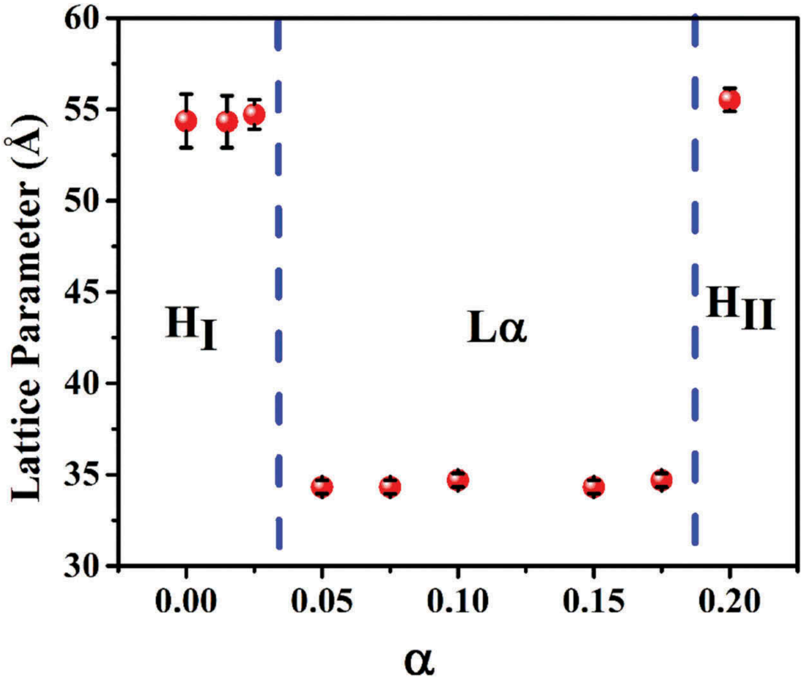

Figure 4. (Colour online) The variation lattice parameter of the first hexagonal (H_I), lamellar (L_α) and second hexagonal (H_{II}) phases obtained as a function of added BMIM-BF$_4$ into the aqueous solution of SDS. The results correspond to the constant value of φ = 0.4 and T = 30°C.

diffraction pattern showing two peaks with their q values in the ratio 1: $\sqrt{3}$ that confirms the presence of hexagonal phase. As shown in Figure 4, the lattice constant of this second hexagonal phase (H_{II}) obtained at this higher value of α = 0.2 is slightly greater than the lattice constant of the first hexagonal phase (H_I) observed at other side of the

Table 1. Lattice parameters of hexagonal (H_I), lamellar (L) and second hexagonal (H_{II}) phases obtained from the small angle x-ray diffraction study of SDS solution in the presence of BMIM-BF4 at varying sample compositions α.

φ	α	Lattice constant (Å)	Phases
0.4	0	54.4 ± 1.5	H_I
	0.015	54.3 ± 1.4	H_I
	0.050	34.3 ± 0.4	L_α
	0.075	34.3 ± 0.4	L_α
	0.100	34.7 ± 0.4	L_α
	0.150	34.3 ± 0.4	L_α
	0.175	34.7 ± 0.4	L_α
	0.200	55.5 ± 0.6	H_{II}

lamellar phase (lower value of α). These lattice parameters of different phases observed at different chemical compositions are given in Table 1 and plotted in Figure 4.

The small angle x-ray diffraction data obtained from the aqueous solution of SDS and the shorter chain (C-2) IL EMIM-BF4 are shown in Figure 5(a). Here, again the total surfactant concentration ($\varphi = 0.4$) was kept fixed and the IL to surfactant molar ratio was varied. At $\alpha = 0.075$, the first Bragg peak corresponding to (1 0) reflection of the two-dimensional hexagonal phase (H_I) of pure SDS solution is found to shift to a lower value of q. Also, the (1 1) peak of the H_I phase is not observed. Instead of that, a new Bragg peak appears at 0.182 $Å^{-1}$. At $\alpha = 0.1$, along with these two peaks, a third peak is observed at $q = 0.226$ $Å^{-1}$. All these three peaks then are best indexed as the reflections from (1 0), (0 1) and (1 1) planes of a rectangular lattice (R) with the corresponding lattice constants 47.0 ± 1.3 and 34.5 ± 0.9 Å. On further increasing of the IL (higher value of α), only a single broad peak appears indicating an isotropic phase (I). In case of longer chain (C-10) IL DMIM-BF4, hexagonal phase (H_I) is observed to transform to a lamellar phase (L_α) on the addition of the IL (Figure 5(b)). This lamellar phase is not found to form another hexagonal phase on further addition of the IL. Instead of that, a broad peak of an isotropic phase (I) is observed. In this context, note that in case of the medium chain (C-4) IL BMIM-BF4, the H_I phase was transformed to another hexagonal phase (H_{II}) at a higher value of α. The lattice parameters of different phases observed for these shorter and longer chain ILs are shown in Table 2.

Rheological behaviour of re-entrant hexagonal phases

The appearance of re-entrant hexagonal phases in the presence of the medium chain (C-4) IL BMIM-BF4 in the SDS solution is the most interesting observation in the present study. To shed more light on the unusual phase sequence, the rheological measurements on the SDS–BMIM-BF4 complexes have been done.

As the evolution of these phases is expected to exhibit distinct rheological behaviour, three samples with α = 0, 0.1 and 0.2 were considered for the measurements as they

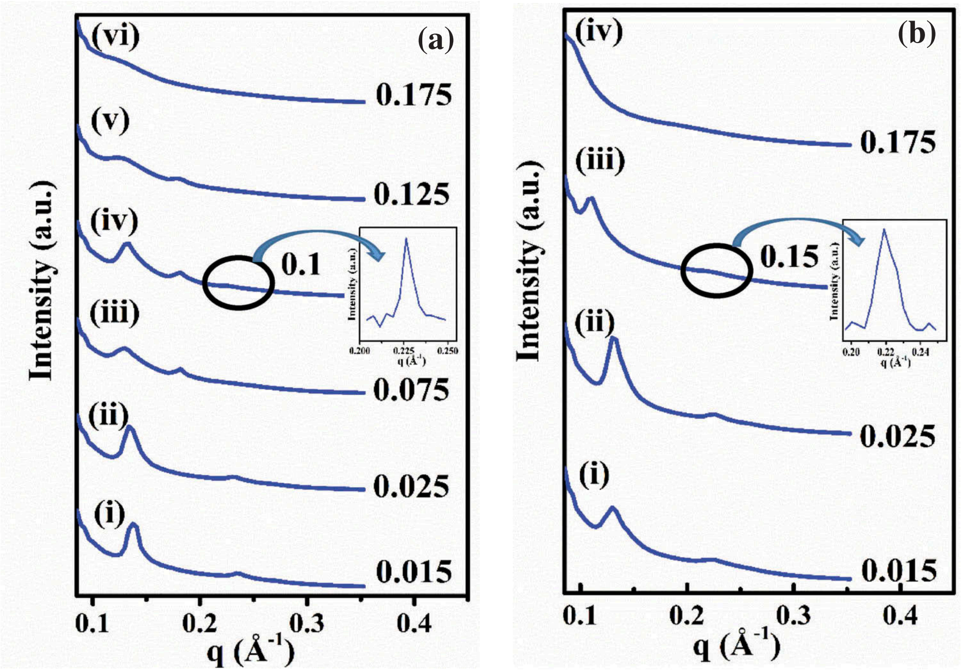

Figure 5. (Colour online) Small angle x-ray diffraction patterns of the different phases at $\varphi = 0.4$. (a) The pattern for shorter chain (C-2) IL EMIM-BF4 at different values of α: (i) 0.015, (ii) 0.025, (iii) 0.075, (iv) 0.1, (v) 0.125 and (vi) 0.175 exhibiting the hexagonal (H_I), rectangular (R) and isotropic (I) phases. (b) The pattern for longer chain (C-10) IL DMIM-BF4 at different values of (i) 0.015, (ii) 0.025, (iii) 0.15 and (iv) 0.175 exhibiting the hexagonal (H_I), lamellar (L) and isotropic (I) phases.

Table 2. Lattice parameters of hexagonal (H_I) and rectangular (*R*) phases of SDS solution in the presence of EMIM-BF4, and hexagonal (H_I) and lamellar (L_α) phases in the presence of DMIM-BF4 obtained from the small angle x-ray diffraction study at varying sample compositions α.

φ	Ionic liquids	α	Lattice constants (Å)	Phases
0.4	EMIM-BF4	0.015	52.8 ± 1.4	H_I
		0.025	54.3 ± 1.5	H_I
		0.075	48.4 ± 1.4 34.5 ± 0.9	*R*
		0.1	47.0 ± 1.3 34.5 ± 0.9	*R*
	DMIM-BF4	0.015	55.9 ± 1.6	H_I
		0.025	55.9 ± 1.6	H_I
		0.15	56.5 ± 1.9	L_α

represent the compositions of the H_I, L_α and H_{II} phases, respectively, keeping φ = 0.4 and T = 30°C fixed. To obtain the linear rheology regime of the samples, the strain amplitude was varied at a constant angular frequency of 10 rad/s and the corresponding storage (G') and loss (G'') moduli were measured. The data are shown in Figure 6. At low values of strain amplitude (γ) (<1%), the storage modulus (G') for all the three phases is found to be higher than that of the loss modulus (G''). The crossover value of the strain amplitude of L_α phase (4.65%) is smaller than both the hexagonal phases. The corresponding values for H_I and H_{II} phases are 10.00% and 25.20%, respectively.

The frequency sweep measurements on all the samples were carried out at a fixed strain amplitude of 0.1% that corresponds to the linear viscoelastic regime (see Figure 6). The frequency (ω) was varied in the range of 0.05–500 Hz. The measured viscoelastic spectra of the moduli G' and G'', again at α = 0, 0.1 and 0.2 corresponding to H_I, L_α and H_{II} phases, respectively, are shown in Figure 7. Even though the values of $G'$and G'' are very close in the low-frequency region, the values of G' becomes higher compared to G'' over the wide range of the frequency. For all these samples, Figure 8 represents the complex viscosity (η^*) as a function of angular frequency (ω). For all the phases, η^*decreases monotonically with ω. Interestingly, the values of η^* for both the hexagonal phases are very similar, while for the lamellar phase, it has a lower value compared to both of the hexagonal phases. This result is observed over the entire range of the angular frequency.

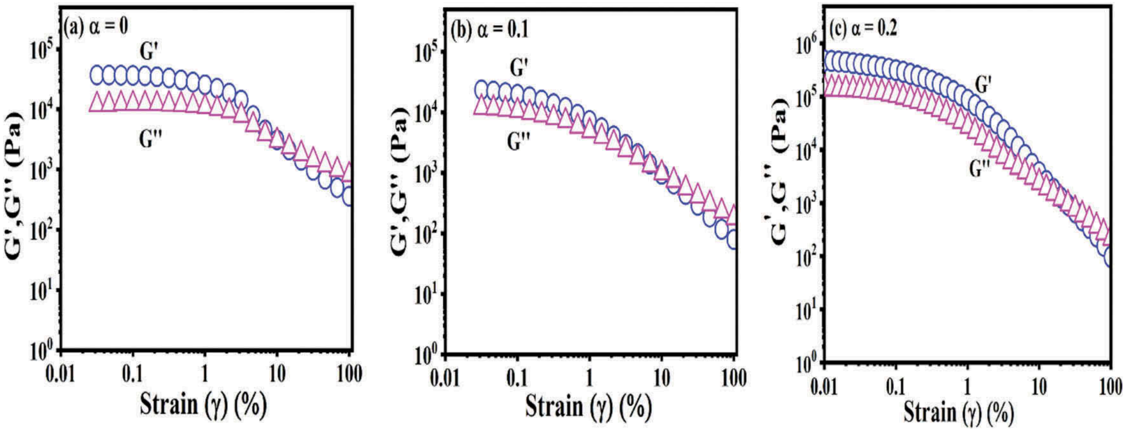

Figure 6. (Colour online) Measurements of storage (G') and loss (G'') moduli of lyotropic liquid crystalline phases: (a) α = 0, (b) α = 0.1 and (c) α = 0.2 corresponding to hexagonal (H_I), lamellar (L_α) and second hexagonal (H_{II}) phases, respectively. φ = 0.4 and T = 30°C were constants.

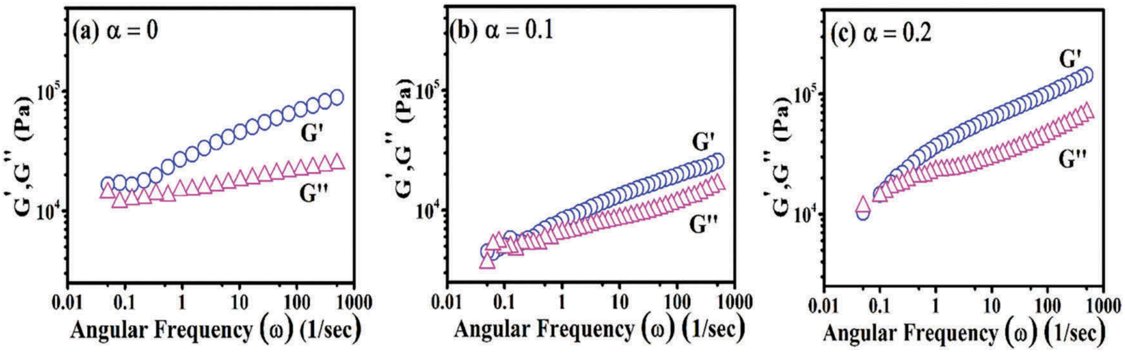

Figure 7. (Colour online) Frequency sweep measurements of lyotropic liquid crystalline phases: (a) α = 0, (b) α = 0.1 and (c) α = 0.2 corresponding to hexagonal (H_I), lamellar (L_α) and second hexagonal (H_{II}) phases, respectively. The strain amplitude 0.1%, φ = 0.4 and T = 30°C were constants.

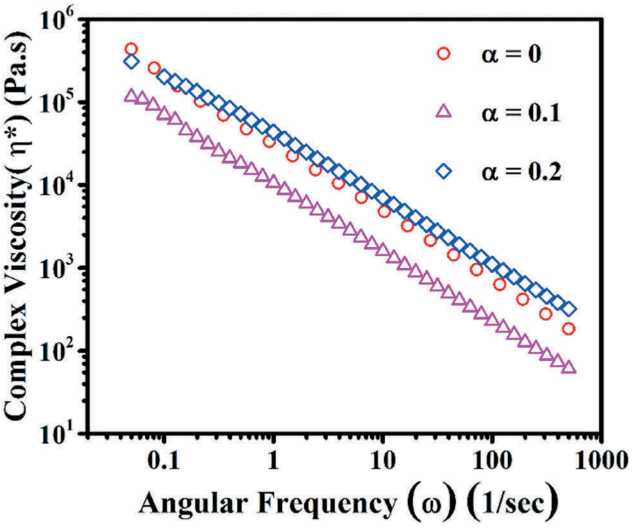

Figure 8. (Colour online) Complex viscosity (η^*) of lyotropic liquid crystalline phases at α = 0 (o), 0.1 (◊) and 0.2 (Δ) corresponding to hexagonal (H_I), lamellar (L_α) and second hexagonal (H_{II}) phases, respectively.

Discussions

Phases in surfactant solutions in the presence of ionic liquids with varying chain length

At a low concentration of surfactants in water, the physical properties of the isotropic solution of micelles are very sensitive to additives, such as organic and inorganic salts, alcohols and co-surfactants. In particular, ionic additives much strongly affect the critical micellar concentration (CMC) of an ionic surfactant, its surface activity and, also the shape and size of the micelles formed by the surfactant [28,29]. As a result, for many of the cases, the viscoelastic properties of the solution are modified due to the formation of long wormlike micelles [30,31]. At a higher concentration of the surfactant in water, there are various liquid crystalline phases, which are altered by additives due to a reshaping and reorganization of the self-assembled aggregates [32,33]. Most interesting phenomenon here is the sequential appearance of structural phases, which is important to comprehend the phase transition in lyotropic liquid crystalline systems. Especially, the transition between the hexagonal phase of cylindrical micelles of positive interfacial curvature and lamellar phase of flat bilayers with zero interfacial curvature has been discussed in literature over decades to understand the topological links between these two phases [28,32,34,35]. In the present study, the small angle x-ray diffraction data show that the two-dimensional hexagonal phase of SDS surfactant transforms into three different phases in the presence of ionic liquids (IL) with same imidazolium head group but of increasing hydrocarbon chain length. Note that all these ILs have same anions (BF_4^-), which are expected to dissociate in the aqueous solution leaving the cations with a hydrocarbon chain attached to it. The cation of C-2 IL has two hydrocarbons in the chain, which may not have a strong effect in modifying the hydrophobic core region of the cylindrical micelles of SDS, which has 12 hydrocarbons in the chain. However, the presence of the cations is expected to reduce the negatively charged head group area of the micelle. This can produce a non-circular cross-sectional micelle as the region of the more populated IL will have less curvature compared to the region of pure SDS. This can produce either a distorted two-dimensional hexagonal or a rectangular lattice [22,24,36]. The data obtained here resembles the rectangular lattice. However, as the electron density contrast between the surfactant complex and the surrounding aqueous medium is poor, low brilliance synchrotron source, which is the case here in the present study, is not good enough to conclude the type of lattice unambiguously. On the other hand, the C-10 IL is expected to influence both the head group and the hydrophobic regions of a SDS micelle as this IL has a comparable chain length. The presence of this IL may screen the repulsive force between the surfactant head groups reducing the head group area, which should reduce the local curvature. At the same time, at higher concentration of the IL, the long chain of the IL does not allow the surfactant chains to come closer. This phenomenon may end up with the transition of the hexagonal phase to a lamellar phase. For medium chain IL (C-4), at low concentration, the head group screening again is expected to produce lamellar phase. However, at higher concentration, the high head group area IL molecule will increase the effective head group area allowing the long chains of the surfactant to come closer. This phenomenon may give rise to the reappearance of the hexagonal phase at this high concentration. The physical explanations given here are the subjects to further systematic experiments and simulation works, which are the future plans of the authors.

The most common intermediate phase between the hexagonal and lamellar phases is the bicontinuous cubic phase with triply period minimal surface characterized by zero mean curvature of the surface [34]. Another well-known phase is the lamellar phase with in-plane curvature defects called the mesh phase [37]. The two-dimensional meshes are also reported to form three-dimensional rhombohedral and tetragonal phases due to the out of plane positional correlation among the in-plane curvature defects of the meshes [36,37]. In all these cases, strongly bounded anionic counterions were used in cationic surfactants to modify the morphology of the aggregates of the surfactants. Kekicheff et al. have reported a detailed phase diagram of SDS-water system where the hexagonal phase was observed to transform to lamellar phase with a number of intermediate phases between these two [26]. However, these intermediate phases were observed over a very narrow range of SDS concentration, unlike the cases in references [37]. In the ternary system of SDS–decanol–water, nematic phases of rod-like and disc-like micelles were reported as the intermediate phases [38,39]. Ghosh et al. have also reported the hexagonal phase of SDS to transform to lamellar phase with the sequential appearance of the nematic phase of rod-like micelles, the isotropic phase of spherical structure and another nematic phase of disc-like micelles at the presence of the strongly binding counterion *p*-toluidine hydrochloride (PTHC) [21]. In none of all these cases of SDS system, the hexagonal to hexagonal transition was reported which is an interesting finding of the present work.

Rheology'of re-entrant hexagonal phases

At high surfactant concentration in water, the viscoelastic properties of the solution highly depend on the type of liquid crystalline phases in the solution. This is reflected in the cross-over values of strain amplitudes here in the three distinct phases (Figure 6). The lowest value of strain amplitude for lamellar phase signifies the least resistance against the applied strain, which is because of the layered structure of the lamellar phase formed by surfactant/IL bilayer. These bilayers can easily flow compared to the cylindrical micelles in both the hexagonal phases.

In the frequency sweep measurements, the values of G' are found to be higher compared to the values of G'' for all three phases (Figure 7). These data suggest the samples to exhibit long relaxation time [40,41]. The values of G' and G'' for H_I phase are 46.0 and 18.0 kPa, while these values for H_{II} phase are 63.3 and 29.6 kPa, respectively, at the frequency 10 s^{-1}. These values indicate the two hexagonal phases to differ in their rheological behaviour.

To distinguish between the H_I and H_{II} hexagonal phases, the magnitude of the complex modulus ($|G^*|$) has been calculated from the values of $G'$and G'' following the equation, $|G^*| = \left(G'^2 + G''^2\right)^{\frac{1}{2}}$. It can be expressed in terms of angular frequency (ω) as,$|G^*| = A\omega^{\frac{1}{z}}$, where z is the coordination number and A is a constant that signifies the strength of interaction among the units constituting a phase [42,43]. From the fits, as shown in Figure 9, the values of z and A for the H_I phase are calculated as 10 and ~32 x 10^3, respectively. The respective values for H_{II} phase are 5.75 and ~85 × 10^3. It shows higher resistive nature of sample at α = 0.2 compared to the sample at α = 0. The relaxation time (τ) for all the samples can be calculated from the slope of the linear fit to the data as shown in Figure 10, where $\frac{G'}{G''}$ is plotted as a function of angular frequency (ω). As expected, the value of τ (~83 ms) for the lamellar phase is smaller compared to H_I (~122 ms) and H_{II} (181 ms) phases. These values, again, indicate the stronger cohesive force among the units of the H_{II} phase compared to the one in H_I phase.

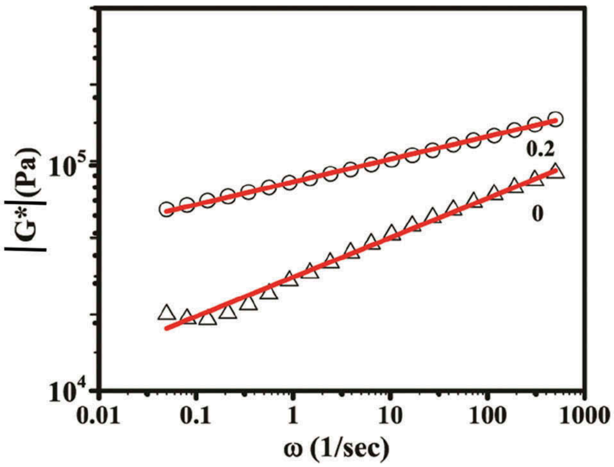

Figure 9. (Colour online) Magnitude of the complex shear modulus ($|G^*|$) of H_I (0) and H_{II} (Δ) hexagonal phases at α = 0 and 0.2, respectively, as a function of angular frequency (ω).

It is known that the addition of salts in the aqueous solution of micelles of charged surfactants produces longer micelles [27]. The curvature of the end-cap of a micelle is more compared to its surface. Hence, it is preferable to increase the length rather than increasing the number of micelles. However, the length cannot be very long as it reduces the entropy of the system. The equilibrium structure depends on both the factors of energy including the effective end-cap energy and the entropy of the system. The present rheological behaviour of H_I and H_{II} phases indicates the formation of longer micelles in case of the H_{II} phase.

In general, on increasing the surfactant concentration in a binary mixture of surfactant-water, the lamellar phase forms hexagonal phase with reverse micelles [44]. This is observed at a very high concentration of surfactant (>80 wt.%) which is not the case in the present study. Here, at a much lower concentration of surfactant (~40 wt.%), the hexagonal (H_{II}) is observed after the lamellar (L_α) by varying the ratio between the ionic liquid and the surfactant, keeping the wt.% constant. Even though the x-ray diffraction confirms the hexagonal lattice in H_{II} sample and the rheology indicates it to be much resistive to shear force compared to H_I sample, it is hard to conclude about the nature of micelles in the H_{II} phase. In the following section, the theoretical calculation will shed light on the issue.

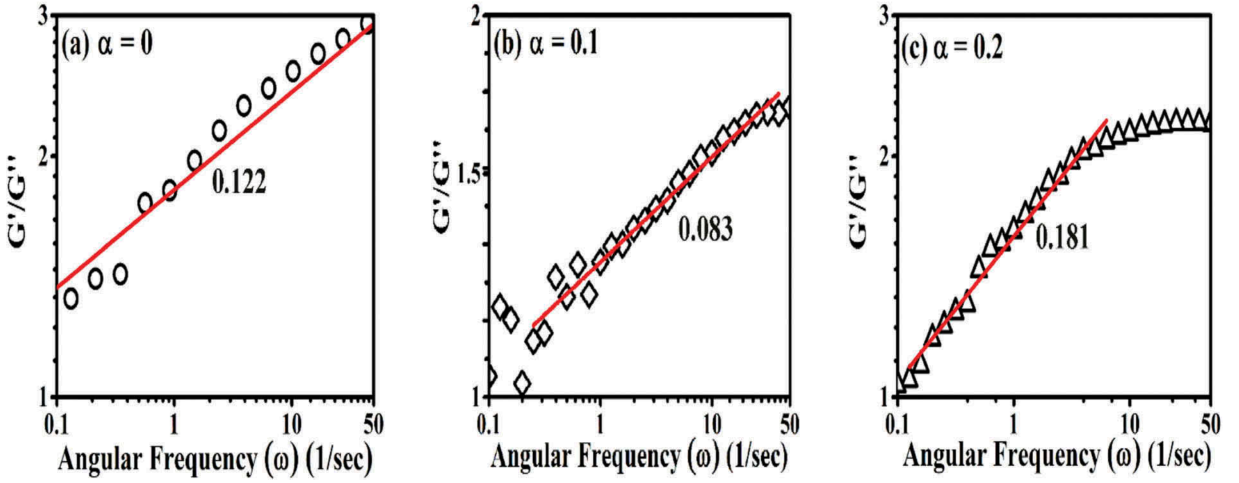

Figure 10. (Colour online) Plot of $\frac{G'}{G''}$ as a function of angular frequency (ω) for the lyotropic liquid crystalline phases: (a) α = 0, (b) α = 0.1 and (c) α = 0.2 corresponding to hexagonal (H_I), lamellar (L_α) and second hexagonal (H_{II}) phases, respectively.

Packing parameters of hexagonal phases

As discussed in the *RESULTS* section, the geometric packing parameter p, of a molecule in an aggregate may influence the nature of micelles in an aggregate [45,46]. In the present study, this parameter has been calculated using the lattice constant of a phase obtained from the x-ray diffraction study.

For a particular sample, one could write the total mass of the sample as, $M_1 + M_2 = \bar{D}V_c$, where M_1 and M_2 are the masses of amphiphilic molecules and water, respectively, $\bar{D}$ the average mass density of the sample and V_c the total volume. The volume of water (V_w) and the amphiphilic molecule (V_s) then, can be written as

$$V_w = \frac{V_c\bar{D}}{\left(\frac{M_1}{M_2} + 1\right)D_w} \tag{1}$$

$$V_s = V_c\left(1 - \frac{\bar{D}}{\left(\frac{M_1}{M_2} + 1\right)D_w}\right) \tag{2}$$

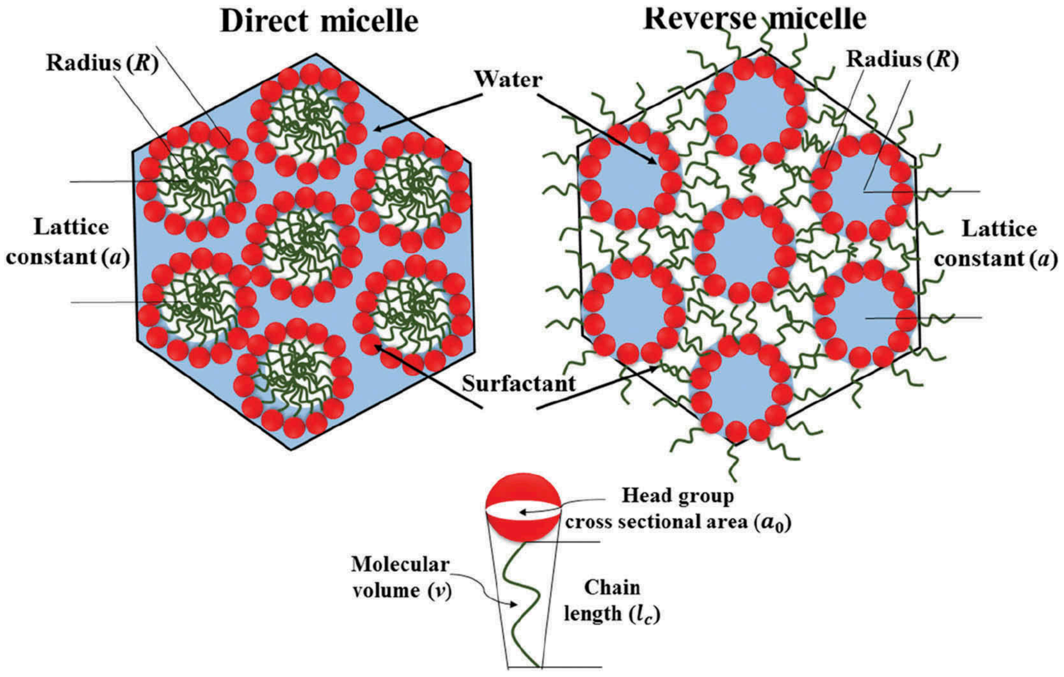

Figure 11. (Colour online) Schematics of hexagonal phases made up of direct micelles (*left*) and reverse micelles *(right)*. The figure represents only the 2D cross-section of cylinders.

where D_w is the mass density of water. For a two-dimensional (2D) phase in a homogeneous surfactant solution, $V_w/V_s\ = S_w/S_s$ where S_w and S_s are the surface areas of the 2D-lattice covered by water and amphiphiles, respectively (Figure 11).

Hexagonal phase (H_I) at α = 0: For the hexagonal phase without IL, the value of S_w/S_s is calculated using equations (1) and (2) and the value is found to be 1.91. Further, for the hexagonal phase, the total surface area of the 2D unit cell is calculated to be, $S_w + S_s = \left(\frac{3\sqrt{3}}{2}\right)a^2 = 5118.37\ AA^2$ using the value of lattice parameter, $a = 54.4\ AA$, which was obtained from diffraction study (Table 1). From these values of S_w/S_s and $S_w + S_s$, one could find the value of the radius (R) of the cylindrical micelles following the relation, $S_s = 3\pi R^2$ as there are effectively three cylindrical micelles in each unit cell. The value of R is found to be 16.74 AA^2 which is very close to the value mentioned in the literature [27]. Considering the average length of a cylinder as L, the mass of total amphiphiles in a unit cell can be calculated from the equation,

$$M_1 = \frac{3\sqrt{3}}{2}a^2L\bar{D} - \left(\frac{3\sqrt{3}}{2}a^2 - 3\pi R^2\right)LD_w \tag{3}$$

The number of the amphiphilic molecule in this mass can be calculated from $N_{SDS} = \frac{M_1}{m_{SDS}}N_A$ where m_{SDS} is the molecular weight of SDS surfactant and N_A the Avogadro's number. The value of the cross-sectional area of the head group of each molecule is then, $a_0 = A/N_{SDS}$, A being the curved surface area ($6\pi RL$) of all the three cylinders. The value of a_0 is calculated to be $44.82AA^2$. The volume of each molecule, $v = 3\pi R^2 L/N_{SDS}$, is found to be $375.17AA^3$. The critical value of chain length is calculated from the equation [28], $l_c = (1.54 + 1.265\ n)\ AA$, where n is the number of carbon atoms in the chain. For SDS molecule with n = 12, the value of l_c = 16.72 AA. Using the values of a_0, v and l_c, the packing parameter, $p = \frac{v}{a_0 l}$, of the SDS molecule is found to be 0.50 which corresponds to the formation of direct cylindrical micelles [27]. It is already known that the hexagonal phase observed in an aqueous solution of SDS at low surfactant content is made up of direct cylindrical micelles [26] (Figure 11). However, this result validates our approach to calculate the value of the packing parameter for the second hexagonal phase (H_{II}) which is observed on the other side of the lamellar phase.

Hexagonal phase (H_{II}) at α = 0.2: As is stated above, the hexagonal phase that appears after the lamellar phase is generally formed by reverse cylindrical micelles as shown in the schematic in Figure 11. Considering reverse cylindrical micelle and following the approach above, the radius (R) of the water cylinder was calculated to be 24.34 Å. The lattice parameter for this phase was, $a = 55.52\ AA$. Here, the expression of the total mass of amphiphiles is composed of SDS and BMIM-BF_4 and the expression is given as

$$M_1 = M_{SDS} + M_{IL} = \frac{3\sqrt{3}}{2}a^2L\bar{D} - 3\pi R^2 LD_w \tag{4}$$

The masses, M_{SDS} and M_{IL} of SDS and IL, respectively, can be calculated from equation (4) and from the molar ratio, $\alpha = \frac{M_{IL}/m_{IL}}{M_{SDS}/m_{SDS}}$ where m_{IL} and m_{SDS} are the molecular weight of BMIM-BF_4 and SDS, respectively.Taking care of contributions from SDS and the IL, the average cross-sectional area (a_o) of the head group and the volume (v) of the amphiphilic molecule were found to be 65.9 7 AA^2 and 349.29 AA^3, respectively, for the sample at *α = 0.2*. The volume (v) is calculated from equation (5) as given below.

$$v = \frac{\frac{3\sqrt{3}}{2}a^2 - 3\pi R^2}{N_{SDS} + N_{IL}} \tag{5}$$

where a is the lattice parameter of the hexagonal lattice and $_{SDS}$ and N_{IL} are the number of SDS and BMIM-BF_4 molecules, respectively. Calculating the average critical chain length, $l_c = 15.03\ AA$, with n = 12 for SDS and 4 for BMIM-BF_4, the packing parameter (p) was found to be 0.35. However, the value of p for a reverse micelle should be ≥1. Hence, the micelle in this hexagonal phase may not be of a reverse type.

Considering the micelle as the direct one and following the approach taken for the sample at *α* = 0, the value of the radius of the cylinder was found to be 16.05 AA. The total mass M_1 was calculated again from Equation (3), however having two components M_{SDS} and M_{IL}. The average cross-sectional area of head group (a_0) and the volume (v) of the amphiphilic molecule were calculated to be 43.49 AA^2 and $348.95AA^3$, respectively. Using the calculated average value of $l_c = 15.03\ AA$, the packing parameter was calculated to be 0.53. This value is close to the packing parameter of a direct micelle. Hence, the micelle in this hexagonal phase is likely to be of the direct type. The calculated parameters for all the phases are given in Table 3. The presence of cations of the IL in the micelles will screen the repulsion between the SDS head groups, which, in turn, may reduce the effective head group area. This is a condition to achieve a reverse micelle. However, in the present case, this head group effect is compensated due to the reduction in the effective volume of the molecule, which may be the reason for observing the direct micelle. It is

Table 3. Calculated parameters of an amphiphilic molecule in hexagonal (H_I), lamellar (L_α) and second hexagonal (H_{II}) phases.

Weight fraction φ	Molar ratio α	Head group area a_0 (Å^2)	Molecular volume v (Å^3)	Chain length l_c (Å)	Packing parameter$p$
0.4	0 (H_I)	44.82 ± 4.26	375.17 ± 19.51	16.72 ± 0.57	0.50 ± 0..06
	0.015 (H_I)	35.52 ± 3.37	260.91 ± 13.57	16.60 ± 0.56	0.44 ± 0.05
	0.2 (H_{II}) (Reverse micelle)	65.97 ± 3.43	349.29 ± 18.16	15.03 ± 0.51	0.35 ± 0.04
	0.2 (H_{II}) (Direct micelle)	43.49 ± 4.13	348.95 ± 18.14	15.03 ± 0.51	0.53 ± 0.06

reported that the IL molecules used in this study insert their chains into the hydrocarbon region of amphiphilic molecules and reduce the effective thickness of the molecular layer [47]. In such an effect in chain length is also evident here as shown in Table 3.

Conclusions

The hexagonal phase of direct cylindrical micelles in an aqueous solution of sodium dodecyl sulfate has been found to transform to rectangular and lamellar phases at the presence of short (two hydrocarbons in the chain) and long (10 hydrocarbons in the chain) hydrophobic chain imidazolium-based ionic liquids, respectively. However, at the presence of a medium chain ionic liquid (four hydrocarbons in the chain) the hexagonal phase of pure surfactant is transformed to another hexagonal phase of direct cylindrical micelles at the presence of few mol% of the ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate. The lamellar phase of stacked bilayers was the intermediate of these two phases. Even though the small angle x-ray diffraction study has revealed the lattice parameters of these hexagonal phases to be comparable to each other, their rheological behaviour has been distinctly different. Generally, the hexagonal phase after the lamellar phase in a phase diagram of a surfactant molecule is known to form by reverse micelle, which is not the case in the present study. Theoretical calculations have established the second hexagonal phase to be made of direct micelles also.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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