Elucidating the effect of additives on the alkyl chain packing of a double tail cationic surfactant

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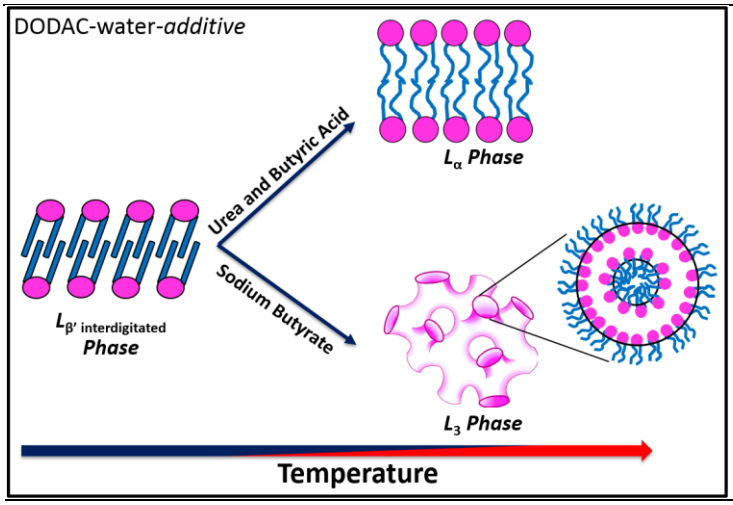
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Some low molecular weight additives can strongly influence the phase behavior of aqueous surfactant systems, and this offers an important handle to control the properties of surfactant solutions and thus to optimize various formulations concerning stability and performance.
Experiments: The surfactant dioctadecyldimethylammonium chloride (DODAC) self-assembles into two lamellar phases in water, the gel phase (L_β) and the liquid crystalline phase (L_α). Here, we present approaches to tune the gel-to-liquid crystalline transition temperature (T_m) with the use of additives. The effects of urea, sodium butyrate and butyric acid on the packing behavior of DODAC were determined. The surfactant phases were characterized using polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small/wide angle X-ray scattering (SWAXS).
Findings: Added urea, sodium butyrate and butyric acid yield a single and stable lamellar phase. Whereas urea and sodium butyrate have only minor effects on T_m, butyric acid gives a large decrease, thus stabilizing the L_α phase with respect to the L_β phase. From the bilayer thickness of the gel phase an interdigitated or tilted packing of the surfactant molecules is indicated. Addition of sodium butyrate gives a strongly interdigitated gel structure and a transition from lamellar liquid crystal to an isotropic L_3 phase.

1. Introduction

Amphiphilic molecules, such as surfactants and polar lipids, can be used for many novel health-care and personal-care applications as solution behavior modifiers [1-5]. Since the first investigations by Kunieda and Shinoda [6] on the solution behavior of long di-alkyl quaternary ammonium salts, there has been much work done to understand the properties of the bilayer structures that dominate the phase diagrams of the binary surfactant-water systems [3, 7-9]. Two types of lamellar structures are found for these systems – the lamellar gel phase (L_β) with highly ordered alkyl chains with little conformational freedom, and the lamellar liquid crystalline phase (L_α) characterized by liquid-like properties of the alkyl chains. The first phase diagram of dioctadecyldimethylammonium chloride (DODAC) in solution was established by Kunieda and Shinoda, and it was found that DODAC and other cationic surfactants with two long alkyl chains displayed relative high stability of the two phase solution, only splitting into two phases with the aid of centrifugation [6]. Laughlin et al. had also performed in-depth studies on the phase behavior of the DODAC-water system [10-12]. They observed the presence of lamellar liquid crystalline phase coexisting with water at temperatures above 45 ^oC, with the surfactant molecules spontaneously self-assembling in bilayer structures. When the solution temperature exceeded 45 ^oC, they also identified a single and stable lamellar phase at a surfactant concentration of around 33 wt. % up to nearly 90 wt. %. The phase behavior of ionic surfactants has enabled them to be potentially useful as drug carriers, wetting agents, and anti-static agents [13]. Carmona-Ribeiro et al. explored the colloidal stability of DODAC vesicles in the presence of electrolytes and microspheres as well as the effect of pH [14-16]. It was found that the bilayers in the fluid-like phase can vary their shape depending on the conditions, whereas in the gel phase the vesicles are more resistant to deformation. Furthermore, the vesicle instability can be related to the asymmetry of charge distribution. Feitosa et al. presented several studies on bilayer surfactant systems in solution and demonstrated variations in the gel-to-liquid transition temperature (T_m) for DODAC in solution with the method of preparation [17-23] in the range between 37.5 and 48 ^oC. The focus in the work was on bilayer-type aggregates in dilute solutions. Recently, Goto et al. [24, 25] confirmed that the gel-to-liquid transition from a stable gel phase (L_β) to a stable liquid crystalline phase (L_α) occurs at 40 ^oC. An increase in the phase complexity with increasing number of carbons in the alkyl chains was also shown [24]. Kodama et al. [26] conducted an investigation in the concentrated regime and established a T_m of 46 ^oC for samples with 80 – 15 wt. % DODAC. Although extensive work reports that DODAC forms lamellar structures, the phase identification is not consistent across various studies in the literature [18, 25, 26], indicating that phase stability, and concentration effects remain ambiguous. In addition, investigations on the DODAC-water phase behavior in the high concentration regime where only the pure lamellar phase exists, without any co-existence of a water phase, are largely lacking.

Double-chain cationic surfactant systems are expected to display many analogies with other double-chain amphiphile systems. Among these amphiphiles, phospholipids, and notably lecithin, have received huge amount of attention and are the most studied in this category. It is for example well known that small polar additives with low vapor pressure may modulate the bilayer structure of this family of surfactants. Considerable work has been reported on the effect of small polar additives on liquid crystalline structures of lipids and block copolymers as well as on the stabilization of the amphiphilic aggregates [2-5, 27-29]. Most significantly, Costa-Balogh et al. demonstrated that the presence of urea has the effect of favoring the liquid crystalline structure of a series of double chain amphiphile systems in solution [2]. In their work, the phase behavior and the interlamellar spacing were determined. In particular, a decrease in the T_m with urea addition to the lecithin system was demonstrated. Furthermore, Björklund et al. showed the potential of urocanic acid and pyrrolidone carboxylic acid in increasing the alkyl chain mobility, resulting in a T_m decrease which can be attributed to the additives residing in the non-polar domains of the lamellae [5]. Sparr and Wennerström also studied the interlamellar forces of a lamellar phospholipid system. They also analyzed the thermodynamic properties and how they relate to the molecular mechanisms of the swelling of the discussed lamellar phases. Hence, the lamellar swelling was found to be entropically driven and the presence of polar solutes resulted in a long-ranged interlamellar repulsion force [3, 30]. Such polar molecules act as stabilizers of the L_α phase, showing a higher swelling potential than the L_β phase [4]. Therefore, many studies have shown the effects of different molecules on the lamellar structure. Depending on their location in the lamellar structure, the additives affect the lamellar structure packing differently. Most of these studies were done on a zwitterionic amphiphile, lecithin, revealing different interactions between the additive and the polar head-group of the surfactant.

We hypothesize that by perturbing the alkyl chain mobility, while keeping the lamellar integrity, with the help of additives we should observe a decrease in the T_m of the ternary DODAC-additive-water systems compared to the binary DODAC-water system. Since the currently used double-tail quaternary ammonium surfactants have relatively high T_m, limiting their applicability, and the effect of additives on the phase behavior has been little investigated, the aim of this work is to provide a model for better understanding of the location of additives and its role in destabilizing and hence reduce the L_β-L_α temperature transition. In view of this we focus on the effects of three additives of quite different nature, urea, butyric acid, and sodium butyrate, on the DODAC lamellar structure. More importantly, we focus on the molecular organization and the effects on the gel-to-liquid phase transition of these three substances in the high concentration regime.

2. Experimental

2.1 Sample preparation

Dioctadecyldimethylammonium chloride (DODAC, 96.7 % purity) was supplied by Evonik Corporation, USA. Urea and sodium butyrate were purchased from Tokyo Chemical Industry Co., Ltd., Japan, while butyric acid was purchased from Sigma-Aldrich, Singapore. These materials were used as received. Ultrapure water of 18 mΩ conductivity was used to prepare the samples.

For the ternary systems, we adopted the fixed surfactant concentration of 35 wt. % corresponding to a pure lamellar phase with no water coexistence, according to the DODAC-water phase diagram [6, 12]. The additives and water, at 80 ^{o}C, were added to the melted surfactant in 20 ml transparent screw-cap glass vials. The samples were prepared with concentrations of additive from 1.3 to 20.0 % in weight. Sample homogeneity was attained using a vortex mixer at 80 ^{o}C followed by a slow cooling down, at a rate of 1 ^{o}C min^{-1} according to the procedure described in Ref. [25]. All the samples were equilibrated at room temperature for, at least, seven days before characterization.

2.2 Polarized optical microscopy

The observation of characteristic optical birefringence patterns [31, 32], due to sample anisotropy, illuminating the samples under crossed polarizers was attained using an Olympus BX53 (Olympus Corporation, Japan) optical microscope with a polarizer filter.

2.3 Differential Scanning Calorimetry

The gel-to-liquid crystalline phase transition temperature (T_m) was determined by using a DSC TA Q10 differential scanning calorimeter (TA Instruments, USA) using a heating rate of 2 ^{o}C min^{-1} from 10 ^{o}C to 60 ^{o}C. The enthalpy of phase transition (ΔH_m) and the width at half-height ($\Delta T_{1/2}$) of the transition peak were obtained by integrating the endothermic peak area by use of the software TA Universal Analysis (TA Instruments, USA). The shape of the main transition peak provides additional information about the phase transition and the $\Delta T_{1/2}$ is associated with the cooperativity of the transition. Thus, the higher the cooperativity, the narrower is the peak. Thermograms under cooling were collected in the same run demonstrating the existence of hysteresis.

2.4 Small/wide angle X-ray scattering

The interlayer spacing (d_{sp}) determination was carried out using a small/wide angle X-ray scattering (SWAXS) system. The measurements were conducted on a SAXSess camera (Anton Paar, Graz, Austria) with a Cu anode X-ray source (PANalytical, PW3830) operating at 40 kV and 50 mA. Cu Kα radiation of

wavelength 0.154 nm was used. The X-ray radiation source is collimated to a line-shaped beam. The sample-to-detector distance was 265 mm. For effective and reliable data collection, the system was kept under vacuum during all measurements minimizing the background scattering. For all samples, the measurements were done at temperatures both below and above the gel-to-liquid crystalline transition temperature. Therefore, the temperature was kept constant at 25 ºC and 50 ºC with a Peltier element. The position of the peaks, for lamellar symmetry, should obey the relationship 1 ÷ 2÷ 3 ÷ …. The interlayer spacing, d_{sp}, is given directly by the position, q^*, of the first and most intense diffraction peak.

3. Results and Discussion

3.1 Conformational analysis

As shown in Fig. 1, the surfactant system was assumed to comprise two regions, the bilayer – containing the surfactant hydrocarbon chains and the non-polar fractions of the additives; and the water layer – containing the water, the surfactant head-groups, the counterions and the polar fraction of the additives.

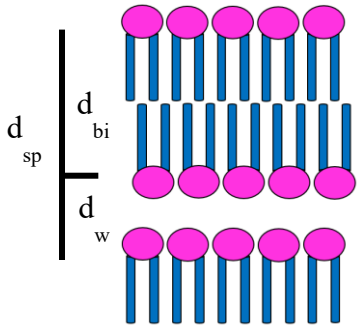

Fig. 1 – Schematic representation of the surfactant lamellar L_β phase packing structure. d_{sp} – interlayer spacing, d_{bi} – bilayer thickness, d_w – polar domain thickness.

Structural parameters of the lamellar phase, such as the interlayer spacing (d_{sp}), the bilayer volume fraction (ϕ_{bi}), the area per polar head-group (a), and the bilayer thickness (d_{bi}), were calculated from SWAXS results, using the following equations [33]:

$$d_{sp} = \frac{2\pi}{q^*} \quad (1)$$

$$q^* = \frac{2\pi}{d_{sp}} = 2\pi\frac{\phi_{bi}}{d_{bi}} = \pi\frac{\phi_{bi}a}{v_{bi}} \quad (2)$$

where q^* is the first-order Bragg peak; ϕ_{bi} is the volume fraction of the total hydrophobic constituents, and v_{bi} is the molar volume of the total amphiphiles present in the bilayer.

The non-polar domain only contains the hydrophobic segments of the surfactant and additives so therefore the ϕ_{bi} can be calculated as [33]:

$$\phi_{bi} = \frac{v_{hc,S} \times \frac{w_S}{M_S} + v_{hc,Add} \times \frac{w_{Add}}{M_{Add}}}{v_S \times \frac{w_S}{M_S} + v_{Add} \times \frac{w_{Add}}{M_{Add}} + v_W \times \frac{w_W}{M_W}} \quad (3)$$

where *w* is the weight fraction, and *M* is the molar mass of the various components denoted as surfactant (*S*), additive (*Add*) and water (*W*); v is the molecular volume given by the sum of the partial molar volume of the hydrocarbon chain (*hc*) and the polar head-group of the molecule. To analyze the SWAXS results we used $v_{hc,S}$ = 1026 Å^3 [34], $v_{hc,sodium\ butyrate} = v_{hc,butyric\ acid}$ = 108 Å^3 [34], v_S = 1126 Å^3 [35], v_{urea} = 74 Å^3 [35], $v_{sodium\ butyrate} = v_{butyric\ acid}$ = 140 Å^3 [36], and v_W = 30 Å^3 [33].

3.2 The binary DODAC-water system

3.2.1 Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were carried out to determine the thermal behavior of the surfactant samples and track the changes in phase behavior. Upon increasing the temperature, a transition from a solid-like to a fluid-like state (L_β-L_α) occurs with the disorder of the alkyl chains increasing. Specifically, a stable planar lamellar structure exhibits a single and relatively broad endothermic peak upon its gel-to-liquid crystalline phase transition (T_m). Table 1 comprises the results obtained after DSC data treatment.

Table 1

Values for the gel-to-liquid crystalline phase transition temperature (T_m) and the enthalpy of phase transition (ΔH_m) for the DODAC-water system.

Composition / wt. %		T_m / °C	ΔH_m / kJ mol^{-1}
DODAC	water		
5.0	95.0	45.5	37.6
7.5	92.5	45.4	39.0
10.0	90.0	46.3	40.2
12.5	87.5	46.2	42.6
15.0	85.0	45.6	40.3
17.5	82.5	45.2	40.9
20.0	80.0	45.5	42.4
22.5	77.5	45.6	38.8
25.0	75.0	45.9	40.2
30.0	70.0	45.6	40.9
32.5	67.5	46.0	42.8
35.0	65.0	45.6	37.5
37.5	62.5	45.4	37.8

The observed value for the enthalpy of the phase transition is in agreement with previously reported results, 40.1 kJ mol^{-1} [25]. The L_α to L_β phase transition temperature was determined to be 45.7 °C, similar to published studies, where a significant variation of the T_m with varying surfactant concentration was not observed [26]. The effect of the concentration was only observed for samples with a concentration below

2mM [18]. Neither the enthalpy per mole of surfactant nor the transition temperature show any significant change with the surfactant concentration suggesting that the surfactant packing is not affected on changing the thickness of the water layers between the surfactant bilayers. To understand how the packing is affected by additives, one has to look at the scattering data. Since concentration has very little effect on the phase transition, we look at structural behavior of the system at a concentration where only one single phase exists, and in this case the concentration is 35 wt. %.

3.2.2 Small/wide angle x-ray scattering (SWAXS)

The structural organization in the samples was analyzed using small and wide angle X-ray scattering at temperatures below (25 °C) and above (50 °C) the T_m. Fig. 3 shows the SWAXS patterns collected from 35 wt. % DODAC in water. Looking at the peak ratio in the small angle region, the presence of a long-range ordered structure can be observed. The characteristic birefringence of anisotropic surfactant samples was visible via polarized optical microscopy. Together with the observation of Bragg reflections of ratio 1 ÷ 2÷ 3 ÷ … [37], the lamellar nature of the surfactant systems was confirmed.

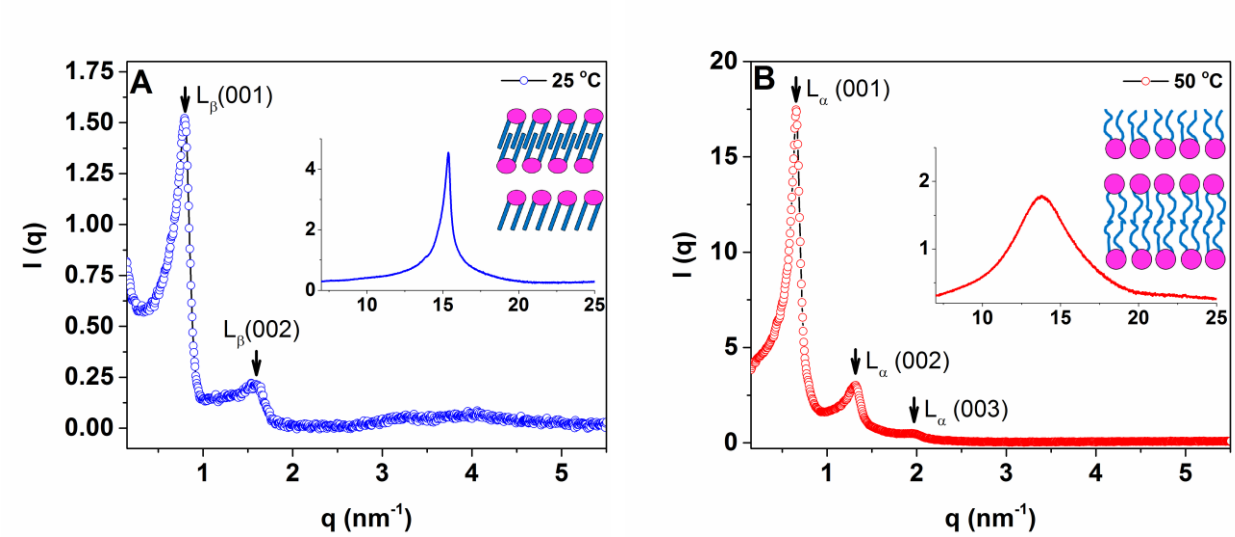

Fig. 2 – SWAXS diffraction profiles for the sample 35 wt. % DODAC – 65 wt. % water: (A) L_β phase, 25 °C; (B) L_α phase, 50 °C.

At 25 °C, the surfactant system is below the T_m (45.6 °C). The sharp peak at 15.4 nm^{-1} corresponds to the alkyl chain-to-chain distance in the gel phase (L_β), 4.1 Å. Above the T_m, at 50 °C, a peak broadening was observed and a slight shift to lower *q* values, 13.7 nm^{-1}, indicating the transition to a liquid crystalline phase (L_α), with a larger hydrocarbon chain-to-chain separation of 4.6 Å [38, 39]. These results are shown in Fig. 2 and it is possible to deduce that the L_β and L_α phases exist below and above the T_m, respectively.

Small angle X-ray diffraction patterns of the lamellar structures of the L_β and L_α phases can be confirmed and are in agreement to what is observed generally for these phases [40]. The d_{sp} increases with the water content for both phases; this corresponds to an increased thickness of the water layers. This

observation is in general as expected for an ionic surfactant, there is large water uptake and swelling; this can be understood from the electrostatic repulsions, mainly the counterion entropy [39, 41].

A comparison between the two phases reveals an interesting difference: d_{sp} values are throughout larger for the liquid crystalline phase. On melting of the surfactant layers there is a change in the conformation of the alkyl chains of the surfactant from an all-trans state to a more disordered one. This would lead to a shorter end-to-end distance of the alkyl chains and an increase in the effective cross-section area. If in the L_β phase, the hydrocarbon chains would adopt a conformation perpendicular to the interface, we predict higher d_{sp} values than those observed for the L_α phase. Thus, the gain in chain mobility in the L_α phase should result in Bragg reflections at higher q values, corresponding to smaller d_{sp} values. However, our results show an opposite behavior, which indicates an alternative chain packing or orientation in the L_β phase. The simplest interpretation of these deviations is that there is interdigitation or tilting of the hydrocarbon chains in the L_β phase, or a combination of these. The existence of a mismatch between the cross-sectional areas of the hydrocarbon chains and the head-group may force the bilayer to change the conformation, avoiding unfavorable interactions [39]. A schematic representation of a possible arrangement is shown in Fig. 3.

In order to study the location of the additives, a structural packing analysis is first performed. The structure of these lamellar phases can be analyzed using different methods and we have included the alternative method in the supportive information. As no major differences between the results from the two methods, Montalvo and Khan method [33] was used, where partial molar volumes were used to define the volumes of the surfactant systems. The values for the thickness of the surfactant bilayer as well as the effective area per surfactant molecules can be calculated. The bilayer thicknesses found are 28 Å at 25 ºC and 33 Å at 50 ºC, and the head-group areas are 81 and 68 $Å^2$ at 25 ºC and 50 ºC, respectively.

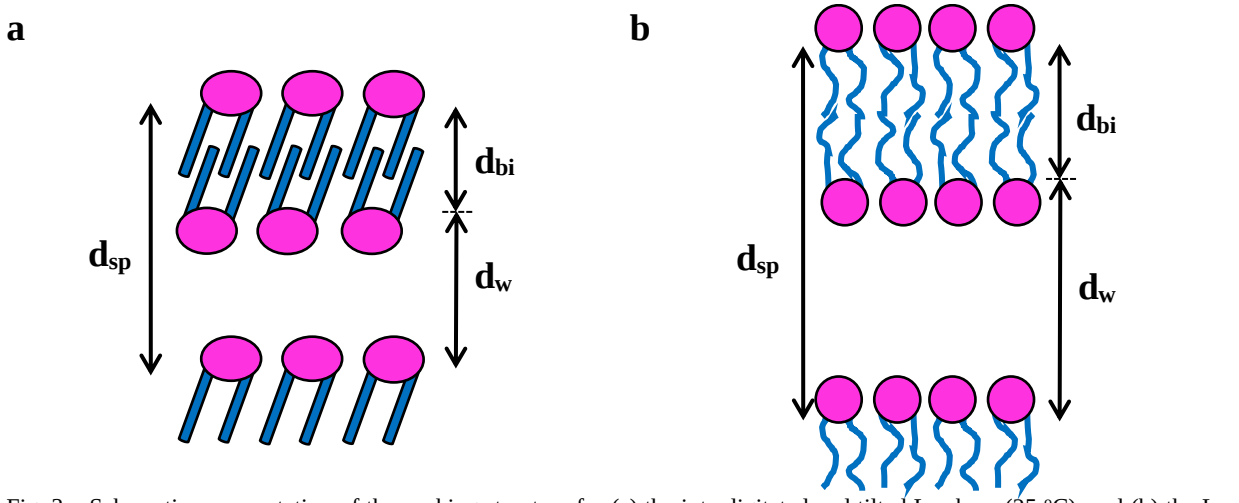

Fig. 3 – Schematic representation of the packing structure for (a) the interdigitated and tilted L_β phase (25 ºC), and (b) the L_α phase (50 ºC) of the studied surfactant systems.

As mentioned, we can expect an increase in the hydrocarbon chain mobility when the temperature is increased and this would result in a decrease of the bilayer thickness and an increase in the area per head-group [7]. However, our results showed a different behavior. The calculated bilayer thickness at 50 ^{o}C of 33 Å is in good agreement with the expected decrease of around 30% of the bilayer thickness from solid-like to fluid-like hydrocarbon state if the chains are in an all-trans conformation and perpendicular to the interface in L_{β} phase [42]. As said, the smaller bilayer thickness for the L_{β} compared to L_{α} phase, might be attributed to a significant tilting and/or interdigitation of the alkyl chains in the gel phase.

The underlying interactions for this phenomenon are not clear at this stage, but mismatches between the cross-sectional areas of the chains and the head-group could lead to variations in the critical packing parameter [43]. If the effect is ascribed to tilting alone, the tilting angle of a hydrocarbon chain must be about 54^{o}, which seems to be an extremely large angle. Therefore, we suggest the existence of a tilted and interdigitated structure in the gel phase ($L_{\beta}{}'_{int}$), as schematically shown in Fig. 3 (a).

3.3 The DODAC-additive-water ternary systems

As mentioned earlier, the effect of additives on the surfactant systems is of fundamental interest and also significant for applications, such as in personal-care application where formulations are complex mixtures. In our studies we have investigated a large number of low molecular weight additives and found quite different types of physico-chemical behavior. In this paper, we will present the results for three additives showing distinctly different characteristics, namely urea, butyric acid and sodium butyrate.

3.3.1 Differential scanning calorimetry (DSC)

The effect of additives on T_m was investigated using DSC. Fig. 4 displays the DSC thermograms of DODAC-additive-water ternary systems, and the various parameters obtained are presented in Table 2. As can be seen from Fig. 4, regardless of the chemical nature of the additive present in the system, only one endothermic phase transition peak was observed. Urea and sodium butyrate had very little effect on the T_m whereas butyric acid displayed a striking ability to lower the transition temperature. For urea and butyric acid, it was established that the phase transition is the same as that observed for the binary surfactant system, i.e. from L_{β} to L_{α}. This was determined using X-ray scattering, which will be discussed below. We also note that with increasing amount of butyric acid the transition becomes less well defined. With 20% of butyric acid the L_{β} phase is not formed; instead there is a macroscopic separation into two phases, the major phase being a clear liquid phase. For sodium butyrate, L_{α} is not formed on melting. The identity of the phase formed is discussed below.

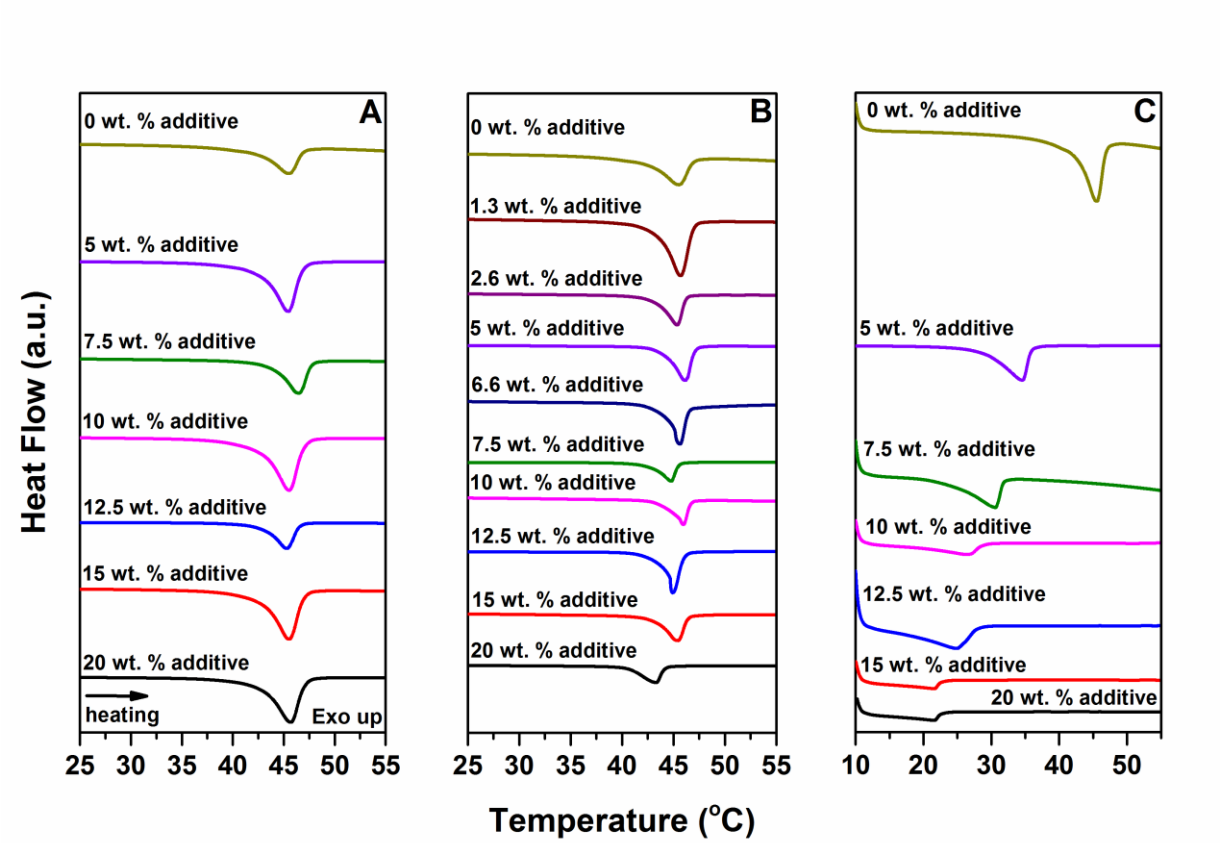

Fig. 4 – Stacked plots of thermograms under heating for the samples 35 wt. % DODAC-water with additives replacing water from 0 wt. % of additive to 20 wt. % of additive. **(A)** – urea; **(B)** – sodium butyrate; **(C)** – butyric acid.

Table 2
Values for the gel-to-liquid crystalline phase transition temperature (T_m) and the enthalpy of phase transition (ΔH_m) for DODAC-additive-water ternary systems.

	Composition / wt. %			T_m / °C	ΔH_m / kJ mol^{-1}
	DODAC	additive	water		
	35.0	0.0	65.0	45.6	37.5
Urea	35.0	5.0	60.0	45.8	42.6
	35.0	7.5	57.5	46.5	42.0
	35.0	10.0	55.0	45.4	46.8
	35.0	12.5	52.5	45.3	39.8
	35.0	15.0	50.0	45.5	43.7
	35.0	20.0	45.0	45.7	44.7
Sodium butyrate	35.0	1.3	63.7	44.8	41.1
	35.0	2.6	62.4	44.8	41.5
	35.0	5.0	60.0	45.0	43.0
	35.0	6.6	58.4	45.0	40.9
	35.0	7.5	57.5	44.8	43.8
	35.0	10.0	55.0	46.0	40.6
	35.0	12.5	52.5	44.9	41.8
	35.0	15.0	50.0	44.3	43.5
	35.0	20.0	45.0	43.2	42.3
Butyric acid	35.0	5.0	60.0	34.6	31.6
	35.0	7.5	57.5	30.6	32.0
	35.0	10.0	55.0	26.5	28.6
	35.0	12.5	52.5	24.9	25.8
	35.0	15.0	50.0	21.6	25.1
	35.0	20.0	45.0	-	-

We can clearly see that the three additives have distinctly different effects on the stability of the surfactant system (Table 2 and Fig. 5). Urea has an essentially insignificant effect on the transition temperature and enthalpy. The transition occurs at an average of 45.7 °C. The shape and intensity of the endothermic peaks are similar across the urea samples. This points to an essentially ideal mixing in the water layers and little tendency for association with the surfactant alkyl chains, not unexpected in view of a very weak amphiphilic character of the urea.

Addition of sodium butyrate, at concentrations above the charge stoichiometry, eliminates the L_α phase, but this additive has no significant effect on the transition temperature. This additive provides the system with the weakly amphiphilic butyrate ions and the sodium ions. The butyrate ions, in excess for most of the samples, are expected to associate rather strongly with the cationic surfactant ions. The increased ionic strength is expected to affect the electrostatic interactions in the system leading to a complex phase behavior. Instead, we find that the transition is virtually unchanged on addition of sodium butyrate with the average T_m = 44.8 °C. As can be seen from Fig. 4, the shape of the thermograms is similar to those when

urea is added, or for the surfactant in water. This is surprising in view of the nature of the additive. In addition, the T_m has been demonstrated to be insensitive to dehydration, as discussed before.

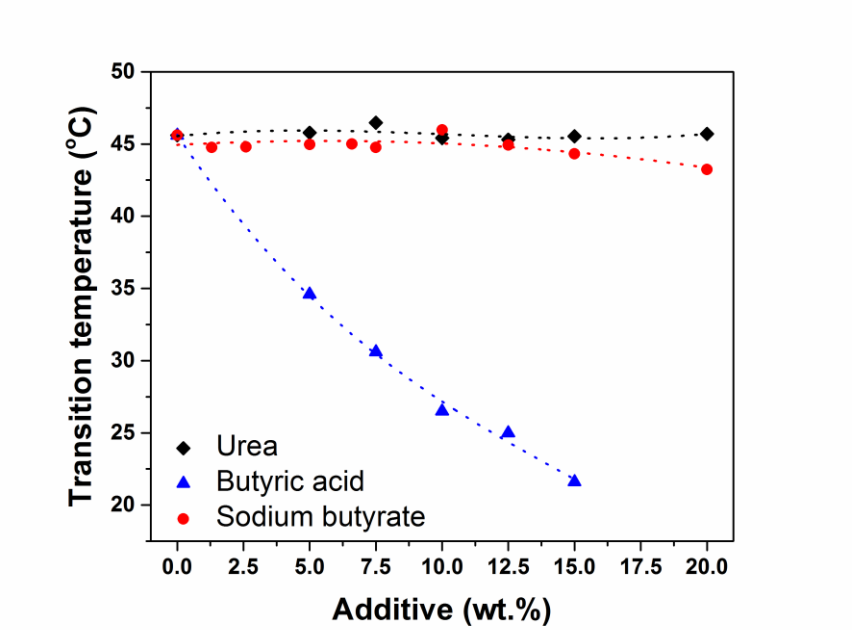

Fig. 5 – Effect of added additives on the gel-to-liquid crystalline phase transition temperature of DODAC (35 wt. %)-additive-water ternary systems. Urea (rhombus), butyric acid (triangle) and sodium butyrate (circle).

Butyric acid addition results in a very significant decrease of T_m , as well as a decrease in the enthalpy change of the phase transition. On top of this, a progressive marked broadening of the peak in DSC is observed. These results seem to indicate a strong interaction between DODAC and butyric acid leading to a lowered stability of the gel phase.

Clearly the effect of additives on the behavior of DODAC can be completely different for different water-soluble additives. For an understanding of the underlying surfactant molecular packing, small and wide angle X-ray diffraction studies were performed.

3.3.2 Small/wide angle X-ray scattering (SWAXS)

Similar to the binary surfactant system, the gel and liquid crystalline structures of the ternary systems were analyzed using small and wide angle X-ray scattering at temperatures below (25 ^oC) and above (50 ^oC) the T_m (Fig. S1, Fig. S2 and Fig. S3). As mentioned previously, the surfactant molecules in the L_β phase might be adopting a tilted and interdigitated structure. Table 3 summarizes the calculated results obtained from SWAXS characterization of the surfactant systems with the various additives.

Table 3
Values for the bilayer volume fraction (Φ_{bi}), the interlayer spacing (d_{sp}), the bilayer thickness (d_{bi}) and the area per surfactant molecule (a) for DODAC systems at 25 ºC and 50 ºC.

	Composition / wt. %			Molar ratio (S:A:W)	Φ_{bi}	25 ºC			50 ºC		
	DODAC (S)	Additive (A)	Water (W)			d_{sp} (Å)	d_{bi} (Å)	a (Å^2)	d_{sp} (Å)	d_{bi} (Å)	a (Å^2)
	35.0	0.0	65.0		0.349	79	28	81	95	33	68
Urea	35.0	5.0	60.0	1: 1.4: 56	0.353	78	28	81	93	33	68
	35.0	7.5	57.5	1: 2.1: 54	0.353	75	26	86	88	31	72
	35.0	10.0	55.0	1: 2.8: 51	0.358	75	27	84	90	32	70
	35.0	12.5	52.5	1: 3.5: 49	0.360	74	27	85	89	32	70
	35.0	15.0	50.0	1: 4.2: 47	0.362	74	27	84	89	32	69
	35.0	20.0	45.0	1: 5.6: 42	0.367	75	28	82	90	33	68
Sodium butyrate	35.0	1.3	63.7	1: 0.2: 60	0.356	65	23	98	82	29	78
	35.0	2.6	62.4	1: 0.4: 58	0.365	46	17	136	78	28	80
	35.0	5.0	60.0	1: 0.8: 56	0.381	35	13	169	55	21	109
	35.0	6.6	58.4	1: 1.0: 54	0.386	35	14	167	52	20	112
	35.0	7.5	57.5	1: 1.1: 53	0.398	35	14	165	-	-	-
	35.0	10.0	55.0	1: 1.5: 51	0.413	35	14	158	-	-	-
	35.0	12.5	52.5	1: 1.9: 49	0.431	36	15	147	-	-	-
	35.0	15.0	50.0	1: 2.3: 47	0.444	37	17	137	-	-	-
	35.0	20.0	45.0	1: 3.1: 42	0.482	38	18	124	-	-	-
Butyric acid	35.0	5.0	60.0	1: 1.0: 56	0.385	73	28	81	77	30	77
	35.0	7.5	57.5	1: 1.5: 54	0.402	72	29	79	70	28	81
	35.0	10.0	55.0	1: 1.9: 51	0.421	72	30	75	69	29	78
	35.0	12.5	52.5	1: 2.4: 49	0.438	74	33	70	72	31	72
	35.0	15.0	50.0	1: 2.9: 47	0.457	69	32	71	66	30	75
	35.0	20.0	45.0	1: 3.8: 42	0.493	-	-	-	-	-	-

As observed in Fig. 6, generally the effect of urea on the spacing and thus on the surfactant layer thickness is negligible. These results are in good agreement with the urea effect on the T_m, where no significant variation was observed. The small variations in the bilayer thickness correspond to small variations in the area per surfactant molecule. The chaotropic effect of urea in water was extensively studied, where changes in the water intermolecular bonding in the presence of urea were observed [44-46]. Since urea is distributed in the aqueous domain, it does not impact the chain packing. Therefore, urea has virtually no effect on the bilayer thickness, or the area per molecule head-group, as shown in Fig. 6. In addition, the L_β and L_α phases were observed to behave in similar ways when urea is present in the system.

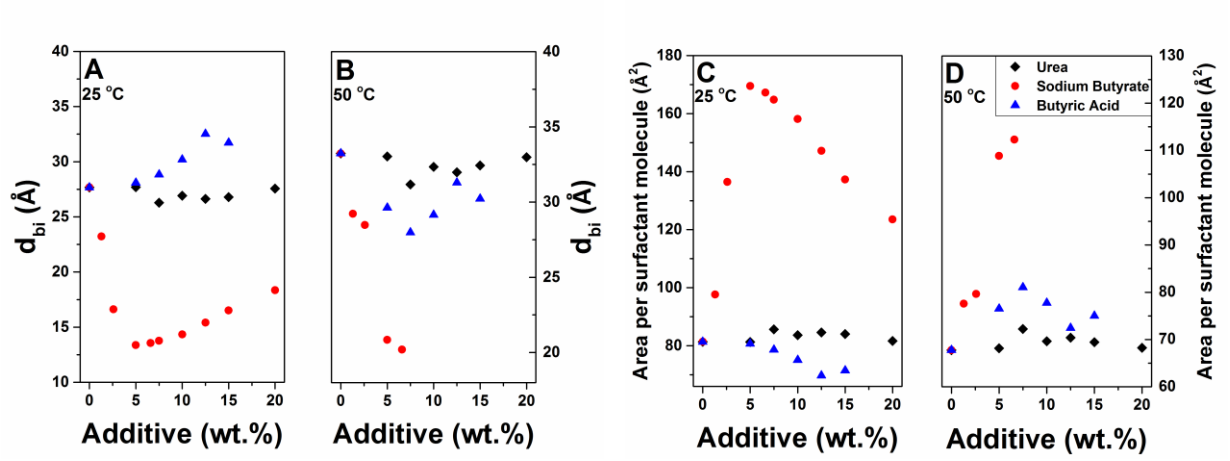

Fig. 6 – Bilayer thickness d_{bi} (A and B) and area per surfactant molecule (C and D) as a function of additive wt. % at 25 °C (A, C) and 50 °C (B, D). Urea (black rhombus), butyric acid (blue triangle) and sodium butyrate (red circle).

With sodium butyrate as additive quite large and interesting effects were observed. As can be inferred from Table 2 relatively small amounts of added butyrate dramatically reduce the spacing in the L_β phase; it reaches values, which are ca. half of those of the surfactant alone. A minimum in spacing is observed around charge stoichiometry between surfactant and butyrate. At higher butyrate contents there is a minor increase. In the calculations of the bilayer thickness and the area per head-group, we assume that sodium butyrate does not differ significantly in volume from butyric acid. To derive the volume, the use of partial molar volume will be not appropriate due to electrostriction effect, leading to smaller volumes per molecule [47]. Therefore, the volume occupied by sodium butyrate was considered to be the same as butyric acid.

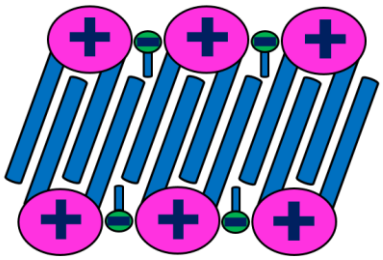

Fig. 7 – Schematic representation of the packing structure for the fully interdigitated DODAC-sodium butyrate-water system.

The deduced values for the bilayer thickness are much smaller with butyrate than for the surfactant alone; actually, they are close to the length of one surfactant molecule rather than two as expected for an "ideal" L_β phase (cf. above). This would correspond to a close to total interdigitation of the surfactant alkyl chains. Such packing, as indicated in Fig. 7, can be understood from the geometric packing restrictions in a system of two surfactants with very different alkyl chain lengths. Thus, butyrate is amphiphilic, and the propyl chain is expected to mix with the surfactant alkyl chains in the bilayers. The resulting structure suggested (Fig. 7) reflects a very minor contribution from butyrate to the hydrophobic volume but a significant contribution to the head-group area. On further inclusion of butyrate, when it is in charge excess, there is a weak progressive increase in the bilayer thickness; the minimum occurs in the region of charge stoichiometry of butyrate and surfactant. It has been suggested previously that specific

interactions are not significant in the formation of an interdigitated structure [48, 49]. Thus, the main driving force is seen to be an increase in the surfactant head-group area.

For the L_α phase in the butyrate system, we observe at small additive amounts a similar picture for the observed spacing and for the bilayer thickness as for the L_β phase and this is attributed to the same type of packing restrictions. However, an important difference compared to the surfactant alone is that the diffraction patterns are less distinct and peaks smeared out (Fig. 8A). This suggests a less ordered L_α phase.

As approximate charge stoichiometry between butyrate and cationic surfactant is attained, the diffraction pattern at 50 ^oC changes completely (Fig. 8B) and no lamellar ordering is indicated. Thus, with sodium butyrate, the melting of the L_β phase does not lead to the L_α phase as observed for the other additives and for the surfactant alone. Instead, the loss of birefringency, as well as of X-ray diffraction peaks, suggests an isotropic phase. There are two possible isotropic phases in this case, a vesicle solution and a sponge (L_3) phase. Vesicle solutions are commonly observed for mixed cationic-anionic surfactant systems but only for dilute solutions [50, 51]. The present systems appear to be too concentrated to allow for vesicles. Only multi-layered vesicles would be possible from geometric packing considerations, and these would show X-ray diffraction peaks. In addition, studies of an anionic double-chain surfactant also demonstrated the effect of electrolytes to induce a transition from lamellar phase to an isotropic phase, identified as the sponge phase [52]. Therefore, it is concluded that a reversed L_3 phase is formed after the phase transition temperature for the samples with excess butyrate ions. The SAXS data was fitted to the Teubner-Strey model [53] for bicontinuous systems allowing the identification of a reversed L_3 phase (Fig. S4). On the other hand, as mentioned it was possible to identify a $L_\beta - L_\alpha$ phase transition when the amount of butyrate was below the charge neutrality, as represented in the Fig. 7. These observations highlight a substantial effect of butyrate ions on the surfactant packing. We note that a transition from an L_α phase to a bicontinuous L_3 phase is expected from simple packing considerations. Thus, the spontaneous curvature of an ionic surfactant film goes from positive (towards the oil part) to negative both as the charge is neutralized (by butyrate ions) and as the ion concentration in the aqueous parts is increased.

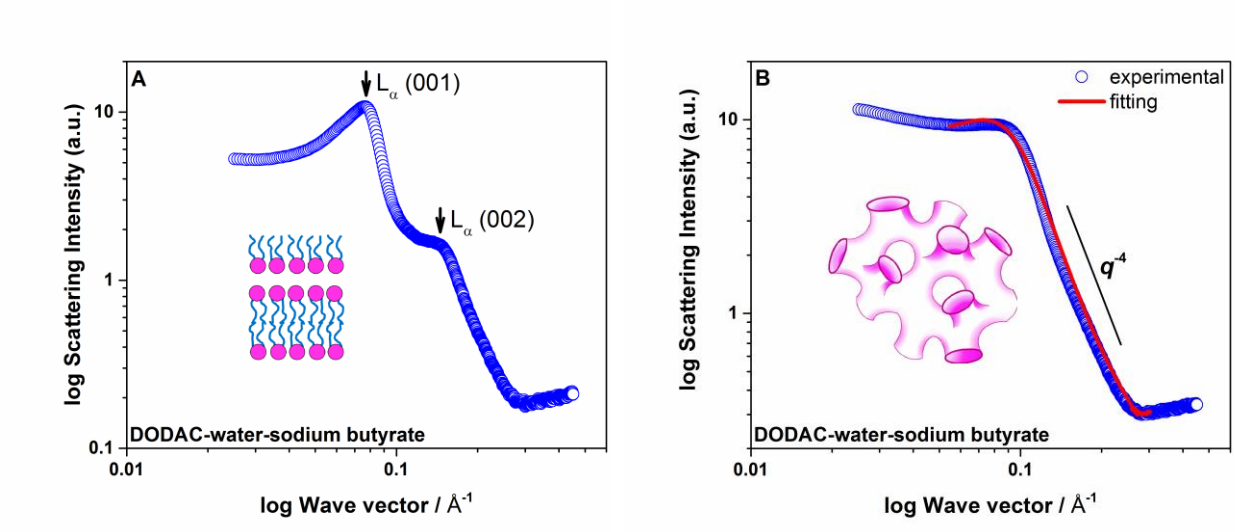

Fig. 8 – SAXS diffraction profiles for the sample: (A) 35 wt. % DODAC – 63.7 wt. % water – 1.3 wt. % sodium butyrate at 50 ^{o}C; (B) 35 wt. % DODAC – 52.5 wt. % water – 12.5 wt. % sodium butyrate at 50 ^{o}C.

Butyric acid molecules are expected to be located at the interface, according to their chemical nature. From the thermograms presented in Fig. 4, it was detected that small quantities of butyric acid gave rise to a very significant reduction in the T_m. These results suggest that butyric acid has a distinct effect on the packing structure. In fact, d_{bi} increases upon butyric acid addition to the system, at 25 ^{o}C, Fig. 6A. Thus, it can be inferred to reduce the chain interdigitation, and a smaller area per surfactant molecule was deduced. At 50 ^{o}C, with the fluid-like nature of the alkyl chains, there is no significant effect on the bilayer thickness. Small variations of the d_{bi} were observed corresponding to variations of *a*. Therefore, a lateral expansion or compression will result into a bilayer thinning or thickening in order to accommodate the same volume.

By analyzing and comparing samples with the same amount of additive (5 wt. %), we can infer distinctly different behavior. On one hand is urea, as a small polar molecule, showing an insignificant effect on the surfactant chain packing. On the other hand, is a short chain fatty acid and its counterpart salt, which have a hydrotrope character and have marked effect on the surfactant bilayers, but in different ways. Interestingly, upon butyric acid addition, there appears to be a reduced interdigitation in the L_β phase. Generally, urea and butyric acid maintain the integrity of the lamellar structure at temperatures below and above the main phase transition, whereas sodium butyrate addition gives rise to an isotropic phase above the T_m. Hence, we highlight the importance of the protonation effect of the additive, which may result in drastic changes in the hydrocarbon chain packing.

4. Conclusion

The effects of urea, sodium butyrate and butyric acid on the alkyl chain packing in the lamellar bilayer structure of DODAC in water were evaluated. The gel-to-liquid phase transition temperature (T_m) was studied using DSC. From the wide angle X-ray scattering curves, the chain-chain distances were deduced; the values are, as expected, and in agreement with studies for different surfactant and lipid systems, larger above than below T_m [39, 54]. The small angle X-ray scattering data show a larger repeat distance for the liquid crystalline (L_α) than for the gel (L_β) phase. With an orientation of the surfactant molecules perpendicular to the bilayers, the opposite situation is predicted. This indicates a considerable tilting and/or interdigitation of the alkyl chains in the L_β phase.

Additives are found to have very different effects on the surfactant system as exemplified here by three cases, urea, sodium butyrate and butyric acid. Whereas urea and sodium butyrate have only minor effects on T_m, similar to other additives [3, 5], butyric acid gives a large decrease, thus stabilizing the L_α phase with respect to the L_β phase. For urea and butyric acid, melting leads to a lamellar phase whereas significant addition of sodium butyrate gives an isotropic phase; it was identified that this is of the bicontinuous or sponge type (often denoted L_3).

The small angle X-ray scattering data imply distinctively different effects of the three additives on the surfactant packing in the gel and liquid crystalline phases. Replacing water by urea has minimal effects on the lamellar spacing both below and above the chain melting temperature. In line with the value of T_m being unaffected, we deduce that the surfactant-surfactant interactions are not appreciably different in water and water-urea environments. Butyric acid has intermediate effects on the bilayer thickness, with a moderate increase for the L_β phase and a moderate decrease for the L_α phase. Butyric acid is a small amphiphilic molecule, which will form mixed aggregates with DODAC. From the reduced average size of the amphiphile, we can understand the lower chain melting temperature. Furthermore, there appears to be a decreased tilting or interdigitation in the gel phase in the presence of butyric acid. In the liquid crystalline phase, the decreased average amphiphile length leads to a minor thinning of the bilayers. Sodium butyrate gives the most complex and interesting behavior and we can identify several factors, which can operate in opposite directions and give cancellation effects. Butyrate will act as a short-chain oppositely charged amphiphile, and it will also give electrostatic screening by acting as an electrolyte. From the SAXS data for the gel phase, we infer a dramatic thinning of the surfactant layers from additions corresponding to rough charge neutrality. For larger additions, the thickness of the surfactant layer increases moderately. Strikingly, the layer thickness over a wide range of compositions corresponds to the length of one surfactant molecule in the all-trans conformation, which would suggest a maximal interdigitation of surfactant molecules. These results show that, although the interdigitation phenomenon has been widely discussed, challenges remain to characterize it.

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