Geometric features in lyotropic liquid crystalline phase transitions observed in aqueous surfactant systems

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ABSTRACT
Lyotropic liquid crystalline phases are widely known to be formed in aqueous surfactant mixtures. Although the phase behavior of several surfactants has been elucidated in the past years, a striking absence of detailed discussion on how molecular geometric parameters vary as different liquid crystals are formed is consistently seen in literature. The current work aimed to partially fill this gap, by determining how several structural parameters changed in a variety of phase transitions previously observed in aqueous surfactant binary and ternary mixtures. The main findings reveal that the cell parameter dimensions are strongly correlated with the packing fraction of small aggregates in each phase; the folding and interpenetration of surfactant hydrocarbon chains are most likely to happen in phases with lower curvature, and can greatly affect other structural parameters; added components can alter the aqueous surfactant phase behavior at different extents; and highly ordered phases are favored by a substantial decrease in the cross-sectional areas per surfactant; among others. The obtained results enable important knowledge on lyotropic liquid crystal formation, in addition to providing detailed information on how to control and obtain such phases, thus prospecting new insights in areas where they are highly desired.

GRAPHICAL ABSTRACT

1. Introduction
Lyotropic liquid crystalline phases, also referred to as mesophases, formed by surfactants in solution have been widely investigated in past years due to their structural complexity and potential applications in a variety of fields. The amphiphilic nature of surfactants drives their self-assembly in a solvent, giving rise to micelles with different shapes, in the dilute regime, and to a rich polymorphism in terms of liquid crystalline structures as the concentration is increased. Several factors govern the type of the resulting mesophases, with the solvent and surfactant molecular structure being the most important ones.[1–3] The solvent defines if the obtained structures, either micelles or liquid crystalline phases, are normal (Type I) or reverse (Type II), for aqueous and nonaqueous media, respectively. The influence of the surfactant molecular structure on its phase behavior is predicted by the well-known theory of critical packing parameter (CPP), where the increase in surfactant concentration leads to the formation of structures with lower curvatures in the expected order: micellar cubic ($I_m$) → hexagonal ($H_d$) → bicontinuous cubic ($Q_2$) → lamellar ($L_a$) → reverse phases.[1–3] Intermediate phases between the hexagonal and lamellar structures may appear but, for the sake of simplicity, they will not be explored here. In a similar manner, the reverse phases will also be excluded of the present study. Such a phase sequence displayed above assumes that the starting micelles formed in the dilute regime are spherical. The micellar cubic ($I_m$) phase, which is described as optically isotropic and very viscous, usually appears between the micellar solution and the hexagonal phase and it is formed by discrete micelles discontinuously arranged in a three-
dimensional cubic array. Micellar cubic phases present several arrangements and one of the most reported lattice types belongs to the Pm3n space group. Although highly debated in the past, the most accepted model for the Pm3n micellar cubic phase is that it consists in eight micelles per unit cell, where two micelles are spherical and the other six are disk-shaped, as displayed in Figure 1.

The hexagonal (H6) phase, with a p6mm space group, consists in cylindrical micelles arranged in a hexagonal pattern in a way that each micelle is surrounded by other six, thus forming a two-dimensional structure. This phase also forms thick fluids, although less viscous than the previous micellar cubic phase, and displays strong birefringence, revealing its anisotropic nature. Its schematic structure is represented in Figure 1.

In some cases, a bicontinuous cubic (QI) phase may appear between the hexagonal and lamellar phases. QI phase is usually based on the la3d space group and is defined by the gyroid periodic minimal surface, consisting of two interwoven, though unconnected, three by three joined network of cylindrical micelles, as displayed in Figure 1. The term “bicontinuous” is employed to describe the QI phase since it is formed by three media, of different polarities, continuously distributed throughout the 3D space.

The lamellar (Lα) phase (Figure 1) is formed by alternated surfactant bilayers and water layers in a one-dimensional structure, where the surfactant chains are in a liquid-like state. It belongs to the pm space group. The Lα phase, with the lowest viscosity if compared with the other three liquid crystalline phases, also presents characteristic birefringent features and is one of the most common surfactant mesophases found elsewhere. At specific conditions, a lamellar (Lβ) phase with distinct surfactant configuration can be formed from the Lα phase.

Although the recent literature contains an enormous amount of studies elucidating the phase behavior of surfactants, in terms of which liquid crystalline phases they form as a function of concentration, temperature and presence of additives, a global picture of the changes that occur in the molecular organization of surfactants as they transit from one to another phase is rarely discussed. Variations in important geometric parameters, including the interfacial molecular area, space occupied by the hydrocarbon chain, polar and nonpolar domain thicknesses, for example, as the surfactant concentration is increased, throughout the phase diagrams, are scarcely found in the literature, and the few examples found are focused on a specific phase, rather than emphasizing a broad discussion involving all phases formed by the investigated amphiphile.

The knowledge of surfactant mesophase structures is a key step in developing industrial applications and an improved understanding of surfactant arrangement in liquid crystalline phases leads to an accurate control over the

Figure 1. Schematic representation of micellar cubic (Pm3n space group), hexagonal (p6mm space group), bicontinuous cubic (la3d space group) and lamellar (pm space group) normal structures with their respective cell parameters (a or d) and bilayer thickness (dhc) for the lamellar phase. The cross-sectional area per surfactant at the hydrophilic-hydrophobic interface (as) and the radius of hydrocarbon chain (rhc) for all phases, are also displayed in the scheme.
surfactant formulations in terms of formation, (colloidal) stability, macroscopic and microscopic characteristics, such as viscosity and encapsulation ability, and performance.[3,16] Based on the above, this study aimed to determine and discuss variations in surfactant geometric parameters, at a molecular level, in mesophases as distinct structures are formed in a variety of systems reported in the literature. Such a broad and deep understanding will contribute to a better evaluation of the rich complexity involved in lyotropic liquid crystal formation, in addition to providing important information for future studies in surfactant formulation processing and designing.

2. Methodology

The current work consisted in calculating geometric parameters of different liquid crystalline phases formed by surfactants in both binary (surfactant/water) and ternary (surfactant/additive/water) systems, and in evaluating the variations in such parameters as the phases transit from one to another. The evaluated phase transitions were: micellar cubic ($L_i$) → hexagonal ($H_i$), hexagonal ($H_i$) → bicontinuous cubic ($Q_i$) → lamellar ($L_d$), hexagonal ($H_d$) → lamellar ($L_d$), and lamellar ($L_d$) → lamellar ($L_d$). The calculations were made for selected studies available in the last 20 years in the literature, regarding systems formed by a variety of surfactants, a broad term that will be used here to englobe all types of surfactants including, cationic, anionic, and non-ionic, as well as amphiphilic ionic liquids and lipids.

The investigated systems were randomly chosen with the condition that the original references presented the exact composition of the investigated samples and the characteristic cell parameters ($d$ for micellar cubic, hexagonal and bicontinuous cubic, and $d$-spacing for lamellar) of each phase, as determined by Small Angle X-ray Scattering (SAXS). In some cases, only SAXS patterns were presented and the cell parameters were calculated by employing the Equations (S1–S5), based on the position of scattering peaks and their respective Miller Indices ($hkl$), as detailed in the Supporting Information (Supplementary material, Table S1). The characteristic cell parameters for each phase are illustrated in Figure 1.

Apart from the $d$ and $d$-spacing values, the composition of the samples is also required for the desired calculations, restricting the study to systems displaying only one homogeneous phase. The available overall compositions were converted to volume fraction of hydrocarbon portion ($\phi_{hc}$), which is calculated based on the assumption that the systems are comprised of a hydrophobic domain, which considers the hydrocarbon molecular volume of both surfactant and additive, and a hydrophilic domain, containing the volume of the headgroup and counterion of surfactant, the hydrophilic volume of the additive, and water.[17] Details on how $\phi_{hc}$ values were calculated are presented in Supporting Information.

For all phases, the radius of hydrocarbon portion $r_{hc}$ and the cross-sectional area per surfactant at the hydrophobic-hydrophilic interface $a_s$ have been calculated. For the lamellar phase, the interlamellar distance $d$, and bilayer thickness $d_{hc}$ were also calculated. The geometric parameters are also illustrated in Figure 1 and were estimated based on the following equations.

**Micellar cubic phase**[18]

\[
r_{hc} = \left( \frac{3d^3 \phi_{hc}}{32\pi} \right)^{1/3} \tag{1}\]

\[
a_s = \frac{3V_{hc}}{r_{hc}} \tag{2}\]

where $V_{hc}$ is the volume occupied by the surfactant hydrocarbon chain (Supplementary material, Table S2). These equations are based on the simple assumption that all micelles composing the micellar cubic phase are spherical.

**Hexagonal Phase**[19]

\[
r_{hc} = \left( \frac{\sqrt{3a^2 \phi_{hc}}}{2\pi} \right)^{1/2} \tag{3}\]

\[
a_s = \frac{2V_{hc}}{r_{hc}} \tag{4}\]

**Bicontinuous cubic phase**[20]

\[
r_{hc} = a_{h} \sqrt{\frac{8\phi_{hc}}{24\pi}} \tag{5}\]

\[
a_s = \frac{48\pi r_{hc}V_{hc}}{\sqrt{8\phi_{hc}a^2}} \tag{6}\]

**Lamellar phase**[19]

\[
d = d - \text{spacing} \tag{7}\]

\[
d_{hc} = d\phi_{hc} \tag{8}\]

\[
r_{hc} = \frac{d_{hc}}{2} \tag{9}\]

\[
a_s = \frac{V_{hc}}{r_{hc}} \tag{10}\]

For comparison purposes, the length $l$ of a fully stretched hydrocarbon surfactant chain, with all-trans configuration, was also calculated employing the Tanford equation:[21]

\[
l = 1.5 + 1.265n \tag{11}\]

with $n$ denoting the number of carbon atoms in the surfactant chain. All calculated parameters are given in units of angstrom (Å). Table 1 presents the systems investigated in the current study, with the abbreviations and notations employed in this work.
3. Results

3.1. Micellar cubic \( \rightarrow \) hexagonal transition

At low concentrations, surfactants may form isotropic solutions containing small micelles. Upon further increase in surfactant concentration, liquid crystalline phases start to form, with their initial structure being dependent on the type of micellar aggregate occurring in the dilute regime. The "crystallization" of spherical micelles results in a discontinuous micellar cubic (I\( _d \)) phase, with the Pm\( 3n \) space group being one of the most occurring arrangements appearing in a variety of aqueous surfactant systems.\(^{34-38} \) This phase transforms into a hexagonal (H\( _d \)) structure as the surfactant concentration is further increased.

Figure 2a indicates the variation in the characteristic cell parameters (\( a \)) of a I\( _d \) phase transition to a H\( _d \) structure as the surfactant concentration is increased in C\( 12 \)C\( \text{C} \)/water mixtures, as calculated based on results displayed in ref. [22]. The transition involves a decrease of nearly 50% in \( a \) values for very similar compositions (Figure 2a). The process also takes place with a significant decrease in the radius of hydrocarbon core (\( r_{hc} \)), with the hexagonal phase consistently displaying smaller \( r_{hc} \) values (Figure 2b). For both micellar cubic and hexagonal phases, the cross-sectional area per surfactant (\( a \)) decreases almost linearly with concentration, with a great diminution near the phase transition (Figure 2c). A similar behavior was also observed for other systems presenting the I\( _d \)-H\( _d \) transition, as illustrated in Table S4 (Supplementary material), for K\( C12 \)G/water mixtures.

3.2. Hexagonal \( \rightarrow \) bicontinuous cubic \( \rightarrow \) lamellar transition

The transition from a hexagonal to a lamellar liquid crystalline phase in binary and ternary surfactant systems is often marked by the appearance of other cubic phases. The normal bicontinuous cubic phase (V\( _d \)), belonging to the I\( a3d \) space group, is the most common structure found between the transitioning phases and is usually found in phase studies involving surfactants with highly hydrated polar headgroups, including carbohydrate-, amino acid- and choline carboxylate-based amphiphiles.\(^{13,22,25,39,40} \) The phase has also been observed for gemini surfactants\(^{41} \) and cationic surfactants with polymeric counterions,\(^{42} \) as well as for amphiphilic block copolymers.\(^{43} \)

Figure 3a shows the variations in the characteristic cell parameters for the H\( _d \), V\( _d \) and L\( _a \) phases formed in C\( 8 \)Mal/water mixtures, calculated based on results displayed in ref. [24]. The \( a \) value is ca. twice larger for the V\( _d \) phase if compared with the H\( _d \) and L\( _a \) phase (\( d \)). The radius of hydrocarbon core (\( r_{hc} \)) decreases almost linearly as the phase transitions occur with the increase in surfactant concentration (Figure 3b). In an opposite manner, no linear relation was observed for the surfactant cross-sectional areas in H\( _d \), V\( _d \) and L\( _a \) phases, as demonstrated in Figure 3c. Again, the \( a \) value observed for the bicontinuous cubic phase is exceptionally large if compared with the other two phases. Such a trend has also been observed for C\( 10 \)EO\( 5 \)Glu/water mixtures, as illustrated in Figure S1 (Supplementary material).

3.3. Hexagonal \( \rightarrow \) lamellar transition

Several aqueous surfactant systems form a hexagonal (H\( _d \)) phase that is directly converted to a lamellar (L\( _a \)) phase as the hydrocarbon concentration is increased, with absence of formation of a bicontinuous cubic phase. Such direct transition is often observed for both binary and ternary surfactant mixtures. Figure 4a shows the variations in the cell parameters (\( a \) for H\( _d \) phase and \( d \) for L\( _a \) phase) near the hexagonal-to-lamellar transition that occurs ca. \( \phi_{hc} = 0.360-0.440 \) for NaC\( 12 \)EO\( 5 \)S-NaC\( 12 \)BzS/water mixtures, as calculated using the results presented in ref. [26]. It is noted that, for both phases, the cell parameters values decrease with \( \phi_{hc} \). When both phases coexist, \( a \) is nearly 20% larger than \( d \) at the same concentration.

For the above-mentioned system, the hexagonal-to-lamellar transition involves a decrease of around 50% in \( r_{hc} \) values, as depicted in Figure 4b. The cross-sectional area per surfactant (\( a \)) decreases almost linearly with \( \phi_{hc} \), as indicated in Figure 4c. The lamellar phase consistently displays smaller \( a \) values if compared with the hexagonal phase (Figure 4c).
similar behavior was also found for C16mimCl/water system,\textsuperscript{27} as demonstrated in Table S5 (Supplementary material). In the two-phase region of NaC12EO3S-NaC12BzS/water system, the structural parameters were not estimated due to uncertainty in the composition of each phase.

3.4. Lamellar ($L_a$) $\rightarrow$ lamellar ($L_d$) transition

One of the most interesting features of lamellar liquid crystalline phases is their ability to swell expressive amounts of water, thus indicating their great stability even at high dilution regimes. The analysis of $d$ values as a function of water concentration, at a given temperature, is the simplest form of studying the swelling behavior of a lamellar phase, as well as in determining in which concentration range the liquid crystalline phase exists as a pure phase or coexists with an isotropic solution. Also, upon the quantitative analysis of such swelling curves, other structural parameters can be derived, including the bilayer thickness ($d_{hc}$).

Figure 5a shows a swelling curve ($d$ versus $\phi_{hc}^{-1}$) for the $L_a$ phase formed in (C12)$_2$DMABr/water system, as determined in ref. [28]. The plot also contains a linear fit for the experimental data points (dashed red line), as well as the predicted swelling pattern (dashed blue line) assuming the bilayer thickness equal to twice $l$ (the length of a dodecyl hydrocarbon chain). Clearly, such prediction fails to fit the experimental data. Also, regarding the experimental data points and the correspondent linear fit, the plot shows a nonmonotonous swelling behavior, indicating in which extent the lamellar phase can be swollen.

Figure 2. Variation in (A). cell parameters ($a$); (B). radius of the hydrocarbon core ($r_{hc}$); and (C). cross-sectional area per surfactant ($a_s$) for the micellar cubic ($I$) and hexagonal ($H$) phases formed as the hydrocarbon volume fraction ($\phi_{hc}$) is increased in ChC12C/water mixtures. Data calculated based on the results presented in ref. [22] Gray dashed lines delimitate the boundary between the two phases.

The $L_d$ phase is one of the most common liquid crystalline phases in surfactant aqueous systems, but may be preceded by another lamellar phase as the system is cooled down to certain temperatures. This phase, usually abbreviated as $L_{d}$, is found in a variety of mixtures at low temperatures and presents several distinct properties when compared with the parent $L_a$ phase formed at higher temperatures. For most part of the systems upon heating, the $L_{d}$-to-$L_a$ phase transition is accompanied by a decrease in the $d$ values, with a remarkable
diminution around the transition temperature. Such variation is exemplified for the 
(C18)2PE/water system, displayed in Figure 5b, with data calculated based on the results presented in ref. [29]. Even though such an interlamellar spacing variation has been reported for several systems, in some cases, the opposite behavior is seen. Figure 5c displays the results calculated for (C18)2DMABr/water system.[30] In this case, the formation of the \( L_a \) phase is followed by an increase in the \( d \) values, as well as an increase in bilayer thickness, also included in Figure 5c. The variation in the cross-sectional area per surfactant \( \left( s \right) \) in (C18)2DMABr/water system is presented in Figure S2 (Supplementary material), which indicates a decrease in \( s \) when the \( L_a \) phase is formed.

The \( L_a \) and \( L_\beta \) lamellar phases may also display distinct geometric features upon the addition of other substances to the binary surfactant/water systems. The literature is rich in examples of the effect of added components on the aqueous phase behavior of surfactants, with a special focus on lamellar phases. Recently, Gonçalves et al.[31] studied the role of different additives, including urea and butyric acid, on the structural properties of lamellar phases formed in (C18)2DMACl/water systems. The calculated parameters demonstrate the distinct effects of the two additives on the lamellar properties of the system (Table 2). By varying the additive-to-surfactant molar ratios \( (n_a/n_s) \), a significant variation in the cross-sectional areas per surfactant and bilayer thicknesses, for both \( L_a \) and \( L_\beta \) lamellar phases, has been found for butyric acid (Table 2). However, the same parameters showed little variations for urea (Table 2).

Some additives can also induce the formation of \( L_\beta \) phase in surfactant aqueous systems at temperatures where only the \( L_a \) phase is supposed to exist. This is the case of ternary systems formed by poly(alkyltrimethylammonium acrylates), long-chain \( n \)-alcohols and water. Previous reports[32,33] have shown that, at certain decanol concentrations, the \( L_\beta \) phase is formed in these mixtures. Figure 6 shows the calculated cross-sectional areas per surfactant \( (s) \) as a function of \( (n_a/n_s) \) for P(C12TAAcr)30/decanol/water and P(C16TAAcr)30/decanol/water mixtures at 25 \(^\circ\)C. A decrease of \( s \) values as the decanol concentration is increased is seen for both investigated systems, which leads to a remarkable observation that the \( L_\beta \) phase only occurs for small values of \( s \). A similar observation was consistently found for the calculated values of \( s \) in systems formed by hexadecyltrimethylammonium cationic

**Figure 3.** Variation in (A). cell parameters \( (a \text{ or } d) \); (B). radius of the hydrocarbon core \( (r_{hc}) \); and (C). cross-sectional area per surfactant \( (s) \) for the hexagonal \( (H_i) \), bicontinuous cubic \( (V_i) \) and lamellar \( (L_a) \) phases formed as the hydrocarbon volume fraction \( \phi_{hc} \) is increased in CaMal/water mixtures. Data calculated based on the results presented in ref. [24] Gray dashed lines delimitate the boundary between the two phases.
surfactants with oligomeric counterions, decanol, and water, as displayed in Table 3. In all cases, the formation of a \( L_b \) phase was confirmed by wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) measurements.

4. Discussion

4.1. Micellar cubic \( \rightarrow \) hexagonal transition

The micellar cubic (\( I_I \)) phase, belonging to the \( Pm3n \) space group, has been found in several systems composed by surfactants with \( n \) ranging from 8 to 16, at low and intermediate concentrations.\[^{[44]}\] Figure 2a showed how the cubic cell parameter varied near the transition to the hexagonal (\( H_I \)) phase and indicated that, even at very similar compositions, \( a \) values for the \( I_I \) phase are larger. This is, mainly, resulted by the relatively low maximum packing fraction of micelles in the micellar cubic phase, which results in a highly hydrated structure. The packing fraction in the \( Pm3n \) cubic structure is 52.4%, while for the hexagonal phase, it is determined as 90.7\%.[^{[45]}] This means that, for the \( H_I \) phase, the excess aqueous volume to be filled is only 9.3% of the total volume of the unit cell, while for the cubic \( Pm3n \) packing of spherical micelles, it has a high value of 47.6%. Such degree of packing frustration limits the variety of systems forming the reverse \( Pm3n \) micellar cubic phase to very few examples in the literature.[^{[46]}]

Results displayed in Figure 2b for \( \text{ChC}_{12}\text{C}/\text{water mixtures} \) show that, for the micellar cubic phase, \( r_{hc} \) values (nearly 18 Å) are comparable to the length of a fully stretched dodecyl chain (\( l = 17 \) Å), indicating no anomalous variability in the packing of surfactant molecules. For the hexagonal phase, \( r_{hc} \) (\( \sim 16 \) Å) is also in good agreement with the value predicted based on \( l \). In \( \text{KCl}_{12}\text{G}/\text{water system} \) (Table S4, Supplementary material), in which the surfactant also possesses a dodecyl chain, \( r_{hc} \) values (\( \sim 18 \) Å) are also somewhat equivalent to \( l \) in the micellar cubic phase, while in the hexagonal phase the hydrocarbon chains are most likely to be partially folded and/or interpenetrated, giving rise to smaller \( r_{hc} \) values (13 Å).

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[^{[44]}]: This text seems to reference a specific concentration range (8 to 16) for the micellar cubic phase.
[^{[45]}]: The percentage value indicates the packing fraction in the hexagonal phase.
[^{[46]}]: Reference to additional literature or data for reverse \( Pm3n \) micellar cubic phase formation.
When comparing the micellar cubic phases formed by ChC\textsubscript{12}C and KC\textsubscript{12}G surfactants (Figure 2c and Table S4, Supplementary material), in compositions where both systems display the same cell parameters \((a/C_24\text{nm})\), the \(a_s\) values increase with the surfactant molecular volume (which is also computed in the hydrocarbon volume fraction calculation), with KC\textsubscript{12}G displaying larger \(a_s\) values if compared with ChC\textsubscript{12}C, as presented in Figure 7, which shows the predicted \(a_s\) values as a function of \(a\) for surfactants with \(n = 12\) at the specified volume fractions. The plot, based on calculations employing Equation (2), also shows that, for constant molecular volume and concentrations, the \(a_s\) values decrease with \(a\).

4.2. Hexagonal \(\rightarrow\) bicontinuous cubic \(\rightarrow\) lamellar transition

The bicontinuous cubic \((V_I)\) phase, with a \(Ia\bar{3}d\) space group, is often observed to occur between the hexagonal and lamellar phases. To date, this is the only normal bicontinuous cubic structure formed in aqueous surfactant mixtures, since the other reported bicontinuous cubic phases, belonging to the \(Pn\bar{3}m\) and \(Im\bar{3}m\) space groups, were found to consist in reverse structures\([9,10,25]\). A consistent observation for binary

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**Table 2.** Variations in the cross-sectional area per surfactant \((a_s)\) and bilayer thickness \((d_{hc})\) for the \(L\alpha\) (50°C) and \(L\beta\) (25°C) phases formed in \((C_{18})_2\)DMACl/water systems upon addition of urea and butyric acid at different additive-to-surfactant molar ratios \((n_a/n_s)\). \(|\text{dif}|\) is the absolute difference in the structural parameter values when comparing the two additive-to-surfactant molar ratios for both additives. In all cases, \(\phi_{he}\) ranged from 0.353 to 0.438. Data calculated based on the results presented in ref. [31].

| Additive | Urea | Butyric acid |
|----------|------|--------------|
| \(n_a/n_s\) | | |
| 1.4 | 2.8 | | |
| \(a_s\) \((L\beta)\) \((\text{Å})\) | 81 | 84 | 3 | 79 | 70 | 9 |
| \(a_s\) \((L\alpha)\) \((\text{Å})\) | 68 | 70 | 2 | 81 | 72 | 9 |
| \(d_{hc}\) \((L\beta)\) \((\text{Å})\) | 28 | 27 | 1 | 29 | 33 | 4 |
| \(d_{hc}\) \((L\alpha)\) \((\text{Å})\) | 33 | 32 | 1 | 28 | 31 | 3 |
surfactant/water mixtures is that the \( V_j \) is frequently formed in systems comprised of surfactants possessing strong headgroup-headgroup and headgroup-water interactions, essentially held by hydrogen bonding between oxygen groups, fact that may explain the formation of the \( V_j \) phase in carbohydrate- and carbohydrate-based surfactants, as well as in (polymeric) surfactants possessing ethylene oxide and ethylene glycol groups.\[^{13,22,25,39,40}\]

Besides that, a common molecular feature found in surfactants forming the normal bicontinuous cubic phase in water is their relatively small hydrocarbon portion, with the polar headgroup occupying a significant part of the total molecular volume. In C\(_{10}\)Mal/water mixtures (Figure 3), the maltoside polar headgroup, consisting of two glucoside units, displays a great volume if compared with the \textit{dimethylacetyl} hydrophobic segment. A similar enhanced contribution of the polar segment to the total molecular volume is also seen in C\(_{10}\)EO\(_3\)Glu/water mixtures (Figure S1, Supplementary material), in which the surfactant is formed by one glucoside unit connected to a tri(ethylene glycol) group, as the hydrophilic moiety, linked to a \textit{decyl} hydrocarbon tail.

During the \( H_J \rightarrow V_J \rightarrow L_x \) transition, a small variation in the characteristic cell parameters for the \( H_J \) and \( L_x \) phases is seen (Figure 3a). The calculated hexagonal \( d \) value, based on its cell parameter in Figure 3a and the Equation (S5) is \( \sim 35 \) Å, in accordance with the value (32 Å) found for the lamellar phase (Figure 3a), indicating that, although the \( V_J \) phase occurs, the formation of a lamellar phase from a hexagonal liquid crystal involves small variations in the characteristic aggregate dimensions. The \( V_J \) phase, in turn, presents a larger value of cell parameter.

For all phases, \( r_{hc} \) values are in good agreement with the length of a fully stretched \textit{octyl} chain \( (l = 12 \) Å, as calculated by Equation (11)), indicating negligible folding and/or interpenetration of hydrocarbon tails. The C\(_{10}\)EO\(_3\)Glu/water mixtures (Figure S1, Supplementary material) presents a similar behavior, although the lamellar phase displays \( r_{hc} = 8 \) Å for a \textit{decyl} chain with \( l = 14 \) Å, which is reasonable, since linear and longer hydrocarbon chains are more prone to be folded and/or interpenetrated. The \( r_{hc}/l \) ratios, as proposed in ref.\[^{25}\] for each phase (Figure 8) illustrates the general observation for both investigated systems.

A persistent observation regarding the cross-sectional area per surfactant \( (a_s) \) is that it is generally larger for the structures that appear near the \( L_x \) phase. The values, displayed in Figure 3c and (Figure S1c, Supplementary material), indeed, show the \( V_J \) structure displaying the largest \( a_s \) for both C\(_{10}\)Mal/water and C\(_{10}\)EO\(_3\)Glu/water mixtures, with the first presenting the greater area requirement for the highly hydratable and voluminous maltoside groups of C\(_{10}\)Mal at the interface.

### 4.3. Hexagonal \( \rightarrow \) lamellar transition

For the hexagonal-to-lamellar phase transition, the \( a \) values decrease as the cylinders that compose the \( H_J \) phase approach to each other, as well as the \( d \) values in the \( L_x \) phase, due to the closer approach between the bilayers. The transition from a 2D cylinder-like structure to a 1D phase formed by stacked surfactant bilayers seems to involve the fragmentation of the initial hexagonal liquid crystal, and a decrease in radius of hydrocarbon core \( (r_{hc}) \) as demonstrated in Figure 4c. These observations indicate that the cylinders fragmentate, owing to the loss of hexagonal order, resulting in a progressing fusion of cylinders, giving rise to the bilayered lamellar phase.\[^{47}\]

The lamellar phase formed \textit{directly} from the hexagonal structure may display remarkably similar \( d \) values if compared with the former 2D phase. Such observation is corroborated by calculating the hexagonal \( d \) value using its cell parameter in the two-phase region of Figure 4a, and Equation (S5). The obtained value of \( d = 37 \) Å is in good agreement with the value for the lamellar phase \( (\sim 35 \) Å) for the same composition (Figure 4a). For C\(_{14}\)mimCl/water (Table S5, Supplementary material), the \( d \) values for the coexisting hexagonal and lamellar phase are ca. 28 Å. A quick view into other works involving the hexagonal-to-lamellar phase transition in ternary mixtures of 1-alkyl-3-methylimidazolium bromides/p-xylene/water\[^{48}\] and Tween

### Table 3. Variation in the \( d \) values and cross-sectional area per surfactant \( (a_s) \) as a function of additive-to-surfactant molar ratios \( (n_a/n_s) \) for the \( L_x \) and \( L_a \) phases formed in surfactant/decanol/water system at 25 °C. \( \phi_{hc} \) ranged from 0.340 to 0.580. Data calculated based on the results presented in ref.\[^{33}\].

| Surfactant          | \( n_a/n_s \) | Lamellar phase | \( d (\text{Å}) \) | \( a_s (\text{Å}^2) \) |
|---------------------|---------------|----------------|-------------------|---------------------|
| \((C_{16}TA)_{2}SUc\) | 4.5           | \( L_a \)      | 45 (\( L_a \))    | 48 (\( L_a \))     |
| \((C_{16}TA)_{4}Ox\) | 8.8           | \( L_a \)      | 50 (\( L_a \))    | 51 (\( L_a \))     |
| \((C_{16}TA)_{3}Cit\) | 13.2         | \( L_x \)      | 53 (\( L_x \))    | 55 (\( L_x \))     |
| \((C_{16}TA)_{2}Ox\) | 13.2         | \( L_x \)      | 56 (\( L_x \))    | 57 (\( L_x \))     |
| \((C_{16}TA)_{2}BTA\) | 19.0         | \( L_x \)      | 59 (\( L_x \))    | 60 (\( L_x \))     |
| \((C_{16}TA)_{2}Cit\) | 10.4         | \( L_x \)      | 56 (\( L_x \))    | 58 (\( L_x \))     |
| \((C_{16}TA)_{2}BTA\) | 17.7         | \( L_x \)      | 59 (\( L_x \))    | 60 (\( L_x \))     |
80/ethyl oleate-fish oil/water mixtures also corroborate the findings.

The smaller lamellar characteristic cell parameter, if compared with the one of the hexagonal phase, at similar compositions, is related to the higher packing fraction of the $L_a$ phase ($\phi_{hc}=0.464$) or $a_{hc}=88\text{Å}$ and $V_{hc}=623\text{Å}^3$). The analysis of the radius of hydrocarbon core ($r_{hc}$), displayed in Figure 4b, seems to indicate that the hydrocarbon chains of the surfactant may be highly folded or even interpenetrated in the hexagonal and lamellar structures. In both phases, $r_{hc}$ values are smaller than the length ($l$) of a fully stretched dodecyl chain, calculated as $17\text{Å}$ by Equation (11). However, the $r_{hc}$ values are twice as large, at some concentration ranges, for the $H_I$ phase as for the $L_a$ phase (Figure 4b).

The surfactant alkyl chains are less likely to be folded and/or interpenetrated in the hexagonal phase due to the increase, at a great extent, in the (entropic and/or electrostatic) repulsion between the polar headgroups, since the arrangement possesses a circular cross-sectional area, in which the diminution of the radius of hydrocarbon core would imply closer contacts between the hydrophilic moieties. The formation of lamellar phases with interpenetrated hydrocarbon chains is often described in the literature and will be detailed in the following topic.

Figure 7. Predicted values of cross-sectional areas occupied by the surfactant ($a_s$) versus the Pm3n micellar cubic cell parameter ($a$) for the specified surfactant molecular volume ($V_s$) and volume fractions ($\phi_{hc}$). The obtained $a_s$ values for $\text{ChC}_9\text{C}/\text{water} (V_s=507\text{Å}^3; \phi_{hc}=0.351; a=88\text{Å})$ and $\text{KC}_{12}\text{G}/\text{water} (V_s=623\text{Å}^3; \phi_{hc}=0.314; a=88\text{Å})$ mixtures are also included as the open and filled triangle points, respectively.

Figure 8. Variation in the ratios of radius of hydrocarbon core-to-surfactant hydrocarbon length ($r_{hc}/l$) within the $H_I-V_I-L_\alpha$ transition observed in $\text{C}_9\text{Mal}/\text{water}$ and $\text{C}_{10}\text{EO}_3\text{Glu}/\text{water}$ mixtures. Dashed black lines are guide to the eyes.

Figure 9. Predicted values of cross-sectional areas occupied by the surfactant ($a_s$) as a function of the number of carbon atoms in the hydrocarbon chain ($n$) in hexagonal phase with $a=33\text{Å}$ and $\phi_{hc}=0.464$ (black full line), in lamellar phase with $d=25\text{Å}$ and $\phi_{hc}=0.600$ (black dashed line), in hexagonal phase with $a=47\text{Å}$ and $\phi_{hc}=0.320$ (gray full line), and in lamellar phase with $d=28\text{Å}$ and $\phi_{hc}=0.652$ (gray dashed line). The calculated $a_s$ values for $\text{NaC}_{12}\text{EO}_3\text{S-NaC}_{12}\text{BzS}/\text{water}$ ($n=12$) and $\text{C}_{10}\text{mimCl}/\text{water}$ ($n=16$) mixtures are also included. The open symbols agree with the predicted values for $\text{C}_{10}\text{mimCl}/\text{water}$ (full and dashed black lines). The filled symbols do not meet the full and dashed gray lines, for $\text{NaC}_{12}\text{EO}_3\text{S-NaC}_{12}\text{BzS}/\text{water}$ mixtures.
4.4. Lamellar ($L_a$) → lamellar ($L_b$) transition

The usual swelling behavior for lamellar phases upon dilution is presented in Figure 5a (open points followed by black dashed lines) for the $L_a$ phase of (C$_{18}$)$_2$DMABr/water system at 25 °C. The increase in water concentration is followed by a linear increase in the $d$ values, with $d \propto \varphi_{hc}^{-1}$ (red dashed line in Figure 5a). By reaching the maximum swelling, a macroscopic phase separation is seen, thus forming a two-phase system, ($L_a$ + excess water), and the $d$ values remain essentially unchanged. Otherwise, water uptake above the swelling limit would cause the disruption of the structure. The calculated $d$ values (blue dashed line in Figure 5a) using the Equation (8) and the bilayer thickness ($d_{hc}$) equal to 34 Å, corresponding to twice the length of the fully stretched dodecyl chain ($l \sim 17$ Å), as estimated by Equation (11), do not agree with the experimental values. The slope of the linear fit gives an experimental value for $d_{hc}$ equal to 23 Å, which corresponds to ca. 70% of the expected value.

The lamellar $L_a$ phase contains the surfactant alkyl chains in a disordered, or liquid-like, state, displaying great molecular motion, thus providing thinner bilayers. Due to the high mobility of the hydrocarbon chains, the $L_a$ phase is usually named as fluid phase and presents enhanced water uptake and diffusion of other molecular and ionic species. Based on these characteristics, the $L_a$ phase is widely used as a model membrane for biological studies, as well as vehicles for encapsulation and delivery of substances, where, in both cases, the phase is used in the dispersed state, that is, vesicles (also refereed as liposomes or niosomes, depending on the lamellar-forming component).

A lamellar phase with “solid-like” chains, $L_b$, is formed by cooling the $L_a$ phase below a transition temperature, abbreviated as $T_{trans}$, which corresponds to the melting of the surfactant hydrocarbon chain. The $L_b$ phase, also referred to as gel or z-gel phase, is highly ordered, viscous, and opaque, thus being employed as rheology modifier in several commercial formulations. Due to its highly ordered packing of hydrocarbon chains, the $L_b$ phase is further characterized by a sharp peak in WAXS with a $d$-spacing of 4.2 Å, corresponding to the hexagonal packing of the surfactant chains.

The variation of $d$ values in the $L_b$-$L_a$ transition may display dissimilarities depending on the investigated system. For (C$_{18}$)$_2$PE/water mixture, at a constant water content, the lamellar spacing decreases as the fluid phase is formed with the increase of temperature (Figure 5b). This can be understood because in the gel phase, the highly ordered alkyl chains are fully, or almost fully, extended, displaying rigid all-trans configuration, thus forming thicker bilayers. The alkyl chains in the fluid phase, having configurations with gauche states, provide to the lamellar liquid crystal smaller $d$ values, as depicted in Figure 10.

Nevertheless, structural features, involved in lamellar phase formation, can change such expected behavior. Figure 5c shows the variation of $d$ and bilayer thickness, $d_{hc}$, for the $L_b$-$L_a$ transition in a (C$_{18}$)$_2$DMABr/water mixture, at a constant water content. The plot clearly shows an opposite trend, with $d$ values increasing as the $L_a$ phase is formed, indicating an alternative chain packing or orientation in the initial phase ($L_b$). The simplest explanation of such deviation commonly found in the literature is because the hydrocarbon chains can be interdigitated, tilted or in both states. The tilted and interdigitated gel ($L_b$) phase, caused by several factor, including electrostatic repulsion between neighboring charged headgroups, is characterized by the interpenetration among the alkyl chains, thus forming thinner bilayers (Figure 5c) and decreased cross-sectional areas (Figure S2, Supplementary material). A schematic representation of this interdigitated and tilted $L_b$ arrangement is shown in Figure 10. Interestingly, for both $L_b$ or $L_b$ gel phases formed in (C$_{18}$)$_2$DMABr and (C$_{18}$)$_2$PE aqueous systems, a variation of ca. 12% in the $d$ values was observed, considering the data available near the transition to the $L_a$ phase.

The addition of a third component may also cause structural variations in lamellar phases formed by surfactant/water systems depending on its molecular characteristics. The effect of urea addition on the $L_b$-$L_a$ transition can change such expected behavior. Figure 5b shows the variation of $d$ and bilayer thickness, $d_{hc}$, for the $L_b$-$L_a$ transition in a (C$_{18}$)$_2$DMABr/water mixture, at a constant water content. The plot clearly shows an opposite trend, with $d$ values increasing as the $L_a$ phase is formed, indicating an alternative chain packing or orientation in the initial phase ($L_b$). The simplest explanation of such deviation commonly found in the literature is because the hydrocarbon chains can be interdigitated, tilted or in both states. The tilted and interdigitated gel ($L_b$) phase, caused by several factor, including electrostatic repulsion between neighboring charged headgroups, is characterized by the interpenetration among the alkyl chains, thus forming thinner bilayers (Figure 5c) and decreased cross-sectional areas (Figure S2, Supplementary material). A schematic representation of this interdigitated and tilted $L_b$ arrangement is shown in Figure 10. Interestingly, for both $L_b$ or $L_b$ gel phases formed in (C$_{18}$)$_2$DMABr and (C$_{18}$)$_2$PE aqueous systems, a variation of ca. 12% in the $d$ values was observed, considering the data available near the transition to the $L_a$ phase.

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with few carbon atoms more and a charged carboxyl group, is mostly located among the surfactant molecules at the bilayer-water interface, changing the packing structure, decreasing the interdigitation, as evidenced by the variation in the cross-sectional area, followed by an increase in bilayer thickness (Table 2). In this case, butyric acid can be classified as a cosurfactant.

Some additives that act as cosurfactants can also favor the formation of the $L_\beta$ phase when added to aqueous surfactant mixtures displaying only the lamellar fluid ($L_\alpha$) phase at a given temperature. It is widely reported in the literature that middle- and long-chain alcohols may induce the formation of gel phases for glycolipids.[30] These results indicate that the $L_\beta$ phase is formed upon addition of decanol, at 25 °C, in the $L_\alpha$ phase of different surfactant/water/decanol systems: A: P(C_{12}TAAcr)$_{30}$; B: P(C_{16}TAAcr)$_{30}$; C: (C$_{16}$TA)$_2$Suc; D: (C$_{16}$TA)$_2$Ox; E: (C$_{16}$TA)$_3$Cit; F: (C$_{16}$TA)$_3$BTA. Values calculated based on the data presented in Figure 6 (last point for $L_\alpha$ and first point for $L_\beta$) and Table S4.

5. Concluding remarks and perspectives

The analysis of the geometric parameter variations as different liquid crystalline phases are formed in surfactant systems leads to several findings, being the most important:

- the cell parameters ($a$ or $d$), at similar compositions, are larger for the mesophases with lower packing fraction of small micelles, with the micellar cubic and lamellar (fluid and gel) phases displaying the largest and smallest values, respectively;
- the lamellar fluid phase is formed by a rearrangement of the hexagonal phase, with its structure resembling characteristics of the 2D former structure, as seen by their similar $d$ values even though a bicontinuous cubic structure appear between both phases;
- the radius of hydrocarbon core ($r_{hc}$) can be similar, larger, or smaller than the length of the fully stretched surfactant chain. Mesophases with lower curvature are more prone to display smaller $r_{hc}$ values, indicating the folding and interpenetration of hydrocarbon chains to a greater extent;
- such a high interpenetration of hydrocarbon chains can dramatically change the variations in the geometric distances of the lamellar phases, with their characteristic molecular parameters being highly dependent on the organization of hydrocarbon chains in the bilayers;
- added components can change the molecular organization in surfactant mesophases depending on how much they are partitioned to the hydrocarbon core and to the aqueous domain;
- the lamellar gel phase is favored by a substantial decrease in the cross-sectional areas per surfactant, thus resulting in the high packing of hydrocarbon chains;
- the geometric parameters of complex structure of the bicontinuous cubic phase do not follow the trends generally predicted by the surfactant phase behavior theories.

Lyotropic liquid crystalline phase formation by amphiphiles, in both bulk and dispersed (i.e., particle dispersions) states, are important for applications in several fields including product formulations, as well as for studies in systems formed by, for example, polyelectrolytes[55] and metal nanoparticles,[56] and in complex phenomena, such as lipid digestion[57] and coacervation.[58] Surfactant liquid crystals can be influenced by a variety of factors, apart from the amphiphile molecular structures covered in the current approach, including the type of solvent, headgroup-headgroup interactions, counterion specificity and presence of electrolytes. Thus, a deep understanding on mesophase formation, considering several different factors, is of great importance for prospecting surfactant formulations and supporting new technological applications.

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Disclosure statement

No potential conflict of interest was reported by the author.

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