

INVITED ARTICLE

## Influence of head group and chain length of surfactants used for stabilizing liquid crystal shells

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### ARTICLE HISTORY

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### ABSTRACT

We investigate the stability and textural development in nematic liquid crystal (LC) shells, with aqueous interior and exterior, as a function of the type and concentration of surfactant stabilizer of the shell interfaces. The LC is the common thermotropic nematic 5CB and the surfactants are commercial, of cat- as well as of anionic type, with varying alkyl chain length. In addition to stabilizing the shell interfaces, surfactants are generally assumed to promote radial (homeotropic) LC alignment, based on prior studies where the surfactant concentration was well above the critical micelle concentration (*CMC*). Here we focus on the low-concentration range, below *CMC*. We find that both cat- and anionic surfactants can stabilize shells, although the higher water solubility of cationics can render stabilization more difficult. We also conclude that surfactants do not necessarily impose homeotropic alignment; if the surfactant concentration is very low, the director may adopt planar alignment at the 5CB–water interface. Interestingly, the threshold concentration where the surfactant takes control of alignment is different for the shell inside and outside. Shells stabilized by solutions of surfactant with concentration near the threshold may therefore adopt a hybrid configuration, with homeotropic inside and planar outside.

### KEYWORDS

Liquid crystal shells; surfactants; stabilizer; multiple emulsions; alignment

## 1. Introduction

Thin microfluidics-produced shells of thermotropic liquid crystal (LC), containing and suspended in aqueous phases, have emerged as a potent new sample geometry for studying the effects of curvature and confinement on liquid crystal self-assembly [1,2]. The self-closing curved surface renders shells ideal for studying the development and interaction of topological defects [3–11], since the Poincaré-Hopf theorem dictates that such defects must develop on a surface with spherical topology if the director field has a component tangential to the shell plane [1,2]. With planar-aligned shells made of short-pitch cholesteric LC, very interesting optical phenomena arise due to the spherical modulation of the Bragg reflection [12–16] as well as the ability of a thin enough cholesteric shell to let light through into its interior, where it experiences internal reflection [17].

In order to prevent merging and/or collapse of shells into droplets, both the inner

and outer interfaces to the surrounding aqueous phases must be stabilized by an additive. This added stabilizer often plays the additional role of controlling the alignment of the liquid crystal director, hence its choice is critical for the outcome [18]. Surprisingly, only a very small set of stabilizers have been explored so far, typically polyvinylalcohol (PVA) for planar alignment (tangential director) and sodium dodecylsulfate (SDS) for homeotropic alignment (radial director).

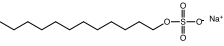
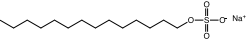
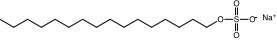
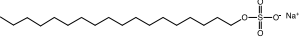
Here we carry out a systematic investigation of the efficiency of surfactants with cat- and anionic headgroups, respectively, in stabilizing and aligning shells of the commonly employed nematic liquid crystal 5CB. The anionic head group is sulfate, with  $\text{Na}^+$  as counter ion, the cationic head group is trimethylammonium, with  $\text{Br}^-$  as counter ion. We vary the length of the hydrophobic alkyl chain for each group from 12 to 18, in steps of 2, and we vary the concentration. Focusing on the extreme low-concentration range, we tune the surfactant concentration from the minimum amount that allows shell production, up to 35% of the critical micelle concentration ( $CMC$ ). For both surfactant groups we find that long-chain surfactants (18 carbons) induce strong homeotropic alignment even at low concentration, whereas short-chain surfactants (12 carbons) can stabilize the shell without influencing alignment at low concentration. This allows tuning from planar to hybrid to homeotropic by changing the concentration. The effect is more pronounced for the cationic than for the anionic surfactants.

## 2. Experimental

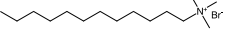
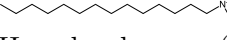
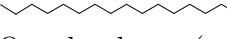
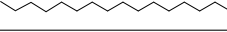
### 2.1. Materials

5CB (4-cyano-4'-pentyl biphenyl) was purchased from Yantai Xianhua Chem-Tech, China. Surfactants were obtained commercially as indicated in Table 1. For reference experiments with planar-aligned shells, aqueous solutions of polyvinylalcohol (PVA) from Sigma-Aldrich, 87-89% hydrolysed and with molar mass in the range 13-23 kg/mol, were used. All chemicals were used as received. Deionized water (resistivity  $18 \text{ M}\Omega\text{cm}^{-1}$ ) from a Sartorius Arium Pro DI was used as solvent for all solutions.

**Table 1.** Overview of the anionic surfactants used in the study. #C stands for the number of carbon atoms in the hydrophobic alkyl chain. Critical Micelle Concentration ( $CMC$ ) values are taken from reference [19], for  $25^\circ\text{C}$  unless otherwise indicated. The Krafft temperatures  $T_K$  are taken from reference [20].

Code	Name and structure	#C	$CMC$ [mM]	$T_K$ [ $^\circ\text{C}$ ]	Source	Purity [%]
SDS	Sodium Dodecyl Sulfate (lauryl) 	12	8	16	Sigma Aldrich	$\geq 98.5(\text{GC})$
STS	Sodium Tetradecyl Sulfate (myristyl) 	14	2	30	Acros Organics	$\geq 95$
SHS	Sodium Hexadecyl Sulfate (cetyl) 	16	0.2	45	Acros Organics	$\geq 98$
SOS	Sodium Octadecyl Sulfate (stearyl) 	18	0.17 @40 $^\circ\text{C}$	56	Acros organics	$\geq 99$

**Table 2.** Overview of the cationic surfactants used in the study. #C stands for the number of carbon atoms in the hydrophobic alkyl chain. Critical Micelle Concentration ( $CMC$ ) values are taken from reference [19], for 25°C. The sources of Krafft temperature  $T_K$  data are given next to each value.

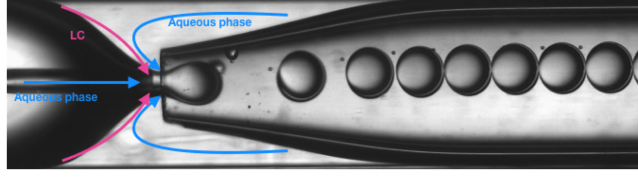
Code	Name and structure	#C	$CMC$ [mM]	$T_K$ [°C]	Source	Purity [%]
DTAB	Dodecyl (lauryl) Trimethyl Ammonium Bromide 	12	14	< 0 [21]	Sigma Life Science	≥98
TTAB	Tetradecyl (myristyl) Trimethyl Ammonium Bromide 	14	4	12.7 [22]	Sigma Life Science	≥99
HTAB	Hexadecyl (cetyl) Trimethyl Ammonium Bromide 	16	0.9	25 [21]	Carl Roth	≥98
OTAB	Octadecyl (stearyl) Trimethyl Ammonium Bromide 	18	0.3	35-36 [21]	Sigma-Aldrich	≥98

## 2.2. Solution preparation

In order to compare the different surfactants investigated in terms of their efficiency in stabilizing and aligning LC shells, we divide the absolute surfactant concentration  $C$  of each solution by the  $CMC$  of the surfactant, thereby defining a normalised concentration as  $C_N = C/CMC$ . In our experiments, we have chosen to investigate  $C_N$  values 0.05, 0.15, 0.25, and 0.35, as this range proves to be of particular interest. The  $CMC$  values are taken from literature [19] and summarized in Table 1 and Table 2. We prepare solutions with the desired  $C_N$  by dissolving the surfactant in deionized water above its Krafft temperature  $T_K$  (also found in the tables), stirring for 5-6 hours.

## 2.3. Shell production

LC shells are produced using a microfluidic setup consisting of coaxially nested glass capillaries, see figure 1, as originally described by Weitz and coworkers [23]. The surfactant solution to be tested is flown through a tapered cylindrical capillary (inlet) with 60  $\mu\text{m}$  diameter orifice. This solution, immiscible with the LC, will be the inner phase of the shells. The LC is flown around it in the same direction, in the interstitial space between the inlet capillary and a square capillary in which it is inserted. Near the inlet orifice, the LC meets the outer phase, which is also flowing in the square capillary but in the opposite direction. Throughout our study, the outer phase composition is identical to that of the inner phase. The LC and the inner phase are flow-focused by the counter-flowing immiscible outer phase to encapsulate the LC in between the aqueous phases. The resulting triple emulsion is collected into another tapered cylindrical capillary (outlet), mounted with its orifice (280  $\mu\text{m}$  diameter) facing that of the inlet capillary, see figure 1. The outlet is connected to a tube that ends in a glass Petri dish functioning as collection bath, containing the same aqueous surfactant solution as used in the production.



**Figure 1.** Snapshot of shell production where blue arrows represent inner and outer aqueous phases and red indicates the LC, flowing as middle phase.

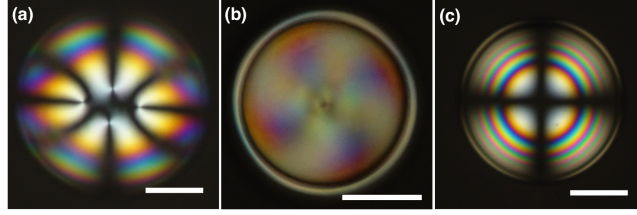
The capillary set-up is placed on a temperature control plate (built in-house) placed on the stage of a Nikon Eclipse TS100 inverted microscope. We monitor the shell emulsification process via a monochrome high-speed camera (IDT NX4-S3) mounted on the microscope. Except when using the surfactants SHS, SOS or OTAB, the surfactant solutions and 5CB are kept at 38°C throughout the shell production process, in order to ensure that 5CB is in its isotropic phase. With the three other surfactants, their high Krafft temperatures  $T_K$  (see Table 1 and Table 2) require further heating to avoid crystallization of the surfactant. Thus, during experiments with SHS, SOS and OTAB, respectively, all fluids are heated to 55°C, 60°C and 43 – 45°C, respectively.

The diameter and thickness of the produced shells are 200–250  $\mu\text{m}$  and  $\sim 10 \mu\text{m}$ , respectively. For polarizing optical microscopy (POM, Nikon Eclipse LV100ND) investigation, shells are either observed directly after production in the collection bath or, for long-term experiments, transferred into a rectangular capillary which is sealed by glue to avoid evaporation of water. The textures of the shells are captured by a Sony FDR AX33 camcorder, mounted on the microscope.

### 3. Results

For each surfactant solution investigated we tested (i) whether shells could be produced, and (ii) which alignment of the nematic phase was obtained in the shell at steady state. The former aspect was assessed during production by observation via the high-speed camera, clearly revealing whether or not the emulsification into shells was successful. As described below, anionic surfactants were found to be slightly more reliable in stabilizing the shells.

The LC alignment was assessed after production by evaluating the polarizing microscopy texture. As reference, we show example textures for fully planar, hybrid and fully homeotropic shells, respectively, in figure 2. These reference samples were produced with identical inner and outer phases for fully planar as well as for fully homeotropic shells. While water itself promotes planar alignment [24], the interfacial tension between 5CB and pure water is too high to allow shell production, hence PVA was added to the aqueous phases for the reference shell shown in figure 2a. The picture is taken with focus on the thin side of the shell, where four half-fold topological defects are located [11]. If either the outer or the inner phase is replaced by a surfactant solution of sufficient concentration, while retaining the PVA solution on the other side, one side of the shell will be planar-aligned, the other homeotropic-aligned. This is because the surfactant adsorbs on the shell–water interface, with the hydrophobic alkyl chain oriented into the LC, promoting the homeotropic (radial) alignment. The resulting hybrid alignment produces a texture in shell geometry as shown in figure 2b, with one integer topological defect at the top and one at the bottom [25]. The photo in figure 2b is taken with focus on the shell equator, hence neither defect is in focus,



**Figure 2.** POM images of (a) planar-aligned shells with 5wt% PVA–water solution on both sides, (b) hybrid-aligned shells with  $C_N=0.35$  SDS outside and 5wt% PVA inside, and (c) homeotropically aligned shell with  $C_N=0.25$  SDS on both sides. The scale bar corresponds to  $50\mu\text{m}$ .

although one of them can be discerned.

If both solutions are surfactant solutions of sufficient concentration, the fully homeotropic texture shown in figure 2c results. No topological defect exists in the shell, as the director has no in-plane component, and instead a pattern with a black cross and multiple colorful concentric rings, reminiscent of conoscopy textures, is seen. This texture reflects the radially oriented optic axis in the shell [26].

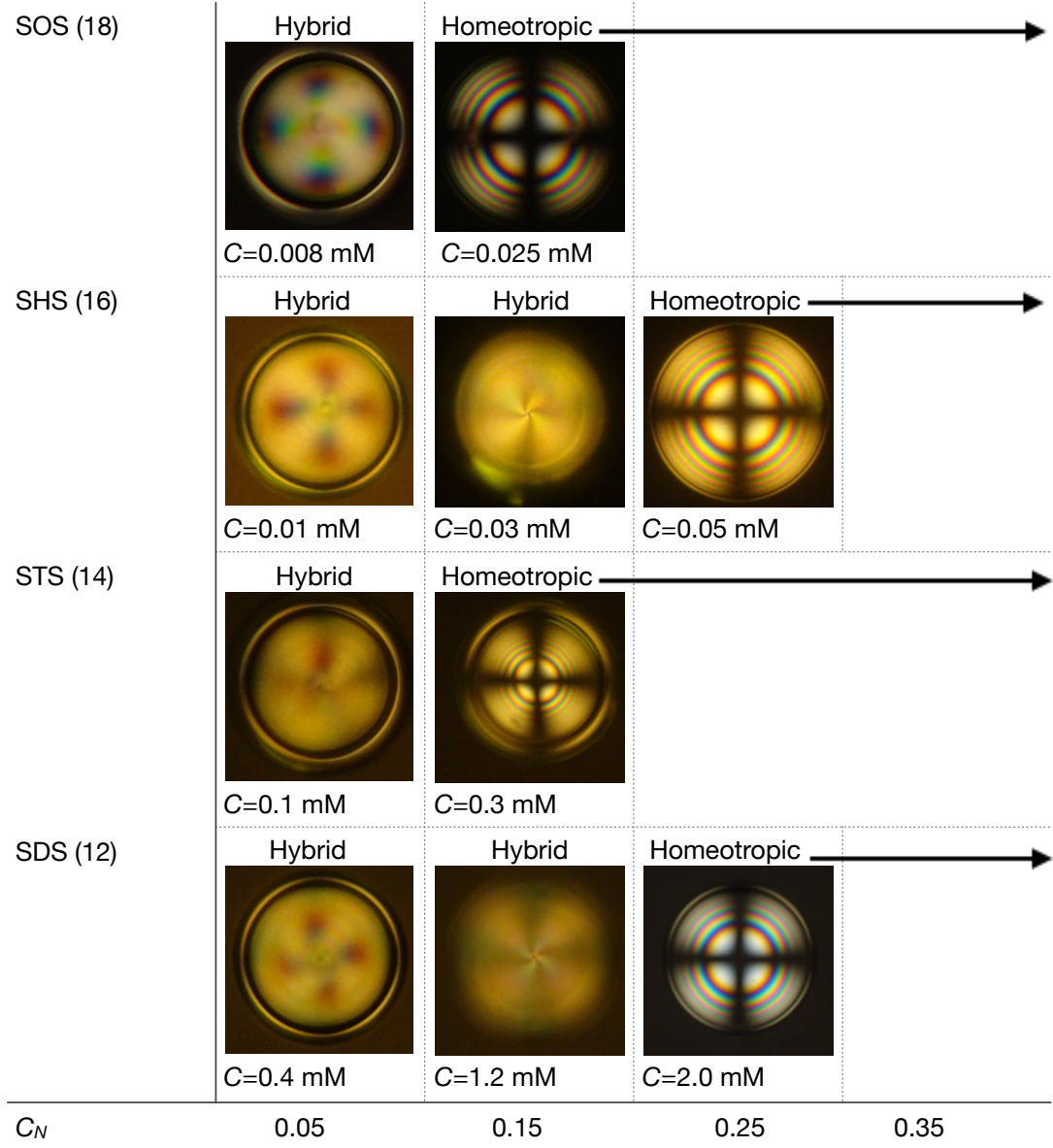
### 3.1. Textures of shells stabilized by anionic surfactants

With all four surfactants in the anionic series (SDS, STS, SHS, and SOS), shells can be produced at all investigated concentrations. Surprisingly, at the lowest concentration,  $C_N = 0.05$ , we find that, irrespective of the chain length of surfactant, the shells display hybrid alignment, see first column in figure 3. Upon increasing  $C_N$  to 0.15, shells stabilized by SDS or SHS remain hybrid-aligned, whereas shells stabilized by STS or SOS are fully homeotropic-aligned. Further increase to  $C_N = 0.25$  ensures homeotropic alignment also with SDS and SHS, see figure 3. Experiments at higher  $C_N$  are not conducted for the anionic surfactants, since already  $C_N = 0.25$  is enough to reach the fully homeotropic state.

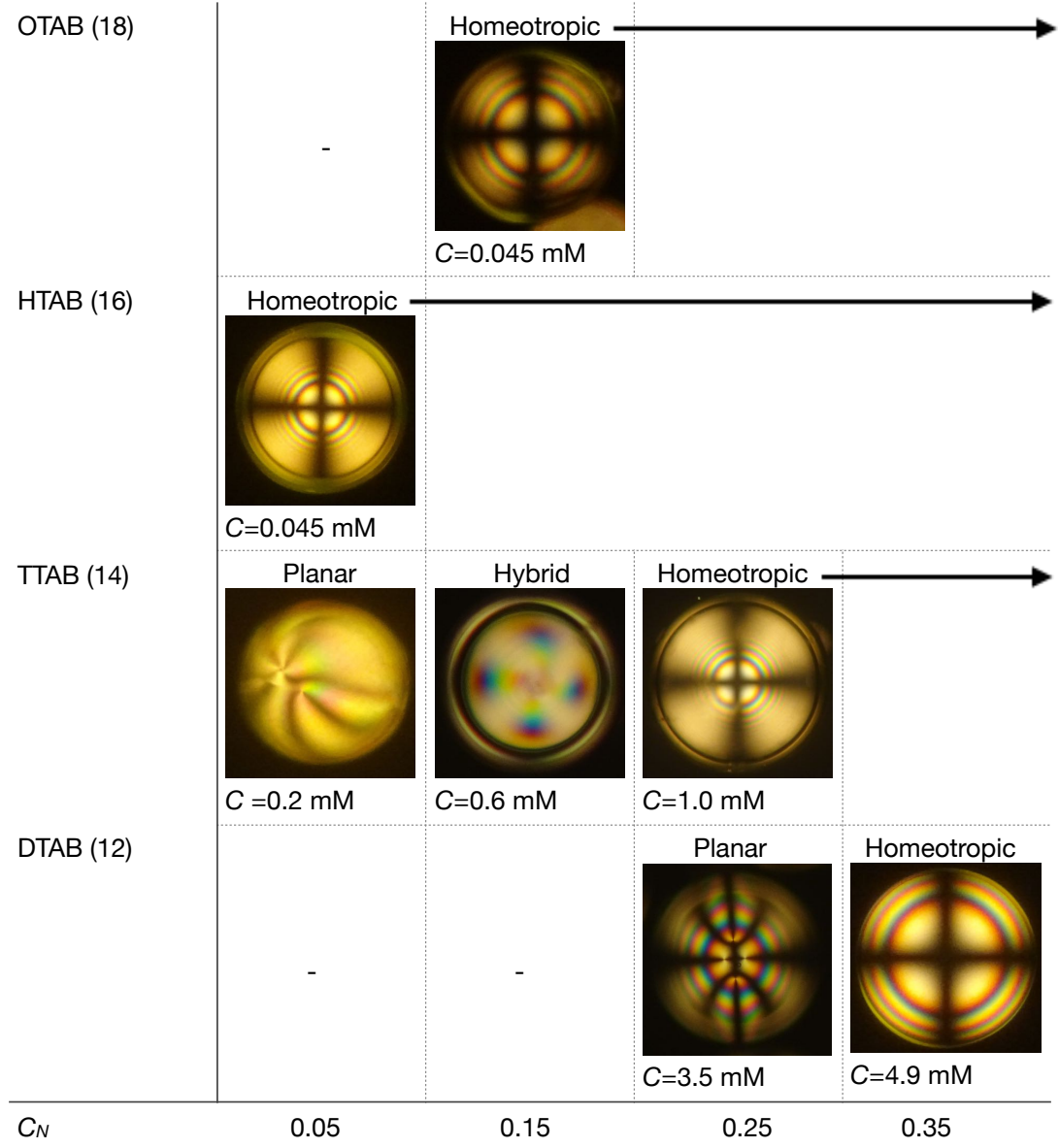
### 3.2. Textures of shells stabilized by cationic surfactants

Shell production with low concentrations of cationic surfactants is notably more challenging than with anionic surfactants. With TTAB and HTAB solutions, shells can be produced reliably at all concentrations, down to  $C_N = 0.05$ . However, both for the longest and for the shortest chain cationic surfactants, OTAB and DTAB, respectively, shell production at  $C_N = 0.05$  was unsuccessful, despite numerous attempts. Raising the concentration of the DTAB solution to  $C_N = 0.25$ , stable shells can be produced and we find that the alignment is planar, as shown in figure 4. We can thus draw the conclusion that also lower concentrations of DTAB would give rise to planar alignment, although we cannot confirm it due to the insufficient stability. For the next higher DTAB concentration,  $C_N = 0.35$ , the shells are fully homeotropic. Possibly, hybrid shells may result at an intermediate concentration, but this was not investigated.

For OTAB, we can successfully produce shells with  $C_N = 0.15$ , displaying homeotropic alignment. We therefore do not investigate shells at higher OTAB concentration, as the saturation alignment has already been reached. For lower concentration the limited shell stability precludes confirmation of alignment, but based on the observation with CTAB at  $C_N = 0.05$ , yielding fully homeotropic shells, we may assume

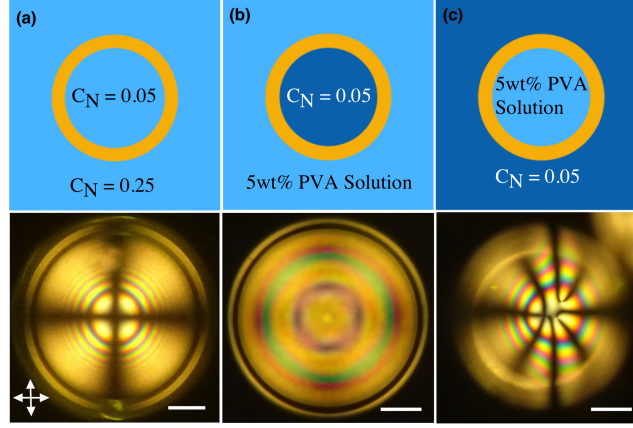


**Figure 3.** Nematic shell alignment induced by anionic surfactants with different chain length at different concentrations. The bottom horizontal row indicates the normalized concentration of surfactant  $C_N$  and the left column indicates the surfactant type, listed in order of increasing chain length from top to bottom.



**Figure 4.** Nematic shell alignment induced by cationic surfactants with different chain length at different concentrations. The bottom horizontal row indicates the normalized concentration of surfactant  $C_N$  and the left column indicates the surfactant type, listed in order of increasing chain length from top to bottom.





**Figure 5.** Schematic drawings and POM pictures of shells stabilized by a  $C_N=0.05$  SDS solution on one side but a different solution on the other side. (a) When the low concentration SDS solution is the inner phase and the outer phase is an SDS solution with  $C_N=0.25$ , the shell alignment is fully homeotropic. (b) With the same inner phase but a water-PVA solution as outer phase, the resulting shell alignment is hybrid. (c) When a water-PVA solution is the inner phase and the  $C_N=0.05$  SDS solution is the outer one, the shell alignment is fully planar. In (a) and (b) the focus is on the equator of the shell whereas in (c) the focus is on the top, revealing the topological defects. The scale bar represents  $50\mu\text{m}$ .

that also OTAB at such low concentration would give homeotropic alignment, had the shells been stable. The most interesting cationic surfactant is TTAB, as this allows shell production at any concentration, and as it displays the richest alignment variation. At  $C_N = 0.05$  the TTAB-stabilized shells are fully planar-aligned, at  $C_N = 0.15$  hybrid alignment results, and at  $C_N = 0.25$  the shell is fully homeotropic. The  $C_N = 0.35$  case was not investigated for TTAB since no further change is expected.

### 3.3. Which kind of hybrid alignment do we have?

As described above and shown in figure 3 and figure 4 we find that shells can develop hybrid alignment over certain concentration ranges for anionic as well as cationic surfactants. This means that only one of the interfaces is homeotropically aligned, while at the other interface the surfactant must be unable to overcome the planar-aligning tendency of water. This brings up the question of *which* interface is homeotropic and which is planar. To find an answer, we perform a series of experiments with SDS-stabilized shells, based on the observation that SDS solutions with  $C_N = 0.05$  on both sides give hybrid shells. We thus use a  $C_N = 0.05$  SDS solution as inner or outer phase, respectively, while changing the composition of the phase on the other side of the shell. First, we prepare shells with the  $C_N = 0.05$  SDS solution inside, using a  $C_N = 0.25$  SDS solution and a 5 wt.% PVA solution as outer phase, respectively. The former outer phase should produce a homeotropic outside, based on the observations in figure 3, and the latter outer phase will give planar alignment, as demonstrated in figure 2a. Next, we use the  $C_N = 0.05$  SDS solution as outer phase, while the 5 wt.% PVA solution is used as inner phase, this time thus ensuring a planar-aligned inside.

The results are shown in figure 5. Panel (a) shows the case with the  $C_N = 0.05$  SDS solution on the inside and the higher concentration,  $C_N = 0.25$ , SDS solution on the outside. The shell is fully homeotropically aligned, demonstrating that the inner interface is homeotropically aligned, even at  $C_N = 0.05$ . When keeping the  $C_N = 0.05$  SDS solution inside but replacing the outer phase with the PVA solution, we find



hybrid alignment, as for the case with  $C_N = 0.05$  SDS solution on both sides. However, if the  $C_N = 0.05$  SDS solution is on the outside, and the PVA solution is on the inside, a fully planar-aligned shell results, as shown in figure 5c. Here the low concentration SDS solution on the outside must thus be unable to induce homeotropic alignment. We can thus conclude from this experiment that the hybrid alignment seen in some cases of shells stabilized by surfactant on both sides must always have the outside planar and the inside homeotropic. This is in agreement with a previous observation of this phenomenon with shells stabilized by water-glycerol solutions of SDS [18].

#### 4. Discussion

The above observations clearly demonstrate that the director configuration of thermotropic LC shells is very sensitive to the choice of surfactant, and that it can be manipulated by varying the surfactant concentration. To analyze the experimental results in some more detail, we describe the surfactant adsorption using the Langmuir equation, which despite its simplicity and multiple approximations works rather well for aqueous surfactant solutions below  $CMC$  in contact with hydrophobic surfaces [27]:

$$\Theta = \frac{KC}{1 + KC} = \frac{KC_N}{1/CMC + KC_N} \quad (1)$$

Here  $\Theta$  is the fraction of the LC–water interface that is covered by surfactant at equilibrium,  $K$  is the equilibrium coefficient for adsorption/desorption of surfactant and  $C$  is the (non-normalized) concentration of surfactant in the aqueous solution.

For the anionic as well as the cationic surfactants, their homeotropic-aligning tendency is not always strong enough at low  $C_N$  to ensure a fully homeotropic director field, even if the concentration is high enough to stabilize the shell from collapse. This effect is most pronounced for short-chain surfactants; indeed, it is clear that the homeotropic-aligning effect is stronger the longer the surfactant chain. This conclusion agrees well with the study by Brake et al. [28], investigating the surfactant chain length effect on the alignment of flat samples of 5CB, placed between a glass slide and an aqueous surfactant solution.

We conjecture that the reason for the chain length effect is that the long hydrophobic chain penetrates further into the LC shell, thereby more effectively influencing the arrangement of the mesogens. Moreover, a longer chain makes the surfactant more hydrophobic, increasing the equilibrium coefficient  $K$  and thus raising  $\Theta$  for the same value of  $C_N$ . For example, at  $C_N = 0.15$ , the interface coverage can be estimated to  $\Theta \approx 60\%$  for a typical value of  $K = 10$ , whereas  $K = 20$  raises the coverage to  $\Theta \approx 75\%$  for the same normalized surfactant concentration, as determined by the "CMC saturation" tool developed by Steven Abbott [29,30]. Since the amphiphilic character of the surfactant promotes a radial adsorption, with the head group protruding into the aqueous phase and the hydrophobic chain orienting into the LC shell, a homeotropic alignment is promoted. In order for a short chain surfactant to have the same effect, the concentration must be high enough to compensate for the lower value of  $K$ , as otherwise  $\Theta$  is insufficient.

The threshold concentration for ensuring sufficient  $\Theta$  to induce homeotropic alignment is thus dictated primarily by  $K$ , but unfortunately the value of the equilibrium coefficient is not readily accessible as it depends on the nature of the oil phase as well

as on the surfactant. However,  $K$  follows a similar trend as a function of chain length as does  $CMC$ . Looking at the variation in  $CMC$  for the different surfactants (Table 1 and Table 2), we can thus understand why the absolute concentration required for effective homeotropic alignment can be orders of magnitude greater for a short-chain than for a long-chain surfactant. For instance, while a 25  $\mu\text{M}$  solution of SOS produces fully homeotropic shells, a 1.2 mM SDS solution produced only hybrid-aligned shells, with the outside planar-aligned. The trend was even stronger for cationics, a 45  $\mu\text{M}$  solution of OTAB yielding homeotropic shells while shells stabilized by 3.5 mM solutions of DTAB were fully planar.

This difference between cat- and anionic surfactants, as well as the larger difficulties in preparing shells with cationic surfactants, begs the question as to why the sign of the surfactant charge would play such an important role. The reason is surely not the charge *per se*, but rather the overall head group. An important hint to the explanation can be found in the significant differences in  $CMC$  and  $T_K$  for cat- and anionic surfactants of identical length, see Table 1 and Table 2. For the same length of alkyl chain, a cationic surfactant has a much lower  $T_K$  and much higher  $CMC$ . Since the alkyl chain is identical, this tells us that the water solubility of the trimethylammonium head group is significantly greater than that of the sulfate head group. One needs to cool further to crystallize out the cationic surfactant (low  $T_K$ ), and a greater amount of the cationic surfactant is required to saturate the water solution and thus trigger micelle formation (high  $CMC$ ). The difference is considerable; throughout the series, an anionic surfactant has  $CMC$  and  $T_K$  comparable to a cationic surfactant with two more carbon atoms in the alkyl chain. For instance, the cationic surfactant best mimicking the behavior of SDS is TTAB.

A highly water soluble head group means a greater hydration sheath and a lower value of  $K$ , i.e. a lower  $\Theta$ . Both aspects suggest that a short-chain surfactant with such a head group is even less likely to impose homeotropic alignment on an LC shell, explaining why shells stabilized by DTAB or TTAB at low concentration even show fully planar alignment, whereas this is never seen with anionic stabilizers within the concentration range studied. The exceptions to this trend in terms of alignment are the surfactants with 16 carbons or more in their hydrophobic chain. While HTAB will only yield fully homeotropic shells, even at  $C_N = 0.05$ , SHS yields hybrid alignment if  $C_N \leq 0.15$ . We speculate that this may be due to the high values of  $T_K$  of SHS and SOS, meaning that the POM investigation of the shells stabilized by these surfactants actually takes place at a temperature well below  $T_K$ , as 5CB is isotropic above  $T_K$ . Possibly, the SHS/SOS partially crystallizes because  $T \ll T_K$ , reducing its interaction with the fluid LC phase and thereby its homeotropic-aligning effect. The effect of the Krafft temperature will be further investigated in a future study.

The difference in water solubility provided by the different head groups is most likely also the reason why cationic surfactants were less effective in stabilizing shells, to the extent that no shells could be produced with low concentrations of OTAB or DTAB. Since a more water soluble surfactant has lower  $K$  it has lower tendency to adsorb at an LC surface when  $C \ll CMC$ , hence it is less effective in stabilizing the shells under these conditions. This effect is particularly severe for DTAB, because here the requirement to heat the solution to 38°C in order to maintain 5CB in its isotropic phase means that the solution is some 40 K above  $T_K$ , raising the water solubility significantly and reducing the tendency for adsorption on the LC shells strongly. The result is that the interfacial tension between the LC and the surrounding aqueous phases should be too high, rendering shell production impossible. We plan to corroborate this conjecture in a future study, using a recently devised technique for measuring interfacial tension

that lends itself very well to the case of water–LC interfaces [31].

Having identified the threshold concentration for each surfactant below which LC shells cannot be produced, we note that the threshold is in fact practically very low for all surfactants, far below  $CMC$ . In particular TTAB comes out as a very interesting surfactant for LC shell use (which has not been applied previously in this context), because it allows stable shell production at such low concentration that it has negligible influence on the LC director field. Thus, by simply adjusting the TTAB concentration, we can tune the director field from planar, via hybrid, to homeotropic. The fact that we can achieve hybrid alignment with identical inner and outer phases is of considerable practical importance, since the usual approach for hybrid alignment, with different inner and outer phases (as in figure 2b), sets up an osmotic pressure across the shell which leads to a continuous thinning or thickening of the shell [10], potential change in the director configuration, as well as limited shell life time [32].

The hybrid alignment, seen with multiple surfactants, anionic as well as cationic, at identical low concentration on the shell inside and outside, is also intriguing from a fundamental point of view. Why does the LC align differently on the inside and outside, even paying the elastic energy cost of the bend that is required to connect a planar and a homeotropic interface, when the solutions on both sides are identical? At the low  $C_N$  values where this phenomenon is observed, the surfactant concentration is apparently sufficient to control the director orientation on the shell inside but not on its outside, as demonstrated in figure 5. It appears that the equilibrium value of  $\Theta$  is greater on the inside than on the outside, i.e.,  $\Theta_{inside} > \Theta_{outside}$ . Since we are using identical surfactant solutions on both sides of the LC,  $C$  (and  $C_N$ ) are the same on the inside and on the outside, hence the explanation for the different  $\Theta$  values must according to the Langmuir equation be sought in different values of  $K$  on the two shell interfaces,  $K_{inside} > K_{outside}$ .

Such a difference can in fact be expected, due to the different signs and magnitudes of curvature on the shell inside and outside. Compared to molecules at a flat phase boundary, molecules at a boundary with positive (convex) curvature experience reduced cohesive forces due to the slightly reduced number of neighbors of identical type. This increases the solubility in the exterior phase, giving rise to Ostwald ripening in polydisperse colloids or foams, with smaller units of disperse phase disappearing while larger increase in prominence due to the greater magnitude of positive curvature of the former. At a boundary with negative curvature, such as on a shell inside, the same argument leads to increased cohesive forces or a decreased solubility in the exterior phase, here water.

Applying this argument to our shells, we can thus conclude that the solubility in the aqueous phase of the hydrophobic tail of the surfactant—which is the part that experiences cohesive forces from the LC if the surfactant resides at the interface—should be slightly greater on the shell outside, due to its weak but positive curvature, than on the shell inside, where the curvature is negative as well as of greater magnitude thanks to the smaller radius. An alternative view is that the different curvatures on the shell’s two interfaces lead to stronger binding of the surfactant into the LC on the inside than on the outside. Either view leads to the conclusion that indeed  $K_{inside} > K_{outside}$ , giving rise to  $\Theta_{inside} > \Theta_{outside}$ , thereby explaining why the inside is homeotropic while the outside is planar. While the differences should be rather subtle at the small magnitudes of curvature in shells with radii on the order of 100  $\mu\text{m}$ , we know from Ostwald ripening of foams, with cell size in the same range, that variations in curvature can have significant consequences even on this scale. In the present case, we would expect an effect only when the surfactant concentration is very close to the

threshold for being able to induce homeotropic alignment, in line with the experimental observations.

## 5. Conclusions

While LC shells with fully homeotropic or hybrid director fields were traditionally prepared using the surfactant SDS as homeotropic-aligning stabilizer, typically at concentration well above  $CMC$ , our systematic study of anionic sulfate-based and cationic trimethylammonium-based surfactants with varying chain lengths shows that they are all very useful stabilizers, working well even for  $C < CMC$ . Interestingly, the higher water solubility of the trimethylammonium head group, and the consequent lower equilibrium adsorption coefficient  $K$ , actually renders cationic surfactants more versatile, as they allow tuning the director configuration by adjusting the concentration. However, the reduced  $K$  and higher water solubility become problematic in case of short-chain cationics since the solutions must be heated to keep the LC in its isotropic state, raising the minimum concentration required for stable shell production.

A particularly interesting stabilizer appears to be TTAB, allowing stable shell production at reduced concentrations as low as  $C_N = 0.05$  and offering the ability to tune the director field from planar, via hybrid, to homeotropic by successively raising  $C_N$ . We identify absolute concentrations of each surfactant at which the resulting shell is planar, hybrid or homeotropically aligned see figure 3 and figure 4. These data will be useful for future studies when stabilisation by surfactant is desired but fully homeotropic is not the only director configuration of interest. Of notable value is the ability to prepare shells with hybrid alignment with identical inner and outer phase compositions, as the absence of osmotic pressure across the shell will allow long-term stability of the shell and its director configuration.

We conclude that the chain length as well as head group of a surfactant are key factors in terms of stabilizing and controlling the alignment of LC shells. Alignment is stronger homeotropic when the chain is longer, at least for temperatures below the Krafft temperature  $T_K$ , an observation we can link to the greater extension into the LC along the radial direction provided by a longer chain. If a firm homeotropic alignment is desired, it is thus advisable to use a long-chain surfactant such as HTAB or SHS. The chain length strongly influences the Krafft temperature  $T_K$  and our study suggests that its value also needs to be taken into account, both for the production of stable shells and for understanding the resulting director configuration. The different water solubilities of the cat- and anionic head groups also significantly affect  $T_K$ , allowing the user to tune the behavior either by chain length or choice of head group.

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## Disclosure statement

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## Notes on contributors

AS carried out all experiments. JL and AS wrote the paper.

## 6. References

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