

**Imperial College  
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Department of Chemical Engineering

**Controlling out-of-equilibrium phase  
transitions in complex surfactant systems**

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for the degree of Doctor of Philosophy at  
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I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and references are given in the list of sources.

Liva Donina (2023)

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## Abstract

Surfactants in solutions self-assemble in a range of structures that are academically and industrially important. In particular, liquid crystalline phases have energies near  $k_B T$  and are generally responsive to external fields, including shear flows and small temperature changes. Lyotropic lamellar  $L_\alpha$  phases can undergo a transformation into multilamellar vesicles (MLVs), which have wide ranging application in protocell models and particle encapsulants. The  $L_\alpha$ -to-MLV transformation exhibits a rich behaviour when co-surfactant and salt is introduced to the system, and thermal energy provided, ranging from vesicle formation to shear-controlled hexagonal vesicle packing. In this thesis, I select sodium dodecyl sulfate (SDS)/octanol/brine (20 g/L NaCl in  $H_2O$ ) as a model system to investigate the equilibrium and non-equilibrium structures attainable by these state and process variables, employing continuous and oscillatory microfluidic flows. Chapter 1 provides an overview of the  $L_\alpha$ -to-MLV transformation in non-ionic and charged surfactant systems and reviews the microfluidic approaches employed in flow-induced transformations. Chapter 2 introduces the experimental techniques used in this work, namely polarised optical microscopy (POM), small angle neutron scattering (SANS), nuclear magnetic resonance (NMR) alongside microdevice design and integration with SANS. Our research sought to answer the following three questions: 1) what are the accessible SDS/octanol/brine solution microstructures? 2) what effect the membrane elastic properties have on the flow induced textures in linear flows? 3) what effect the microfluidic flow field has on SDS/octanol/brine flow induced textures. In Chapter 3, I investigate the solution structure of SDS/octanol/brine system across the lamellar ( $L_\alpha$ ), vesicle ( $L_4$ ) and micellar ( $L_1$ ) phases employing small angle neutron scattering (SANS), optical microscopy and nuclear magnetic resonance (NMR). Chapter 4 quantifies the effect of  $L_\alpha$  elastic properties on the shear induced  $L_\alpha$ -to-MLV transformation by utilising continuous flow microfluidics on a long serpentine chip. Chapter 5 focuses on the effect of continuous and oscillatory microfluidic contraction-expansion flows on the formation of MLVs. Chapter 6 describes an outreach activity at the intersection of surfactant science and art, first developed for the Great Exhibition Road Festival 2022 and refined since. The final chapter reflects on the key findings of this PhD project and provides an outlook for future research.

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- L. Donina, L. Porcar and J.T. Cabral. Composition and temperature effects on the solution structure of SDS/octanol/brine by SANS, NMR and microscopy, submitted (2023).

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To my family

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Everything flows.  
Heraclitus

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# Chapter 1

## Introduction

Soft materials encompass a large range of naturally occurring and man-made materials. While the mathematical theories to describe these materials were established in the 1950s, what we describe as soft matter has been present since the dawn of ancient civilisations in the form of clay, inks, soap and other inventions [1]. The field of soft condensed matter studies things that are viscoelastic, neither in a simple liquid state nor crystalline. This includes a variety of materials, ranging from plastics, paints and polymer melts to living organisms [2]. For example, DNA is a biological polymer while cell membranes are assembled from phospholipids, which are amphiphilic molecules classed as surfactants [2]. Surfactants (surface active agents) are amphiphilic molecules with hydrophilic head groups and hydrophobic tails that can self-assemble in a range of different structures (phases). Unsurprisingly, surfactants have a significant industrial and academic relevance often found in personal care and cleaning products, foods and protocell models. Similarly to other soft matter systems, the structures formed by surfactants are responsive to external stimuli at  $k_B T$ . One way to induce a phase transition dynamically is via application of flow. The formation of these flow induced structures is often not well understood, therefore a question of how to study them arises. Most often flow induced transitions are studied with the aid of rheology by measuring bulk properties, such as viscosity. However, the advent of microfluidics [3] has facilitated the manufacture of very small devices with fine tuned flow fields and couple them with an array of analytical techniques, such as microscopy

[4], scattering techniques [5], [6] and nuclear magnetic resonance [7]. These technological advancements offer a potential to study phase transitions in situ while accessing flows that would not have been otherwise achieved in bulk. This research project focuses on studying flow-induced phase transitions in surfactant systems with the aid of microfluidics, specifically complex surfactant mixture containing the widely used surfactant sodium dodecyl sulfate (SDS), in the lamellar phase region. The main aim of this research is to understand and control the flow-induced phase formation and potentially induce new unexpected phases transitions. This is relevant to both academic and industrial research where many of the processes and product performance are directly related to the applied flow.

The following chapter provides an overview of surfactant phases and flow induced structural rearrangements, specifically in the lyotropic lamellar phases. First, an overview of our current understanding of the widely studied lamellar-to multilamellar vesicle ( $L_\alpha$ -to-MLV) transformation is provided with a particular emphasis on SDS-based systems. Next, microfluidic technology and an up-to-date understanding of the structural rearrangements feasible with lab-on-a-chip devices is described. Finally, the yet unexplored areas of shear induced  $L_\alpha$ -to-MLV phase transitions are outlined followed by the key objectives of this work.

## 1.1 Supramolecular assembly of amphiphilic molecules

A striking property of soft matter systems is their ability to spontaneously self-assemble in structures of different length scales. The most common molecules partaking in this assembly are amphiphiles, molecules that have a part that hydrophilic and a part that is hydrophobic. The most commonly known amphiphiles are surfactants and can be categorised based on the charge on their headgroup (e.g. cationic, anionic, non-anionic and amphoteric) and by the number of hydrophobic tails. Chemically, the most common surfactants will have a quaternary ammonium (cationic), sulphate (anionic), sulphonate (anionic), ethoxy- (non-ionic) or quaternary ammonium-carboxyl headgroups (amphoteric)

[8].

In solution, surfactants are adsorbed at the air-water interface to lower the free energy of the phase boundary which describes the work required to expand the interface. The surfactant headgroup interacts with the water molecules while the hydrophobic tail is pushed out of water. When the monomeric surfactants added to the solution can no longer lower the free energy, they will form aggregates in the bulk of solution called micelles [8]. Micellisation takes place when the surfactant concentration is above critical micelle concentration (cmc) and Kraft temperature [2]. The formation of micelles is accompanied with a decrease in surface tension, molar conductivity, diffusion coefficient and an increase in conductivity and chemical shift in  $^1\text{H}$  NMR [9], [10].

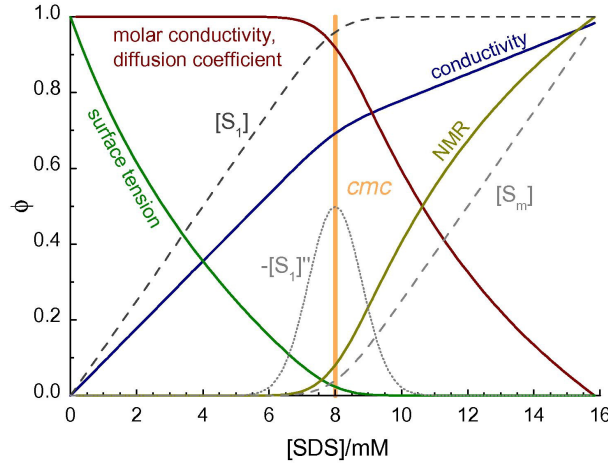


Figure 1.1:  $\phi_v$  represents normalised physical and chemical properties plotted vs  $[\text{SDS}]$ .  $[S_m]$  and  $[S_1]$  show the concentration of SDS in micellar phase and free surfactant phase respectively.  $-[S_1]''$  is the second derivative of  $[S_1]$  indicating cmc. Reproduced with permission from [9].

The shape of the micelles formed in a solution can be described by critical packing parameter (Eq. 1.1), where  $V$  is the surfactant tail volume,  $a_0$  is the equilibrium area per molecule and  $l_c$  is the surfactant tail length [11].

$$CPP = \frac{V}{a_0 l_c} \quad (1.1)$$

If CPP is  $\leq \frac{1}{3}$ , cone shaped micellar packing is observed (e.g. spherical micelles), while  $\frac{1}{3} \leq CPP \leq \frac{1}{2}$  would lead to cylindrical assemblies (cylindrical micelles) and  $CPP > 1$

leads to wedge shaped packing (reverse micelles) [11], [12]. The shape of the molecule will also influence the more highly ordered structures, e.g. lamellar phases (Fig. 1.2).

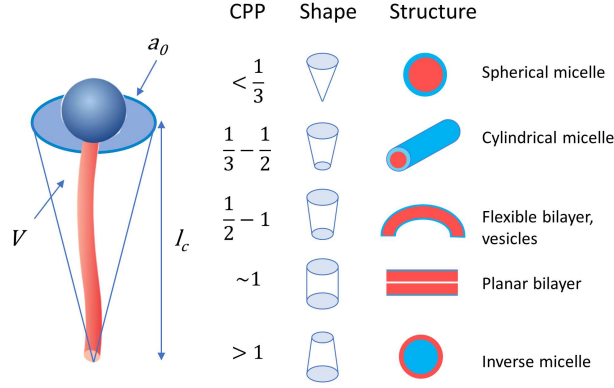


Figure 1.2: Surfactant critical packing parameter (CPP) and corresponding phases. Modified from [12].

## 1.2 Lyotropic Liquid Crystalline Phases

With increasing concentration, surfactant molecules will self assemble into liquid crystalline phases. Liquid crystallinity occurs at equilibrium when amphiphilic molecules are arranged with a degree of order, but without the long range order exhibited by hard condensed materials [2]. This is given by a temperature-concentration phase diagram, which describes the equilibrium structures present in surfactant solutions. An example of sodium dodecyl sulfate (SDS) phase diagram is given in Fig. 1.3 [13]. A typical binary surfactant phase diagram will generally display isotropic (micellar), hexagonal, cubic and lamellar phases depending on the surfactant concentration and temperature [8].

The lamellar phase, which will be of studied in this thesis, consists of a bilayer surfactant membrane of thickness  $\delta$  separated by a solvent layer of thickness  $d$  (0.1-100nm) and has the symmetry of a smectic liquid crystal A phase (Fig. 1.4) [15]. These bilayers can also assemble in subtypes of  $L_\alpha$ , namely MLV (or  $L_4$ ) phase and sponge phase  $L_3$  Fig. 1.4, determined by the membrane elastic properties discussed later in Section 1.4. In a binary surfactant/water system lamellar phase forms only at very high surfactant concentrations (70-90%), while addition of co-surfactants (e.g. long chain alcohols 5C+)

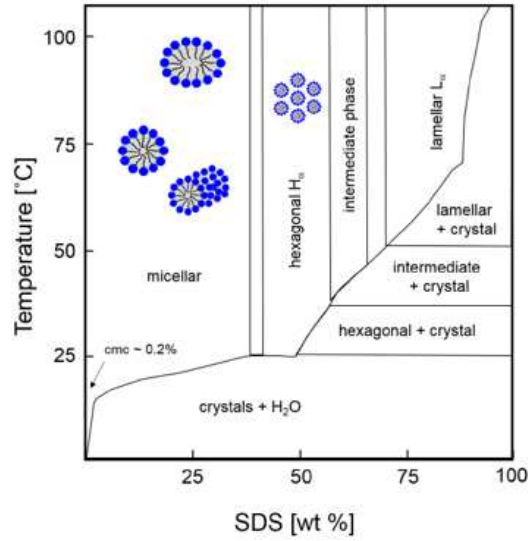


Figure 1.3: An example of surfactant phase diagram. SDS will assemble in micellar above cmc of 8 mM or 0.2% w/w, hexagonal and lamellar phases. Reproduced with permission from [13], [14].

lowers the concentration required to form  $L_\alpha$  phase [16]. Much of the research so far has focused on understanding equilibrium behaviour of lamellar phases by studying membrane undulations and stabilisation [17]–[19]. While these systems have largely been understood both on a macroscopic and microscopic scale, their out-of-equilibrium flow phenomena still pose unresolved challenges which I will discuss next.

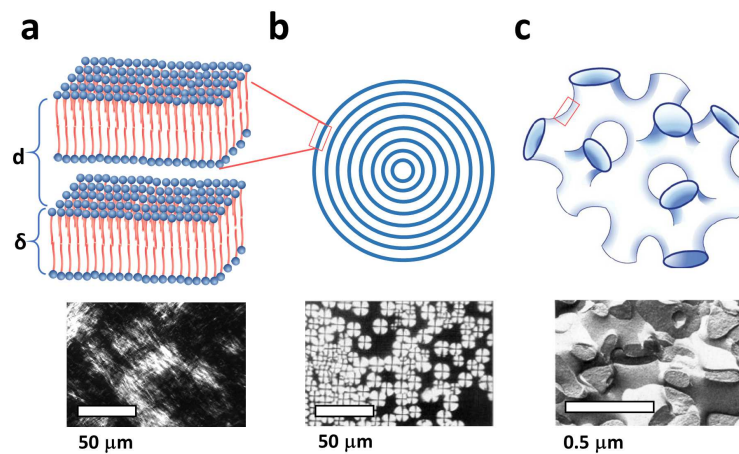


Figure 1.4: Lamellar phases morphologies. a) Stacked fluid lamellar sheets  $L_\alpha$ ; b) Multi-lamellar vesicle phase  $L_4$ ; c) Bicontinuous sponge phase  $L_3$ . Bilayer lamellar phase  $L_\alpha$  and MLVs are birefringent and can be visualised under polarised optical microscopy (in polarised optical microscopy images shown below), while sponge phase  $L_3$  is isotropic (structure shown in freeze fracture micrograph). Modified with permission from [20]–[22].

### 1.3 Rheology and flow behaviour characterisation

Understanding surfactant solution flow behaviour is crucial to identify molecular level textural/phase transformations and is revealed by rheology. This field of science shares its name with the Greek word for flow ("rhein") [1] and describes how materials respond to deformation (shear) applied to it. In idealised scenario, solids exhibit Hookean behaviour, where applied shear stress  $\sigma$  induces shear strain  $\gamma$  with constant proportionality given by shear modulus  $G$ , i.e. elastic response. On the other hand, ideal liquids exhibit Newtonian response when  $\sigma$  induces flow with constant  $\gamma$  with proportionality given by viscosity  $\eta$ , i.e. viscous response [2]. Soft materials, including surfactant liquid crystalline phases, can behave either as liquids or solids at different timescales, described by relaxation time  $\tau$ . This property is called viscoelasticity [2]. Dynamic viscosity  $\eta$  which describes the fluids resistance to deformation by internal friction can be measured with a rheometer. The flow applied by the rheometer is described by two parallel plates, one of which is stationary whilst other is moving at a constant speed in one direction separated by a distance  $h$  (Fig. 1.5). Fluid that is in contact with the walls is assumed to have the same velocity as the walls (assuming there's no slip between the fluid and the plate, aka no slip boundary condition). This flow is called Couette or shear flow and the velocity gradient  $v_x$  along the  $z$  direction is given by [23],

$$v_x(z) = v_0 \frac{z}{h} \quad (1.2)$$

where  $v_0$  is a fixed velocity of the moving plate.

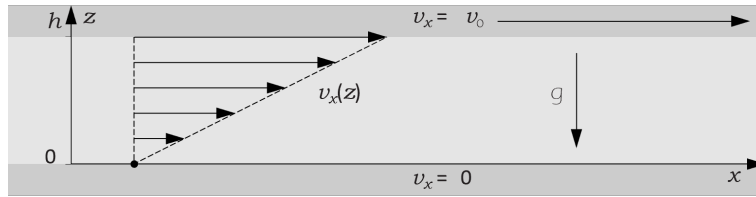


Figure 1.5: Couette flow. Reproduced with permission from [23].

The force  $F$  required to move the moving plate informs about the *viscous part* of viscoelastic

properties of the material between the plates and is given by,

$$F = \eta \frac{v_0 A}{h} \quad (1.3)$$

where  $\eta$  is viscosity of the fluid. Since shear stress  $\sigma$  is given by  $F/A$  and shear strain  $\dot{\gamma}$  is given by  $v_0/h$ , rearranging for viscosity we obtain [24]

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (1.4)$$

Larger  $\eta$  means that a greater shear stress  $\sigma$  is required to make the material flow. If the relationship between  $\dot{\gamma}$  and  $\sigma$  is linear the fluid is called Newtonian whereas a non-linear relationships indicates a non-Newtonian fluid. If  $\sigma$  decreases with increasing  $\dot{\gamma}$ , a fluid is shear thinning whereas increase in  $\sigma$  with increasing  $\dot{\gamma}$  indicates a shear thickening behaviour [24].

### 1.3.1 Lyotropic liquid crystalline phase transitions under flow

Complex soft matter systems exhibit a range of intriguing properties, among one of which is a great viscoelastic response to a minor perturbation. A common way to induce this response is through application of shear (or flow). In surfactants, flow induced structures have been studied for both isotropic (micellar) and lyotropic liquid crystalline phases (nematic, hexagonal, lamellar) [25]. For example, wormlike micelles can form networks under flow [26], [27] while the sponge phase has been observed to transition to the lamellar phase [28] as well as the cubic  $Q_{II}$  phase [29]. The lamellar phase also exhibits rich flow behaviour with the most characterised transformation being  $L_\alpha$  to multilamellar vesicle (MLV) transformation which was first described by Diat and Roux in 1993 [30].

## 1.4 $L_\alpha$ -to-MLV transformation

MLVs can form spontaneously in surfactant systems [17], [31], [32]. However, these phase regions are very narrow and can often be only formed in specific surfactant systems. Spontaneous formation of vesicles relies on membrane curvature energy that can only be accessed at specific surfactant concentrations. Another, perhaps a more appealing way to form vesicles is by input of energy to deform the membrane i.e. application of shear. Lamellar phases at equilibrium are stable across a broad range of concentrations thereby allowing more control over the formulation of the vesicles. Research on lamellar-to-MLV phase transformations was pioneered by French physicist Didier Roux in 1990s [33], [34] when he described the formation of shear/temperature controlled MLVs in SDS/alcohol (octanol and pentanol) lamellar phase in a rheometer.

The stability of surfactant membrane bilayer is governed by their elastic properties and was first described by Helfrich [35]. The bending energy per unit area required  $F$  to deform the membrane is given by the quadratic approximation,

$$F = \frac{1}{2}\kappa\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 + \bar{\kappa}\frac{1}{R_1R_2} \quad (1.5)$$

$\frac{1}{R_1}$  and  $\frac{1}{R_2}$  are the principal curvatures,  $\kappa$  is the membrane bending modulus responsible for the membrane fluctuations while  $\bar{\kappa}$  is the Gaussian modulus describing the curvature of the membrane and defines whether the membrane would be planar or spherical (vesicles) [35]. In the case of vesicles, the principal curvatures will be identical  $\frac{1}{R_1} = \frac{1}{R_2} = \frac{1}{R}$  and substituting in Eq. 1.5 will give the following [36],

$$F_{Va} = (2\kappa + \bar{\kappa})\frac{1}{R^2} \quad (1.6)$$

and estimating the energy for an area of sphere  $A = 4\pi R^2$  using Eq.1.6 will give a total bending energy  $F_V = 4\pi(2\kappa + \bar{\kappa})$ . The relationship between  $\kappa$  and  $\bar{\kappa}$  values indicates the shape of the bilayer structure. In planar bilayers,  $2\kappa > -\bar{\kappa}$ , in spheres  $\bar{\kappa} < -2\kappa$  and in

bicontinuous (sponge) phases,  $\bar{\kappa} > 0$  [15].

From the work by Diat *et al.* [34], [37], the following relationships between applied shear rate  $\dot{\gamma}$  and vesicle size  $R$  has been derived,

$$R \simeq \sqrt{\frac{4\pi(2\kappa + \bar{\kappa})}{\eta d \dot{\gamma}}} \quad (1.7)$$

where  $\eta$  is the dynamic viscosity of the fluid,  $d$  is the  $L_\alpha$  repeat distance. From this,  $R \propto \dot{\gamma}^{-\frac{1}{2}} \propto \phi_v^2$  follows, where  $\phi_v$  is membrane volume fraction related to  $d$  by the dilution law  $\phi_v = \frac{\delta}{d}$ , where  $\delta$  is membrane thickness. This proportionality seems to be somewhat universal and has been reported in work by other researchers [38], [39].

### 1.4.1 Experimental studies on $L_\alpha$ -to-MLV transformation

Since the first characterisation of  $L_\alpha$ -to-MLV transformation under flow, there have been countless studies investigating this phenomenon in a range of surfactant systems, i.e. non-ionic, cationic, anionic and in block co-polymers. Most of the studies have focused on one or several of the following physical variables; shear rate  $\dot{\gamma}$  or shear stress  $\sigma$ , temperature, flow type (continuous vs oscillatory) or addition of dopants to manipulate the membrane physical properties. An overview of research performed over the past three decades of the most commonly studied surfactants, non-ionic (surfactants of  $C_xE_y$  type containing polar ether groups) and SDS (anionic), is provided in Table 1.1 with their associated characterisation techniques, scattering and rheology.

Table 1.1: Overview of  $L_\alpha$ -to-MLV phase transformations reported in literature 1993-2023.

\* next to technique denotes an oscillatory flow experiment.

| Surfactant                            | Alcohol                                     | Solvent                                                    | d, Å    | T, °C | $\dot{\gamma}$ , s <sup>-1</sup> | Technique                | Ref. |
|---------------------------------------|---------------------------------------------|------------------------------------------------------------|---------|-------|----------------------------------|--------------------------|------|
| 40% C <sub>10</sub> E <sub>3</sub>    | n/a                                         | D <sub>2</sub> O                                           | 60      | 25-36 | 0-10                             | <sup>2</sup> H NMR       | [40] |
|                                       | n/a                                         | D <sub>2</sub> O                                           | 60      | 25-38 | 2-100                            | SALS/SANS                | [41] |
|                                       | n/a                                         | H <sub>2</sub> O                                           | 60      | 32-42 | 0.1-100                          | rheology                 | [42] |
|                                       | n/a                                         | D <sub>2</sub> O                                           | 60      | 25    | 10-60                            | <sup>2</sup> H NMR/SALS* | [43] |
|                                       | n/a                                         | D <sub>2</sub> O                                           | 60      | 25    | 1-50                             | SALS/SANS                | [44] |
|                                       | n/a                                         | D <sub>2</sub> O                                           | 60      | 36-42 | 5                                | <sup>2</sup> H NMR       | [45] |
|                                       | n/a                                         | D <sub>2</sub> O                                           | 60      | 25    | 5, 10                            | SALS/SANS*               | [46] |
| 44% C <sub>10</sub> E <sub>3</sub>    | n/a                                         | D <sub>2</sub> O                                           | 69      | 25-40 | 10, 1000                         | SALS/SANS                | [47] |
| 50% C <sub>12</sub> E <sub>3</sub>    | n/a                                         | H <sub>2</sub> O                                           | 69      | 34    | 0.1-100                          | SALS                     | [48] |
| 40-60% C <sub>12</sub> E <sub>3</sub> | n/a                                         | D <sub>2</sub> O                                           | 60      | 24-42 | 2-60                             | SANS                     | [49] |
| 40% C <sub>12</sub> E <sub>3</sub>    | n/a                                         | D <sub>2</sub> O                                           | 69      | 24-40 | 0.1-100                          | <sup>2</sup> H NMR/SANS  | [50] |
| 40% C <sub>12</sub> E <sub>4</sub>    | n/a                                         | D <sub>2</sub> O                                           | 68      | 25-38 | 2-100                            | SALS/SANS                | [41] |
|                                       | n/a                                         | D <sub>2</sub> O                                           | n/a     | 25-47 | 10-100                           | SALS/SAXS                | [51] |
|                                       | n/a                                         | D <sub>2</sub> O                                           | n/a     | 25    | 0.1-80                           | <sup>2</sup> H NMR/SALS  | [52] |
|                                       | n/a                                         | D <sub>2</sub> O                                           | 78-85   | 20-40 | 0.1-100                          | SALS/SAXS                | [53] |
|                                       | n/a                                         | D <sub>2</sub> O                                           | 78.5    | 55    | 10-200                           | SALS/SANS                | [54] |
| 40% C <sub>12</sub> E <sub>5</sub>    | n/a                                         | D <sub>2</sub> O                                           | 55      | 63    | 0-10                             | <sup>2</sup> H NMR/SANS  | [55] |
| 50-55% C <sub>14</sub> E <sub>5</sub> | n/a                                         | D <sub>2</sub> O                                           | 57-67   | 25-75 | 3                                | SAXS                     | [56] |
| 40% C <sub>16</sub> E <sub>4</sub>    | n/a                                         | D <sub>2</sub> O                                           | 62.8    | 40-55 | 2-100                            | SALS/SANS                | [57] |
| 48-55% C <sub>16</sub> E <sub>7</sub> | n/a                                         | D <sub>2</sub> O                                           | 60-65   | 55-75 | 1-10                             | SALS/SAXS                | [58] |
| 48% C <sub>16</sub> E <sub>7</sub>    | n/a                                         | D <sub>2</sub> O                                           | 70-79   | 66-69 | 0.05-30                          | SALS/SAXS                | [59] |
| 9% SDS                                | 10-11% C <sub>8</sub> H <sub>17</sub> OH    | H <sub>2</sub> O (2% NaCl)                                 | n/a     | 20    | 70,94                            | SALS*                    | [60] |
|                                       |                                             |                                                            | n/a     | 20    | 47                               | SALS*                    | [61] |
|                                       |                                             |                                                            | 114     | 25    | 1-1070                           | SALS/SANS                | [62] |
| 7% SDS                                | 8% C <sub>8</sub> H <sub>17</sub> OH        | D <sub>2</sub> O (2% NaCl)                                 | 120-165 | 27-28 | 50-1000                          | SANS                     | [63] |
| 6.5% SDS                              | 7.9% C <sub>8</sub> H <sub>17</sub> OH      | D <sub>2</sub> O (2% NaCl)                                 | n/a     | 23    | 1.5-80                           | <sup>2</sup> H NMR       | [64] |
|                                       |                                             |                                                            | n/a     | 26-31 | 10-80                            | SALS                     | [65] |
|                                       |                                             |                                                            | n/a     | 24-28 | 1-500                            | SALS                     | [33] |
|                                       |                                             |                                                            | n/a     | 22-29 | 30                               | SALS*                    | [66] |
|                                       |                                             |                                                            |         |       |                                  |                          |      |
| 15.8% SDS                             | 14.8% C <sub>5</sub> H <sub>11</sub> OH     | 45% C <sub>12</sub> H <sub>26</sub> 24.4% H <sub>2</sub> O | 80      | 25    | 5-200                            | SALS                     | [67] |
| 15.1% SDS                             | 14.6% C <sub>5</sub> H <sub>11</sub> OH     | 47% C <sub>12</sub> H <sub>26</sub> 23.3% H <sub>2</sub> O | 95      | 25    | 1-40                             | SALS                     | [68] |
| 20% SDS                               | 18% C <sub>5</sub> H <sub>11</sub> OH       | 31% C <sub>12</sub> H <sub>26</sub> 31% D <sub>2</sub> O   | 40-400  | 25    | 0-8000                           | SALS/SANS                | [34] |
| 22.7-26.8% SDS                        | 5.9-9.9% C <sub>10</sub> H <sub>21</sub> OH | D <sub>2</sub> O                                           | 59-78   | 25    | 5-1100                           | SALS/SANS                | [69] |
| 20% AOT                               | n/a                                         | H <sub>2</sub> O (1.6% NaCl)                               | 100     | 25    | 2-300                            | SALS                     | [70] |

For now, I will focus on the findings of the studies rather than the working principles behind these techniques that will be described later in Chapter 2. Generally, the concentrations for C<sub>x</sub>E<sub>y</sub> type surfactants are in the 40-60% w/w range as these most commonly are binary surfactant/water systems, while anionic surfactant concentrations are in the 6-15% w/w range since most of these systems are ternary/quaternary where the addition of dopants (e.g. salt, co-surfactant) extends the lamellar phase stability region. This is reflected in the d-spacing, which is smaller for the non-ionic C<sub>x</sub>E<sub>y</sub> surfactants when compared to anionic surfactants, following the dilution law  $d = \frac{\delta}{\phi_v}$ . An overview of shear diagrams is given in Fig. 1.6a,(of non-ionic C<sub>x</sub>E<sub>y</sub>) and Fig. 1.6b,(of anionic SDS), followed by a closer look at the experimental design and key insights from these shear studies.

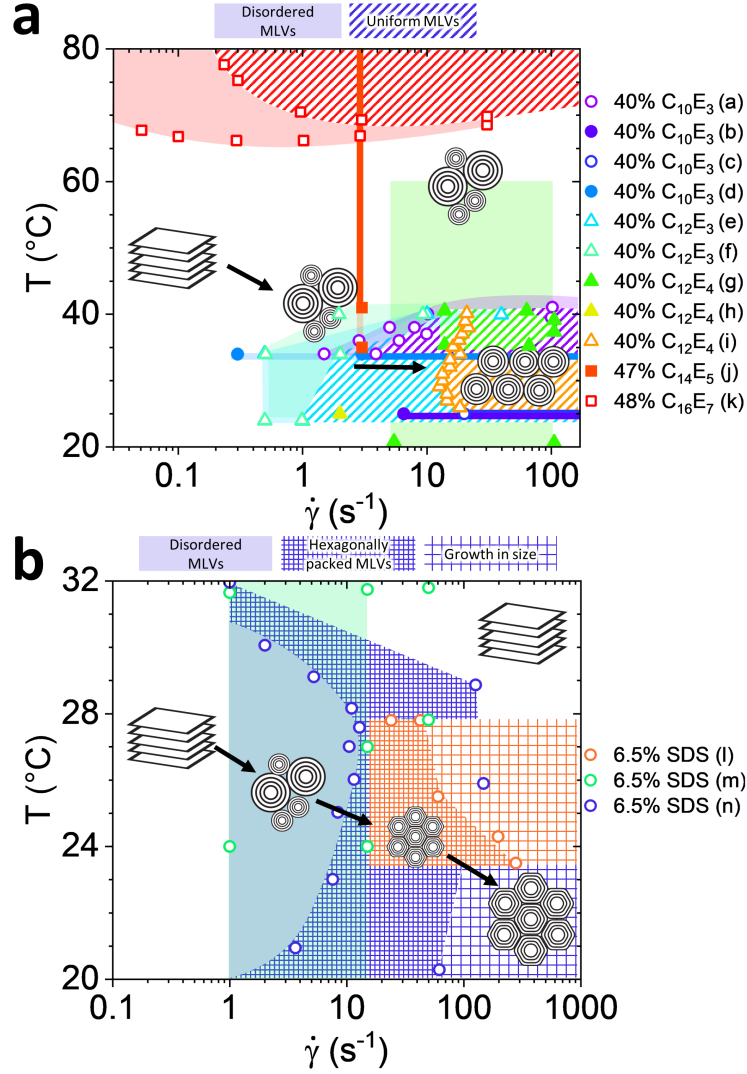


Figure 1.6: Shear diagrams. a) shear diagram for  $C_xE_y$ -type surfactants summarising data from a - [42], b - [46], c - [43], d - [48], e - [50], f - [49], g - [51], h - [71], i - [53], j - [56], k - [59]; b) shear diagram for SDS/octanol/brine summarising data from l - [33], m - [65], n - [66].

### Effect of flow type

Naturally, flow is at the centre of all of the  $L_\alpha$ -to-MLV transformation studies, where it is either described by applied shear rate  $\dot{\gamma}$  or shear stress  $\sigma$ . The design of a shear experiment can have an effect on the pathway of MLV formation, for example by introducing oscillatory shear flows or by shear quench. In oscillatory shear experiments sinusoidal shear rate is applied achieved by a back-and-forth rotating rheometer spindle. The studies that have been carried out using oscillatory shear experiments have often found a change in the

transition pathway where intermediate structures, such as tilted lamellae and multilamellar cylinders, are not formed [43]. Additionally, oscillatory shear experiments can be a way to induce more ordered phases [66], such as hexagonally packed MLVs. Another way of introducing a more complex shear flow is by shear quench, a rapid cessation or decrease in applied shear flow. In a study by Koschoreck *et al.*, growth in MLV size was observed following a shear quench [44].

### Effect of temperature in non-ionic surfactant $L_\alpha$ phases under flow

The effect of temperature is most frequently studied in non-ionic surfactant systems since their lamellar phases are stable across broad temperature range, 25 to 50-80 °C depending on hydrocarbon tail length, unlike SDS-octanol-brine lamellar phases that are only stable up to 30 °C. Temperature in non-ionic surfactant systems plays a similar role to added co-surfactants and salt in anionic surfactant systems as it modulates the membrane elastic properties, i.e. membrane spontaneous curvature  $\bar{\kappa}$  [72]. In a study by Nettesheim *et al.* 40% w/w  $C_{10}E_3$   $L_\alpha$  phase showed formation of the intermediate multilamellar cylinder phase between 1-2  $s^{-1}$  and to ordered vesicle state above 5  $s^{-1}$  at 25 °C and no transformation to MLVs above 38 °C [41]. The shear diagram in Fig. 1.6a corroborates this behaviour in  $C_{10-12}E_y$  type surfactants where above  $\approx 40$  °C transformation into MLVs is not observed irrespective of shear rate and increase in temperature shifts the shear rate  $\dot{\gamma}$  and shear stress  $\sigma$  to higher values [53]. Concentration (not shown in the shear diagram), will have a similar effect where 60% w/w  $C_{12}E_3$  will require higher shear rates ( $\dot{\gamma}$  above 60  $s^{-1}$ ) for MLV formation [49].

### Effect of dopants

The phase behaviour of bilayer structures can be manipulated by addition of dopants, i.e. mid-to-long chain alcohols and by addition of salts. This will lead to a change in membrane charge and in turn spontaneous curvature  $\bar{\kappa}$  and consequently the phase structure [72]. As a result, MLV formation can be achieved in anionic systems even without application

of shear [73], [74]. Furthermore, addition of dopants to anionic surfactant  $L_\alpha$  phases leads to decrease in membrane bending rigidity  $\kappa$  [75], while the opposite effect is observed for non-ionic surfactants [76], [77]. In the context of flow, decreasing membrane bending rigidity  $\kappa$  has been associated with decrease in the critical shear rate  $\dot{\gamma}_c$  required for MLV formation [77].

### 1.4.2 MLV formation mechanisms

In the following section, I will describe the theoretical models underpinning the flow-induced formations of MLVs. In brief, the formation of MLVs from  $L_\alpha$  phase has been attributed to dilational strain caused either by non-uniformities caused by the equipment (rheometer) [78] or undulations of the membrane [79].

Oswald attributed the origin of MLV formation to the shear apparatus [78]. The spacing between the moving and stationary parts of a rheometer are fixed to a specific distance, 0.5-2 mm. However, on a nanoscale, there are non-uniformities in the gap spacing. This non-uniformity will cause the lamellar membrane dislocations as sheets are attempting to fill the gap between the stationary and moving part of the rheometer. At a critical shear rate  $\dot{\gamma}_c$ , the dislocations will not be able to follow the flow giving rise to undulations leading to the formation of MLVs [78]. Simultaneously, the dislocations lead to an increase of dynamic viscosity  $\eta$  due to energy dissipation caused by dilative strain [15]. However, the theoretical estimates are  $10^3$  smaller than the experimentally observed  $\dot{\gamma}_c$  ( $1-10 \text{ s}^{-1}$ ) [80].

Zilman and Granek argued that undulation instability from the shear apparatus proposed by Oswald is unlikely to trigger MLV formation, since the transition characteristics could vary from instrumental setup and sample preparation. In their model, Zilman and Granek consider short range undulations in uniform lamellar membranes that interact with the shear flow at low shear rates [79]. When shear is applied, it suppresses the undulations (Fig. 1.7a) which would cause the  $L_\alpha$  sheets to extend (Fig. 1.7b). However, the fixed geometry of the shear apparatus prevents this and instead the sheets become laterally

compressed (Fig. 1.7c) and above the critical shear rate  $\dot{\gamma}_c$  the  $L_\alpha$  sheets buckle (Fig. 1.7d,e) and break up into MLVs (Fig. 1.7f) [72], [79].

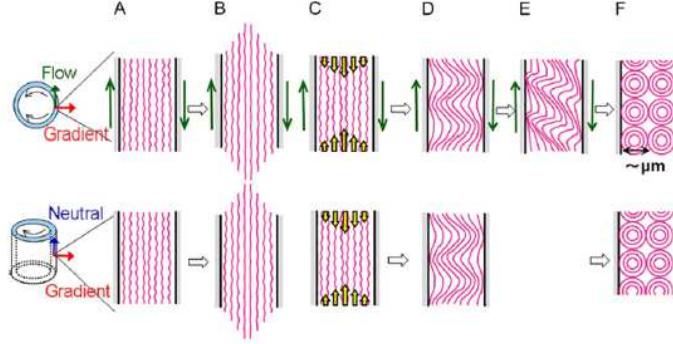


Figure 1.7: Model for  $L_\alpha$ -to-MLV transformation described by Zilman and Granek. a) Suppression of undulations under shear; b)  $L_\alpha$  sheets want to extend under flow; c) Extension is prevented by the overall  $L_\alpha$  geometry causing the sheets to compress laterally; d) sheets start to buckle; e) critical shear rate  $\dot{\gamma}_c$  is reached and f) sheets break up into MLVs. Reproduced with permission from [72].

Zilman and Granek calculated the critical shear rate for MLV formation to be a balance between the stress generated on the bilayer membrane surface and the elasticity required to stretch the bilayer. They established a relationship between critical shear rate  $\dot{\gamma}_c$ , viscosity of the solution  $\eta$ , interlamellar spacing  $d$ , and the gap between two plates  $D$  as follows [79],

$$\dot{\gamma}_c \approx \frac{0.7k_B T}{\eta d^{5/2} D^{1/2}} \quad (1.8)$$

When taking into account the increase in viscosity  $\eta$  of the compressed  $L_\alpha$ , the model comparison to experimental data [34] was in good agreement with  $\dot{\gamma}_c \approx 3 \text{ s}^{-1}$  [79]. However, the model does not take into account lamellar phase defects and the difference of timescales between membrane relaxation time and experimental shear rate [81].

A recent simulation study by Shiba *et al.*, observed unilamellar vesicle formation at membrane fractions  $\phi_v \leq 0.15$  and low  $\dot{\gamma}_c$  ( $\leq 10^{-2} \text{ s}^{-1}$ ) and formation of multilamellar cylinders and rolled up lamellae above  $\phi_v \geq 0.15$  for shear rates  $\dot{\gamma}_c \leq 10^{-2} \text{ s}^{-1}$  and  $\leq 10^{-1} \text{ s}^{-1}$  respectively [82].

### 1.4.3 SDS/octanol/brine flow induced phase transformations

This project focuses on selecting multiple flow induced phase transformation pathways, hence SDS/octanol/brine system will be studied (equilibrium phase map shown in Fig. 1.8a).  $L_\alpha$  phase of SDS/octanol/brine pseudo-quaternary phase undergoes multiple flow-induced transformations depending on the shear rate  $\dot{\gamma}$  and temperature. Above  $2 \text{ s}^{-1}$ , a composition containing  $\approx 6.5\%$  SDS and  $\approx 7.9\%$  octanol forms disordered MLVs (Fig. 1.8b, I) that decrease in size as  $\dot{\gamma}$  is increased until around  $50 \text{ s}^{-1}$ , where a uniform hexagonally packed MLV phase emerges (evidenced by emergence of 6 equidistant first order scattering dots in SALS pattern, Fig. 1.8b, II). This persists until shear rate is increased to  $200 \text{ s}^{-1}$  when a jump in MLV size is observed (Fig. 1.8b, III) as evidenced by decrease in distance between scattering peaks in SALS, and conversely an increase in MLV size [33]. The growth in size is discontinuous (the observed "jump" in Fig. 1.8b from II to III) at  $24.3^\circ\text{C}$  but becomes continuous for temperatures above  $26.5^\circ\text{C}$  [30], [33].

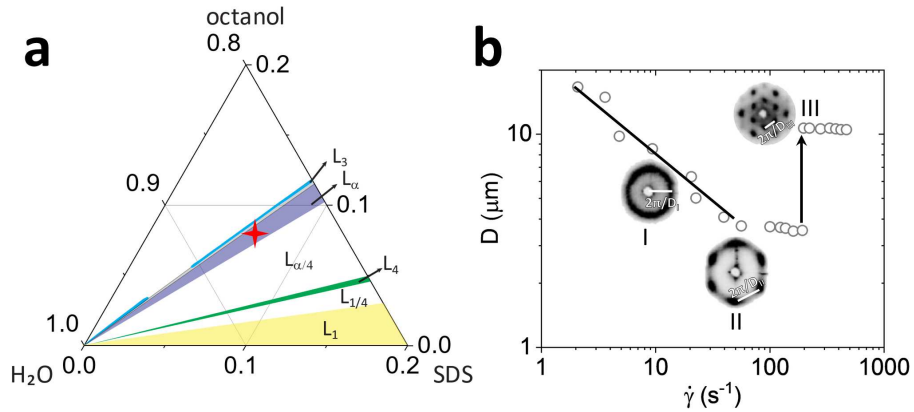


Figure 1.8: SDS/octanol/brine equilibrium and dynamic phase maps. a) Water-rich corner of SDS/octanol/brine phase map. The red star indicates the composition of the sample studied here. This corresponds to 6.5% SDS, 7.9% octanol and 85.6% brine w/w.  $L_1$  and  $L_\alpha$  correspond to micellar and lamellar phases respectively.  $L_3$  and  $L_4$  are narrow phase regions of sponge and dilute MLV phase respectively. The  $L_\alpha$  dimensions are  $\delta=2.4 \text{ nm}$  and  $d=15 \text{ nm}$  [30]; b) Shear phase diagram at  $24.3^\circ\text{C}$  of MLV transition from disordered (I) to hexagonally packed (II) to growth in size (III) of MLVs. Discontinuous transition between small and big vesicles is observed up to  $26.5^\circ\text{C}$ . Modified form [17], [83] and [33].

## 1.5 Microfluidics

As described earlier, complex surfactant systems can be manipulated via applied flow. Microfluidics is a technology that allows the manipulation of small sample volumes (typically on a nanoscale) in a microchannel [3]. The scaling down the the flow geometries leads to a great decrease in volume forces (gravity, inertia) while the surface forces (surface tension, viscosity) remain unchanged. This can be described by the scaling law,

$$\frac{\text{surface forces}}{\text{volume forces}} = \frac{l^2}{l^3} = l^{-1} \xrightarrow{l \rightarrow 0} \infty \quad (1.9)$$

where volume forces  $\rightarrow 0$  leading to surfaces forces becoming predominant [23].

The scaling laws in microfluidics can be described by several dimensionless parameters. One of the most commonly used dimensionless parameter is the Reynolds number,  $Re$ , which describes the relationship between inertial and viscous forces,

$$Re = \frac{\rho u l_0}{\eta} \quad (1.10)$$

where  $\rho$  is the fluid density,  $u$  is the fluid velocity and  $l_0$  is the characteristic length, given by the smallest lengthscale in the microfluidic channel (e.g. channel width) [23]. Flows where  $Re > 4000$  are described as turbulent and laminar when  $Re < 2300$  with nearly all flows in microfluidic systems belonging to the latter [84].

### 1.5.1 Microfluidic devices with different flow types

The benefit of studying soft matter with microfluidics is the potential to design fine-tuned flow fields and probing length scales of a few 100  $\mu\text{m}$ . To certain degree, the field of microfluidic rheology addresses many of the questions concerning devices with defined flow fields. These devices are generally classed by the type of flow they provide: capillary, stagnation point and contraction (Fig. 1.9) [85].

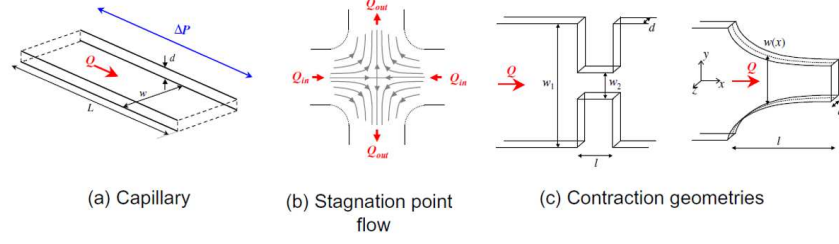


Figure 1.9: Device designs for microfluidic rheometry. a) Steady shear flow in a capillary; b) Device with a stagnation point for extensional flows; c) Device with contraction-expansion geometry for extensional flows. Reproduced with permission from [85].

An intriguing prospect is to have a microfluidic device where flows can be tuned depending on the inlet and outlet flow velocity and flow direction. There have been several examples in recent literature of microfluidic four roll mills that can achieve these requirements [86]–[88]. These devices (Fig. 1.10) are inspired by Taylor’s four roll mill [89] and allow accessing pure shear ( $\Lambda=0$ ), rotational ( $\Lambda=-1$ ) and extensional ( $\Lambda=1$ ) flows ( $\Lambda$  is the flow type parameter defined by strain-rate and vorticity tensors). The benefit of a such device would not only be a well defined flow field, but also a decrease in the device design and manufacturing process and the potential to study the influence of cumulative flow effects (similar to a traditional rheometer).

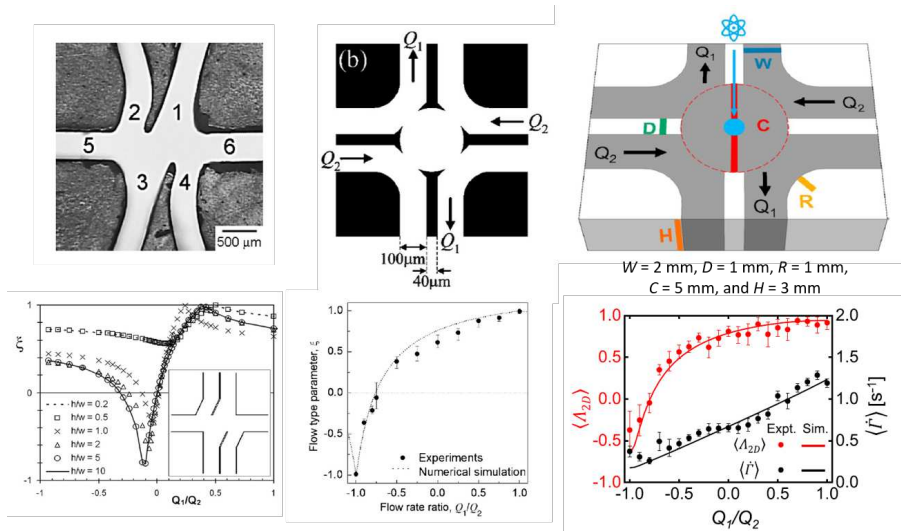


Figure 1.10: Microfluidic four roll mill devices. Modified with permission from [86]–[88].

### 1.5.2 Flow-induced assembly with microfluidics

The advent of microfluidics and the ease of their fabrication has lead to an abundance of lab-on-a-chip devices that can execute a series of tasks, such as complex reaction sequences ranging from organic synthesis [90] to studies of cells [91] to equilibrium phase mapping [4], [92]. Microfluidics can also be integrated with analytical devices, such as High Pressure Liquid Chromatography (HPLC) [93], Infrared (IR) Spectroscopy [94], Mass Spectrometry [95] and Dynamic Light Scattering [96] to name a few, allowing on-line analysis of the experiment. More recently, microfluidic devices have been integrated with more complex analytical methods such as NMR [7], [97] and small angle neutron/x-ray scattering [5], [98] which historically require larger sample volumes for analysis.

Microfluidics have been often used in nano- and micro- particle design. The ways microfluidics can facilitate manufacturing of these particles is via pathway selection or flow processing (Fig. 1.11) [99]. Microfluidics allows control of the sequence of self-assembly steps and form equilibrium and metastable structures. Microfluidics also offers access to different flow types and flow-induced structure formation [99]. The latter will be the focus in this thesis.

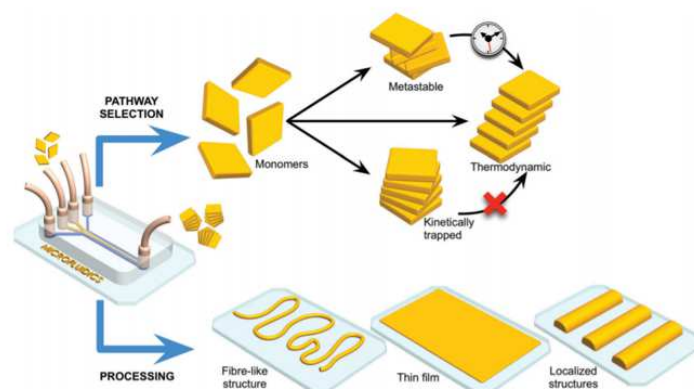


Figure 1.11: Directed assembly under flow. Microfluidics facilitate pathway selection of self-assembled structures and/or thermodynamic states, that can be either in equilibrium or non-equilibrium states (metastable or kinetically arrested). Simultaneously, microfluidics allows processing of already self-assembled materials into new arrangements, e.g. plastic in 3D printed devices, formation of thin films or localised patterns. Reproduced with permission from [99].

There have been several analytical tool (microscopy, SAXS/SANS, PIV) coupled microflu-

idic studies investigating flow induced structural transformations in surfactant phases. These transformations have been typically studied by introducing extensional flows in a form of contraction-expansion or micropost array. Generally, the flow induced structures have been studied in micellar, lamellar or vesicles phases. The micellar studies have primarily focused on the formation of gel-like micellar networks after CTAB/NaSal solution has been passed through a micropost array [100]–[105]. Lamellar  $L_\alpha$  transformations on a chip so far have focused on lamellar reorientation following an extension [5], [6], [98], shear induced vesicle formation [106] and lamellar formation from sponge phase  $L_3$  [107]. Studies investigating surfactant vesicles (unilamellar or multilamellar) have focused on their deformation under complex flow fields generated by a microfluidic four roll mill [108]. The flow rates scanned in these studies ranged from 0.03–15 mL h<sup>-1</sup> with wall shear rates  $\dot{\gamma}$  reaching 37000 s<sup>-1</sup> with the exception of  $L_3$  to  $L_\alpha$ , where flow rates reached 1800 mL h<sup>-1</sup> and wall shear rates  $\dot{\gamma}$  reaching 10<sup>5</sup> s<sup>-1</sup> [107].

## 1.6 Motivation for this work

So far I have described the formation, structural parameters and microstructural rearrangements of liquid crystalline surfactant phases, namely  $L_\alpha$ -to-MLV phase transformation which has been previously studied extensively in a range of surfactant systems, including charged and uncharged binary, tertiary and quaternary systems. Some of these systems, specifically SDS/octanol/brine display rich flow phase behaviour forming vesicles of various sizes and higher order packing as a function of shear rate and temperature. Microfluidic technology offers a platform to investigate flow induced phase transformations with complex flow fields that are more relevant to industrial applications where complex flow fields are prevalent. To date the research effort of microfluidic-facilitated structural rearrangements in surfactant systems has focused on long-lived flow induced structured phase (FISP) formation from micellar-to-wormlike, micelles-to-wormlike micellar bundles and short-lived phase formation such as deformation of vesicles under flow, lamellar phase orientational flip under extension,  $L_3$ -to-lamellar phase transformation.

The overall aim of this thesis is to integrate the lamellar-to-MLV flow induced textural transformation on microfluidic devices with linear and extensional flow geometries and elucidate the role of the physical properties of the lamellar membrane and the applied flow field on the formation of MLVs.

The objectives for my thesis work were:

- Understand how the molecular scale physical properties of surfactant lamellar phase link to its microfluidic flow behaviour;
- Demonstrate the feasibility of studying lamellar-to-MLV phase transformation under microfluidic flow;
- Understand the role of different flow geometries in lamellar-to-MLV phase transformation.

My thesis is divided into methods, three experimental chapters focusing on the equilibrium and flow phase behaviour in model SDS/octanol/brine system and an additional chapter focusing on the outreach work I have done to explain the role of surfactants and surface tension via the activity of paper marbling.

Chapter three will look at the equilibrium phase behaviour of SDS/octanol/brine system and build on previously published phase map. I will describe the role of addition of dopants, i.e. co-surfactant octanol and temperature on the nanostructure of the phases.

Chapter four will focus on understanding the role of charge on lamellar membrane physical properties and how membrane rigidity affects the flow induced phase transformations.

Chapter five will look at the role of flow field in a contraction-expansion microfluidic device where I will investigate the role of linear and oscillatory shear flows and timescales for the lamellar-to-MLV phase transformation.

Finally, chapter six will offer an outlook on how surfactant science can be used in societal engagement by combining the science with the art of paper marbling and how the general public can gain insights in interfacial and surfactant science via hands-on

activities. The case study described here focuses on the activity carried out for the Great Exhibition Road Festival 2022. I show how the reciprocity often sought out in societal engagement activities can offer tangible experimental results that can be analysed and compared in a laboratory setting.

# Chapter 2

## Methods

In this chapter I will look at the key experimental techniques used to characterise lamellar structures under quiescent and flow conditions. I will first look at optical microscopy, SANS and NMR for bulk characterisation. Following that, I will briefly introduce microfluidic technology, its principles and device fabrication. Finally, the requirements for coupling microfluidics with small angle neutron scattering and microscopy will be elucidated.

### 2.1 Optical microscopy

Optical microscopy allows the visualisation of objects that the human eye cannot discern (about  $40\text{ }\mu\text{m}$ , width of a fine hair). In optical microscopy, incident light is focused on the object of interest through a series of lenses whereby it can be reflected, absorbed or transmitted. The resolution of optical microscopy corresponds to the wavelengths of visible light,  $\sim 0.5\text{ }\mu\text{m}$  [109].

#### Principles of microscopy

The simplest microscope consists of an objective lens and eyepiece (ocular) [110].

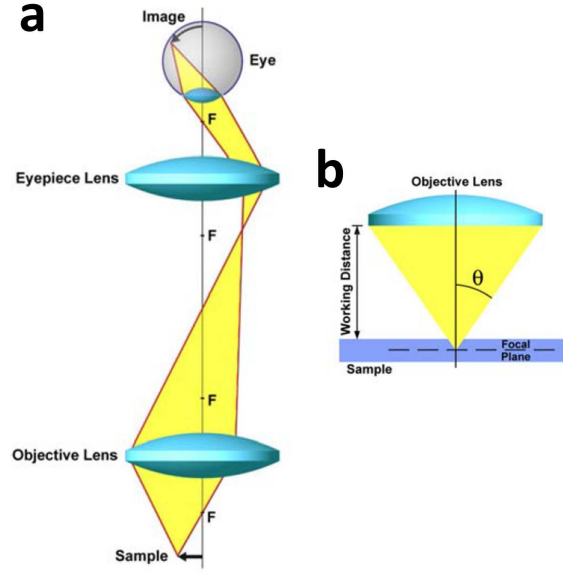


Figure 2.1: Optical microscopy. Modified from [110]

The working principles behind the simplest lens are capture in the thin lens equation [111] which captures the relationship between the distance of the object  $d_o$  and the image  $d_i$ ,

$$\frac{1}{d_f} = \frac{1}{d_i} + \frac{1}{d_o} \quad (2.1)$$

The focal length of the lens,  $d_f$ , is the point at which the light passing through the lens converges (convex lens) or diverges (concave lens). The magnification  $M$  of a given lens is defined as [111],

$$M = \frac{d_i}{d_o} = \frac{d_f}{d_i - d_f} = \frac{d_o - d_f}{d_f} \quad (2.2)$$

In microscopy, the objective is the most crucial optical component and its performance is described by numerical aperture (NA) [110]. NA determines which angles the objective lens can accept the incoming visible light and is defined as,

$$NA = n \sin(\theta) \quad (2.3)$$

where  $n$  is the refractive index of the medium between the sample and the objective lens

(usually air, 1.002, but 1.51 for immersion microscopy oils) and  $\theta$  is the half-angle of the cone of light accessible for entering or exiting the objective lens [110].

From the numerical aperture, the lateral resolution  $r_{lateral}$  of the objective can be estimated as follows,

$$r_{lateral} = \frac{0.61\lambda}{NA} \quad (2.4)$$

where  $\lambda$  is wavelength of light. Objectives with higher lateral resolution can resolve finer details, however, the resolution is still on the same order of magnitude as the light used for imaging. The resolution can be greatly enhanced by the use of confocal or fluorescence microscopies [110].

### **Polarised Optical Microscopy**

Natural light is uniaxial, i.e. its electric field vectors vibrate in all possible angles from the axis of propagation [109]. When the incident beam encounters a polarising filter, the electric field vectors in the resulting beam will be in the same plane. A filter that produces polarised light is called a polariser and a filter that adjust the angle of polarised light is called analyser. In the case of cross-polarised light the alignment between analyser and polariser is  $90^\circ$ . Polarisers are typically made out of transparent crystals, e.g. calcite that are oriented in the same direction [109].

Polarised optical microscopy (POM) allows to capture the submicroscopic molecular order that leads to birefringence [109] and is often used to study birefringent materials such as liquid crystals [110]. Birefringence is a property of a molecularly ordered material to split the incident beam of light in two orientations meaning the material displays more than one refractive index. There are several mechanisms behind birefringence, but this work will be looking more closely at structural birefringence that emerges due to ordered macromolecular arrangements (e.g. lamellar crystals) and flow birefringence where application of flow induces macromolecular alignment [109].

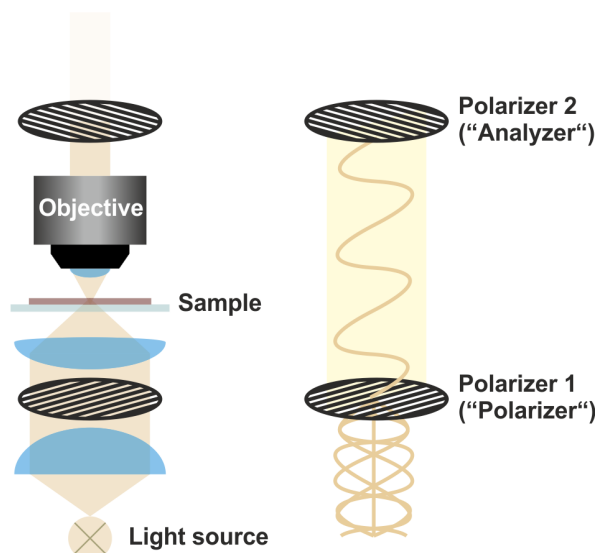


Figure 2.2: Cross-polarised optical microscopy. The polariser is positioned after the light source while the analyser after the light has passed through the sample. Reproduced with permission from [112].

As a result, the polarised light travelling through the anisotropic crystal (the sample) is divided into two sinusoidal light waves (Fig. 2.2). When the light hits the second polariser (analyser), only the waves parallel to the analyser will pass through. The light emerging from the analyser is then detected by the microscope camera yielding the cross-polarised image [112].

In the context of lamellar to MLV transition, POM is often used as a complimentary technique to scattering or NMR. MLVs form a characteristic Maltese cross pattern under cross-polarised light. If MLVs are small (about a micron), the optical texture is speckled and uniformly grey (Fig. 2.3) [81].

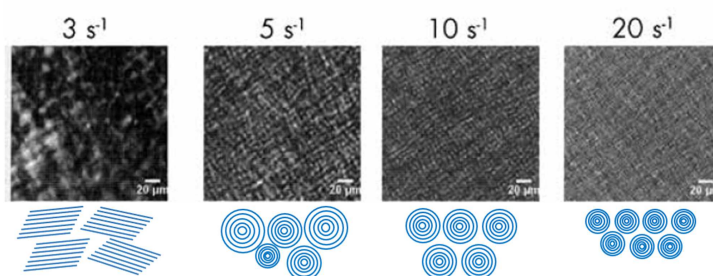


Figure 2.3: Formation of MLVs from 40wt%  $C_{10}E_3$  lamellar phase. Modified with permission from [81].

## 2.2 Small Angle Neutron Scattering

### 2.2.1 Probing matter by scattering particles

On molecular lengthscales, objects will exhibit both particle- and wave-like properties, i.e. wave-particle duality, at the fundamental level captured by Planck's equation (Eq. 2.5), where energy  $E$  is given by

$$E = h\nu \quad (2.5)$$

where  $h$  is Planck's constant and  $\nu$  is oscillation frequency of the wave and de Broglie's equation which states that a particle with momentum  $p$  possesses a wavelegnth  $\lambda$  (Eq. 2.6)

$$\lambda = \frac{h}{p} \quad (2.6)$$

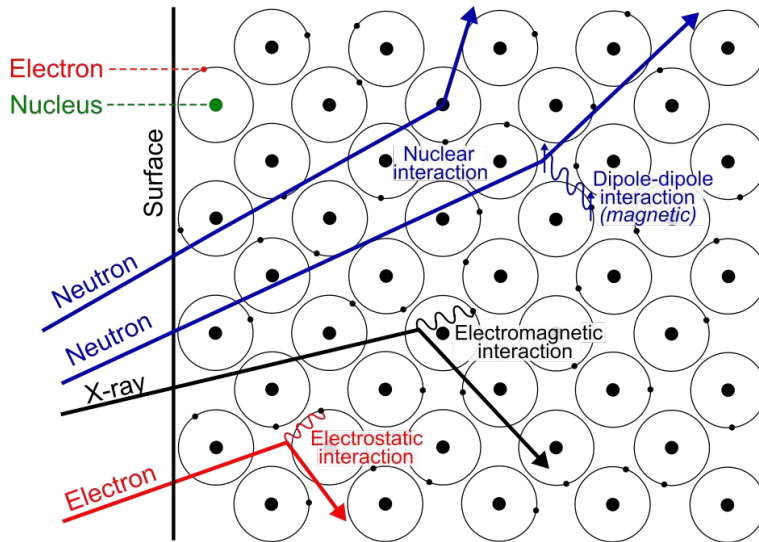


Figure 2.4: Types of scattering. The distance from the surface shows the penetration depth of each type of particles. Reproduced with permission from [113], [114].

In a scattering experiment, a beam of particles with a wavelength  $\lambda$  and energy  $E$ , impinges on the particles of the sample resulting in a change in scattering direction which is described by  $Q$ , the wave vector transfer [115]. The mechanism of the way the incident

Table 2.1: Radiation of scattering experiments. Modified from [116].

|                           | Visible light          | X-rays               | Neutrons                      |
|---------------------------|------------------------|----------------------|-------------------------------|
| Type                      | Electromagnetic wave   | Electromagnetic wave | Particle/wave                 |
| Wavelength, $\lambda$     | 400-600 nm             | 0.01-2 nm            | 0.01-2 nm                     |
| Distances probed          | $\geq 0.1 \mu\text{m}$ | nm to $\mu\text{m}$  | nm to $0.3 \mu\text{m}$       |
| Scattered by variation of | Refractive index       | Electron Density     | Nuclear scattering properties |
| Techniques                | DLS, SLS, SALS         | SAXS                 | SANS                          |

beam of particles will interact with the sample is dependent on the particles which make up the beam (Fig. 2.4). For example, in electron scattering, the incident beam will interact with the orbital electrons of the scattering particle hence will only be able to penetrate the surface (e.g. a few  $\mu\text{m}$  of Al). An X-ray photon while uncharged, possesses an electromagnetic field and will interact with the sample particle electron orbitals, but will penetrate the matter more easily (e.g. a few mm of Al). A beam of neutrons is uncharged and hence will be unaffected by the sample electron orbitals and therefore will be able to penetrate matter deeply (e.g. a few cm of Al). This offers the benefit of understanding the bulk properties of the material, albeit suffers from poor scattering signal and therefore require high concentrations of the sample [115]. Neutrons can also interact magnetically with unpaired electrons in the sample via spin-based dipole-dipole which is the basis behind neutron spin-echo scattering studies and nuclear magnetic resonance spectroscopy [115].

### 2.2.2 Elastic neutron scattering

Neutron scattering is characterised by the change of momentum  $P$  and energy  $E$  of the incident beam  $k_i$  and can be expressed as,

$$P = \frac{h}{2\pi} |k_s - k_i| \quad (2.7)$$

$$E = \frac{h}{2\pi} |\omega_s - \omega_i| \quad (2.8)$$

where  $k_s$  is the scattered wavevector and  $\omega_i$  is angular frequency after the scattering event.

When scattering is elastic, there is no change in energy meaning that  $|k_i| = |k_f| = \frac{2\pi}{\lambda}$ . In a neutron scattering experiment (Fig. 2.5) collimated incident beam  $k_i$  interacts with the neutrons in the sample and is scattered as  $k_s$ .

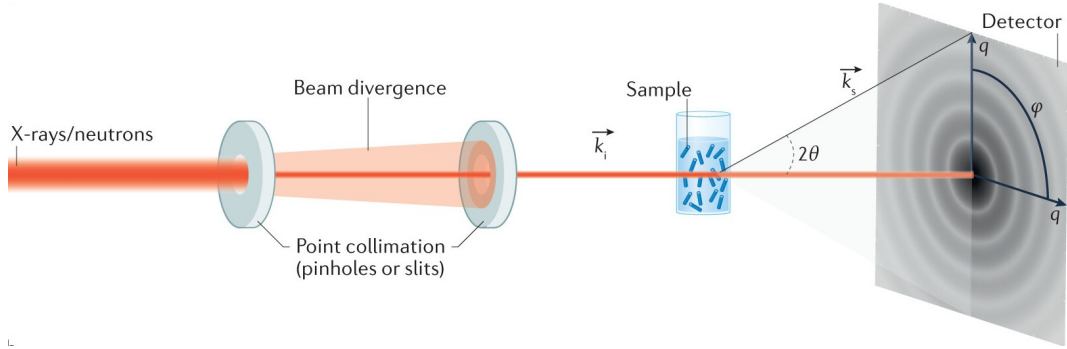


Figure 2.5: Principle of scattering experiment. Transmission geometry set-up for small angle neutron scattering (SANS) displaying a collimated beam interacting with a sample. As the incident beam,  $k_i$ , travels through a sample, an extremely small portion of it interacts with the atoms to generate scattering events,  $k_s$ . The intensity of the scattered radiation is collected on a detector, the angular dependence of which is expressed in terms of momentum transfer,  $q$ . Reproduced with permission from [117].

The scattering wavevector  $Q$ , derived from 2.6 and 2.7 is given by 2.9 where  $\theta$  is the angle of the scattered wavevector  $Q$

$$Q = |k_s - k_i| = \frac{4\pi \sin\theta}{\lambda} \quad (2.9)$$

### Scattering length density

The magnitude of scattering of incident neutrons is determined by the scattering length of the neutron it is interacting with and is given by Eq. 2.10,

$$\frac{b}{R} = 1 - \frac{\tan(qR)}{qR} \quad (2.10)$$

Table 2.2: Neutron scattering lengths  $b_i$  for nuclei present in chemicals used in this project. Values taken from [118]

| Element | $b_i, \text{\AA} \times 10^{-5}$ |
|---------|----------------------------------|
| H       | -3.739                           |
| D       | 6.671                            |
| C       | 6.646                            |
| O       | 5.803                            |
| Na      | 3.63                             |
| S       | 2.849                            |
| Cl      | 9.577                            |

where  $R$  is the radius of the nuclei and  $q$  is given by  $\frac{2\pi}{h} \sqrt{2m(E_i + V_0)}$ , the summed energy of incident neutron  $E_i$  and square well potential  $V_0$  for a neutron with a mass  $m$  [118]. The magnitude of scattering length is predicated on the strength of the interactions between the incident neutron and the neutron(s) found in the sample [117]. Neutron scattering lengths for relevant atoms constituting surfactants used in this work are given in Table 2.2. Note that the  $b_i$  value for H and D atoms has different signs, which enables distinguishing these nuclei in a scattering experiment and becomes important when carrying out contrast variation [118].

Neutron scattering length density  $SLD$  measures the scattering of the sample and is given by

$$SLD = \frac{\sum_{i=1}^N b_i}{V_m} \quad (2.11)$$

where  $b_i$  is the scattering length density of an atom in the sample,  $N$  is the number of atoms in the sample and  $V_m$  is the molecular volume given by  $V_m = \frac{M_w}{N_A \rho_m}$  where  $M_w$  is the molecular weight of the sample and  $\rho_m$  is the density of the sample [115], [118].

### Scattering cross-section

Scattering wavevector  $Q$  will determine the scattering intensity  $I_s(Q)$  of the sample and is given by Eq. 2.12,

$$I_s(Q) = I_0(\lambda)T(\lambda)d\frac{d\Sigma(Q)}{d\Omega}\Delta\Omega \quad (2.12)$$

where  $d$  is sample thickness,  $T(\lambda)$  is the sample transmission,  $\frac{d\Sigma(Q)}{d\Omega}$  is the macroscopic scattering cross-section, where  $d\Omega$  represents the fraction of neutrons scattered at angle  $\theta$ ,  $\Delta\Omega$  the solid angle that subtends detector coil and  $I_0$  is the empty beam transmission is given by Eq. 2.13,

$$I_0 = \phi_v(\lambda)A_2\epsilon(\lambda)t \quad (2.13)$$

where  $\phi_v(\lambda)$  is the neutron flux,  $A_2$  the illuminated area,  $\epsilon(\lambda)$  the detector efficiency and  $t$  counting time normalised to set number of monitor counts [118].

Coherent scattering macroscopic cross-section  $I_{coh}(Q)$  ( $\frac{d\Sigma(Q)}{d\Omega}$ ) for a system with identical particles is be given by

$$I_{coh}(Q) = n\Delta\rho^2V^2P(Q)S(Q) \quad (2.14)$$

where  $n$  is the number density of particles,  $\Delta\rho^2$  is the scattering contrast,  $V$  is the volume of a single particle,  $P(Q)$  is form factor that describes the shape of the particle and  $S(Q)$  is structure factor that describes the inter-distance within the particle [117], [118]. Incoherent scattering (Q-independent) is given by:

$$I_{incoh}(Q) = \frac{\sum_i}{4\pi} \quad (2.15)$$

## Neutron sources

Neutrons are generated either by high energy particle accelerators or nuclear reactors. Neutrons generated are too high in energy and have to be cooled/slowed down by either H<sub>2</sub>O or liquid H<sub>2</sub>. This allows the neutrons to reach energies around 25 meV, corresponding to 1.8 Å wavelength  $\lambda$  [113]. Neutrons generated in a nuclear reactor (such as ILL in

Grenoble), are produced by fission of heavy atoms from uranium (U-235). For most scattering experiments, the neutrons are reduced to a monochromatic beam by passing them through a highly reflective or crystalline material, e.g. pyrolytic graphite, germanium or copper. In the case of high energy particle accelerators, i.e. spallation sources (such as ISIS in Oxfordshire), the neutrons are generated by proton collision with a heavy metal, tungsten (W-183) or uranium (U-238). Since the release of neutrons in a spallation source is not continuous, monochromatic mirrors are not used, but instead time-of-flight (TOF) is used to determine the wavelength of neutrons [113].

## 2.3 SANS models used in this thesis

### 2.3.1 SLD calculations

Fig. 2.6 shows the scattering length density *SLD* calculations by employing Eq. 2.11. These calculations reflect the SLD values for SDS/octanol/brine lamellar phases described in Chapters 3, 4, 5 and micellar phases described in Chapter 3.

### 2.3.2 Structure of SDS/octanol/brine sponge phase $L_3$

Quantitative description of sponge phase  $L_3$  for the molar octanol:SDS ratio of 0.27 (or 1.2 w/w) was achieved by fitting structure factor  $S(q)$  model (Eq. 2.16) described by Lei [120],

$$S(q) = 1 + \frac{A \arctan[q\xi_{io}/2]}{q} + \frac{B}{\xi_3^{-2} + (q - q_3)^2} \quad (2.16)$$

where  $\xi_{io}$  is inside/outside correlation length which describes correlation on a large scale much larger than  $\xi_3$  which describes sponge pore correlation length.  $q_3$  is the position of the Bragg peak (conversely, average sponge pore size is  $\xi = 2\pi/q_3$ ) and A and B are  $S(q)$  prefactors. The structure factor is dominated by the second term (prefactor B) because

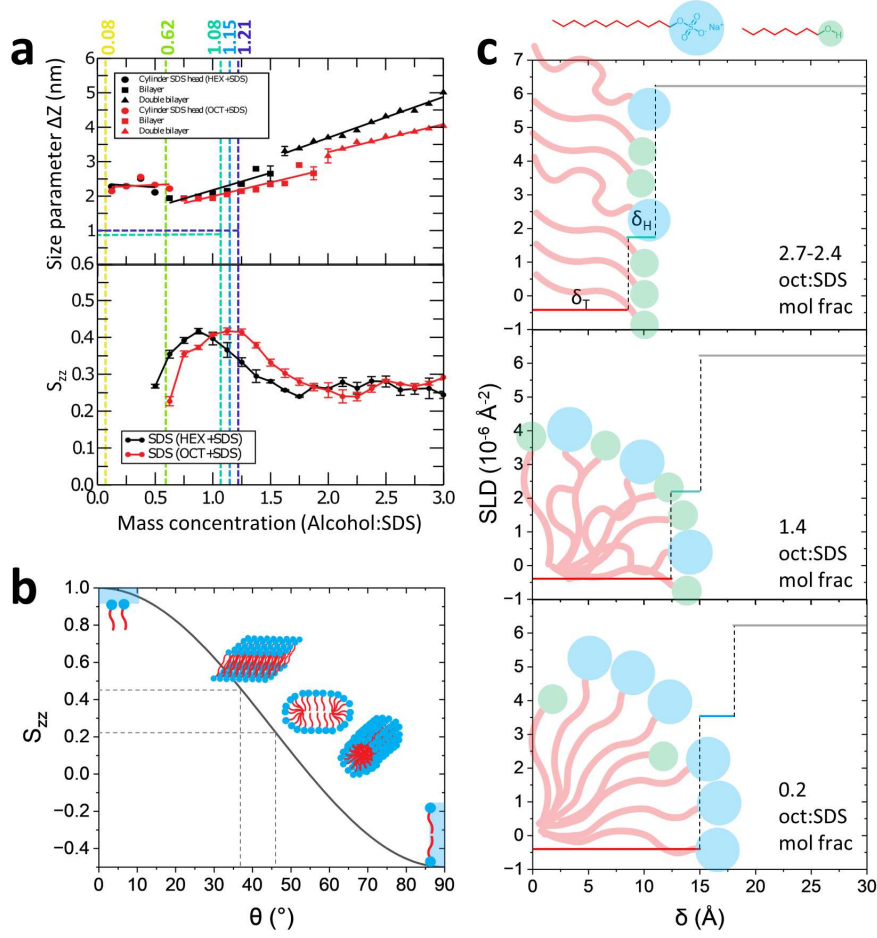


Figure 2.6: Molecular dimensions and SLDs for samples with oct:SDS ratios of 1.21, 1.15, 1.08, 0.62 and 0.08. a)  $\Delta Z$ , which corresponds to membrane thickness or micellar radius as a function of octanol concentration (top),  $S_{zz}$  parameter as a function of octanol concentration (bottom) describing the surfactant tail tilt, -0.5 corresponds to tails parallel to water interface while 1.0 corresponds to tails normal to water interface taken from [119], b) Surfactant tail tilt in the systems of interest; c) SLD calculations of lamellar 1.08-1.21 (top), mixed 0.62 (middle) and micellar 0.08 (bottom).

the membrane concentration is relatively small. Porcar *et al.* [121] report  $\xi_3$  of values around 85 Å which are the values fitted for SDS/octanol/brine system.

Analytic approximation describing membrane "discoids" (Eq. 2.17) was employed to describe the form factor  $P(q)$  [121],

$$P(q) = 4(\pi\sigma^2\Delta\rho)^2 \frac{1 - \cos[qt_0] \exp[-q^2 t_0^2/32]/q^2}{q^2\sigma^2 + 2 \exp[-q\sigma^2/6]} \quad (2.17)$$

where  $\sigma$  is the radius of gyration of the discoid,  $t_0$  thickness of membrane's hydrocarbon core, which in this case is between 17-30 Å and  $\Delta\rho$  is the neutron contrast between the

hydrocarbon tail and solvent has been estimated to be  $5.9 \text{ \AA}^{-2} 10^{-6}$  from the molecular volume. Overall thickness of sponge phase membrane  $\delta$  is  $t_0 + 5$ .

The observed coherent scattering  $I_{coh}$  is as follows (Eq. 2.18),

$$I_{coh}(q) = NS(q)P(q) \quad (2.18)$$

where  $N = \phi_v / \pi \sigma^2 \delta$  where  $\phi_v$  is membrane volume fraction calculated as  $(V_{octanol} + V_{SDS}) / V_{total}$

### 2.3.3 Structure of SDS/octanol/brine lamellar phase $L_\alpha$

Lamellar structures were fitted with the Caillé structure factor model [122] preprogrammed in SASView considering scattering from surfactant head and tail groups separately. The structure factor (Eq. 2.19) is given by

$$S(q) = 1 + 2 \sum_{n=1}^{N-1} \left(1 - \frac{n}{N}\right) \cos(q dn) \exp\left(-\frac{2q^2 d^2 \alpha(n)}{2}\right) \quad (2.19)$$

where  $N$  is number of lamellar stacks and  $\alpha(n)$  (Eq. 2.20)

$$\alpha(n) = \frac{\eta_{cp}}{4\pi^2} (\ln(\pi n) + \gamma_E) \quad (2.20)$$

with  $\eta_{cp} = \frac{q_0^2 k_B T}{8\pi \sqrt{KB}}$  being Caillé parameter where  $K$  is the membrane bending rigidity  $\bar{B}$  is the membrane compression modulus.  $\gamma_E$  is Euler's constant with value of 0.58.

Form factor is given by (Eq. 2.21)

$$P(q) = \frac{4}{q^2} \Delta\rho_H^2 (\sin[q(\delta_H + \delta_T)])^2 - \Delta\rho_T^2 (\sin(q\delta_T))^2 \quad (2.21)$$

Where  $\Delta\rho_H$  is  $SLD_H - SLD_{brine}$  and  $\Delta\rho_T$  is  $SLD_{tail} - SLD_H$ ;  $\delta_H$  is the thickness of the headgroup ( $-OH$ ) and  $-SO_4Na$ ) and  $\delta_T$  is the hydrocarbon chain of octanol and SDS.

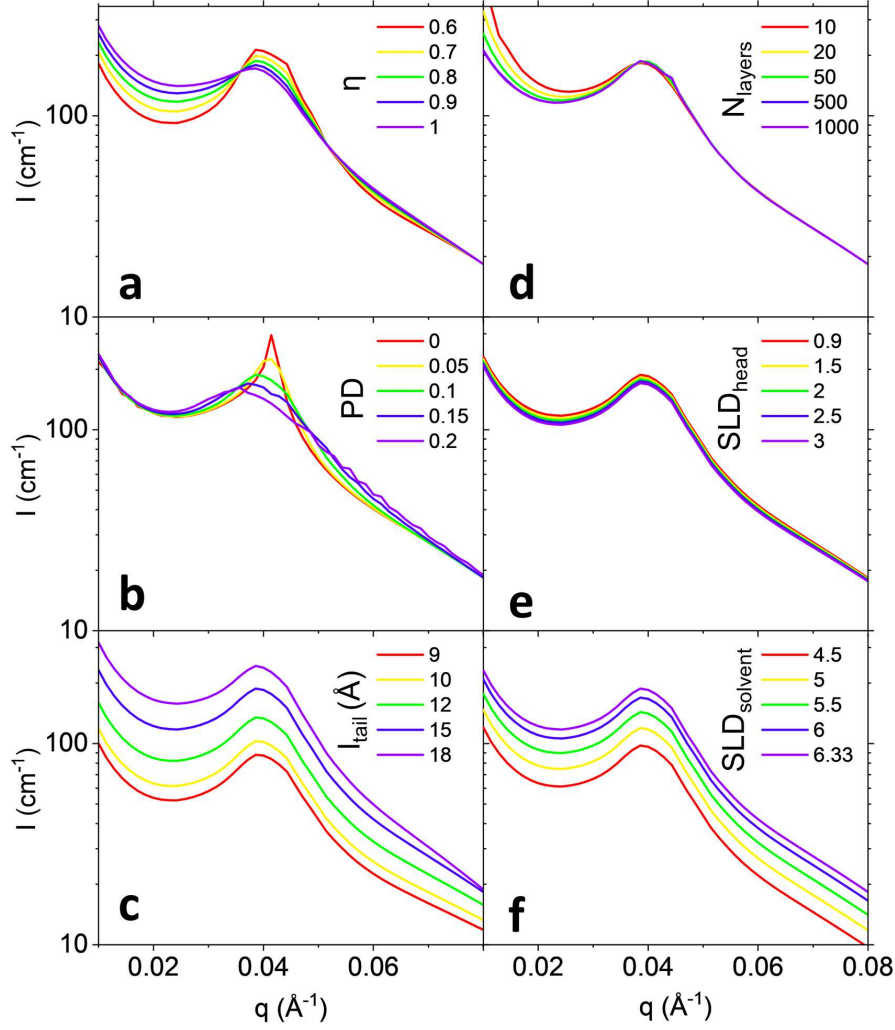


Figure 2.7: Parameters in Caillé model. a) Caillé parameter ( $\eta = 0.6 - 1.0$ ) describing lamellar membrane physical properties; b) Polydispersity of d-spacing ( $p_D = 0 - 0.25$ ) describing Gaussian d-spacing distribution; c) Surfactant hydrocarbon tail length ( $l_{tail} = 9 - 18 \text{ \AA}$ ); d) Number of lamellar stacks ( $N_{layers} = 10 - 1000$ ); e) Scattering length density for the headgroup consisting of  $-SO_4$  and  $-OH$  ( $SLD_{head} = 0.9 - 3 \cdot 10^{-6} \text{ \AA}^{-2}$ ); f) Scattering length density for the solvent ( $D_2O$  and  $NaCl$ ) ( $SLD_{head} = 4.5 - 6.33 \cdot 10^{-6} \text{ \AA}^{-2}$ ).

The coherent scattering  $I_{coh}$  is given by (Eq. 2.22)

$$I(q) = 2\pi \frac{P(q)S(q)}{q^2 \delta} \quad (2.22)$$

### 2.3.4 Structure of SDS/octanol/brine micellar phase $L_1$

The addition of salt  $NaCl$  and mid-to-long chain 1-alcohol such as 1-octanol favours the formation of wormlike micelles. To describe these structures, core-shell cylinder model

[123] available on SasView was fitted. The form factor is given by Eq. 2.23

$$F(q, \alpha) = (\rho_c - \rho_s)V_c \frac{\sin(q\frac{1}{2}L \cos \alpha)}{q\frac{1}{2}L \cos \alpha} \frac{2J_1(qR \sin \alpha)}{qR \sin \alpha} + (\rho_s - \rho_{solv})V_s \frac{\sin(q(\frac{1}{2}L + T) \cos \alpha)}{q(\frac{1}{2}L + T) \cos \alpha} \frac{2J_1(q(R + T) \sin \alpha)}{q(R + T) \sin \alpha} \quad (2.23)$$

and

$$V_s = \pi(R + T)^2(L + 2T) \quad (2.24)$$

where  $\alpha$  is the angle between the cylinder and the scattering vector  $q$ ,  $\rho_c$  is the scattering length density of the hydrocarbon core,  $\rho_s$  is the scattering length density of the headgroup shell and  $\rho_{solv}$  is the scattering length density of the solvent,  $V_s$  is the total volume of the cylinder,  $V_c$  is the the volume of the core (Eq. 2.24),  $R$  is the radius of the core,  $L$  in the length of the core and  $T$  is the thickness oft the shell. The outer radius is given by  $R + T$  and the total length including shell is  $L + 2T$ ;  $J_1$  is first order Bessel function. The coherent scattering is then is given by:

$$I(q, \alpha) = \frac{scale}{V_s} F^2(q, \alpha) \sin(\alpha) + I_{incoh} \quad (2.25)$$

### 2.3.5 Nuclear Magnetic Resonance for lamellar to MLV transformation

Nuclear Magnetic Resonance (NMR) is a widely used technique in chemistry for structure determination, purity of the compound and even complex mixture e.g. soil, metabolites, natural products characterisation with a suite of multidimesional NMR techniques [124]. In NMR transition occurs by application of bulk magnetisation and nuclear spin alignment with this external applied magnetic field. Unlike other spectroscopic techniques that measure the change in energy levels, the energy difference in NMR arises from spin populations [125].

NMR is widely used technique to study soft matter, particularly liquid crystals. Since liquid crystals are partially ordered, NMR signal with arise not only from Zeeman interactions ( $H_z$ ) and spin-spin coupling ( $H_J$ ), but also form dipolar interactions ( $H_D$ ) from the nuclei in close proximity and quadrupolar interactions ( $H_Q$ ) when quadrupolar nuclei with magnetic spin greater that  $1/2$  are present [126].

One example of quadrupolar nucleus that has been widely used for supramolecular mesophase determination and distribution is Deuterium ( $^2\text{H}$ ). D has a magnetic spin of 1 and  $^2\text{H}$  NMR quadrupolar splitting patterns are very useful for surfactant in water ( $\text{D}_2\text{O}$  in NMR experiment) phase determination (Fig. 2.8) [127].

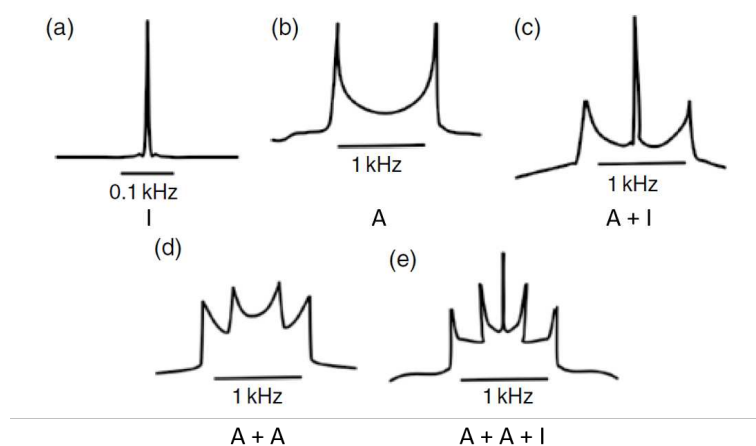


Figure 2.8: Quadrupolar splitting patterns in  $^2\text{H}$  NMR. I=isotropic phases, A=anisotropic phases. a) Narrow singlet for isotropic phases: micellar, sponge phase, cubic, microemulsion; b) Doublet for anisotropic phases: lamellar, hexagonal. The magnitude of splitting depends on the degree of anisotropy; twice the magnitude for lamellar than hexagonal; c) Mixed phase consisting of isotropic and anisotropic phases; d) Two anisotropic phases; e) Two anisotropic and one isotropic phase. Modified from [127].

While MLVs belong to lamellar phase, the quadrupolar splitting pattern of MLVs is a singlet. This arises because of the diffusion of  $\text{D}_2\text{O}$ . In the case of lamellar phase,  $\text{D}_2\text{O}$  has no rotational component, while in the case of MLVs the membrane curvature causes  $\text{D}_2\text{O}$  to rotate resulting in signal averaging and eventually the collapse of quadrupolar splitting pattern into a singlet. This difference in  $^2\text{H}$  NMR spectra allows the phase transition of lamellar to MLVs to be studied with NMR coupled with rheometer [40].

## 2.4 Microfluidics

Microfluidics is a technology that studies fluids on 100  $\mu\text{m}$  lengthscales and offer the ability to design more complex flow fields beyond simple shear flows, such as microfluidic four roll mill [86].

### 2.4.1 Microfluidic device fabrication

With the rise of microfluidics, numerous chip fabrication procedures have been developed. Broadly, these techniques can be categorised as photomask-based (PDMS, NOA-81, glass etching) or photomask-free (3D printing, laser cutting, embossing) [128]. The most common chip fabrication techniques, photolithography, soft lithography, laser etching and glass etching, have been summarised in Table 2.3.

The device for experiments carried out in this work had to satisfy two requirements - be optically transparent and have high transmission in SANS, which was the reason behind opting for fabrication in crown glass [132]. Device fabrication by wet glass etching was outsourced to Dolomite Microfluidics. The process of glass etching is outlined in Fig. 2.9a alongside fabricated device designs (Fig. 2.9b, c). Wet etching relies on several fabrication steps. First, photoresist is applied on chrome bonded glass, then a positive photomask is placed on top and irradiated with UV. Second, the uncured photoresist is washed away with developer, leaving an imprint of the channel where photoresist was not cured. Third, the channel design is etched in chrome and following that, etched in glass with hydrofluoric acid (HF). When photoresist and chrome layers have been removed, the exposed channel is sealed by bonding a coverslide at 640 °C either via plasma activated or fusion bonding [133]. Device designs were selected based on two experimental approaches. The serpentine device was used to decouple vesicle formation on the chip in time and space (Fig. 2.9b) and was selected as it is already commercially available. Custom linear contraction-expansion device (Fig. 2.9c) was designed to investigate the effect of extensional flow and time required to complete the lamellar-to-MLV transformation. The

Table 2.3: Common microfluidic chip fabrication techniques. Figure compiled from [128]–[131].

| Technique        | Material       | Procedure                                                                                                                                                                                                                                                                           | Solvent compatibility                                                  |
|------------------|----------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------|
| Photolithography | NOA-81         | Positive transparency is placed over the material and exposed to UV light. In areas where the acetate was transparent the material is cured (hardened) and vice versa [128]                                                                                                         | Compatible with organic solvents [129]                                 |
| Soft lithography | PDMS           | Siloxane oligomer is mixed with curing base (10:1), degassed under vacuum and poured over a SU-8 master. To accelerate the curing process, PDMS is placed in over at 70-80 °C for 1-2h. To close the channels, the chip is bonded to a base by air or oxygen plasma treatment [129] | Incompatible with non-polar organic solvents (e.g. toluene, DCM) [130] |
| Laser etching    | PMMA           | The channel is machined by laser ablation and sealed by heat between two dry resist films (DRF) [131]                                                                                                                                                                               | Incompatible with organic solvents [130]                               |
| Wet Etching      | Silicon, glass | Achieved with HF (hence outsourced to specialised companies, e.g. Dolomite). The mask is typically gold or chromium [128]                                                                                                                                                           | Compatible with organic solvents                                       |

dimensions of the contraction-expansion were governed by the limitations in glass etching with features no smaller than 0.3 mm and no larger than 1.6 mm, which is the size of the inlet tubing and the commercially available Dolomite gaskets.

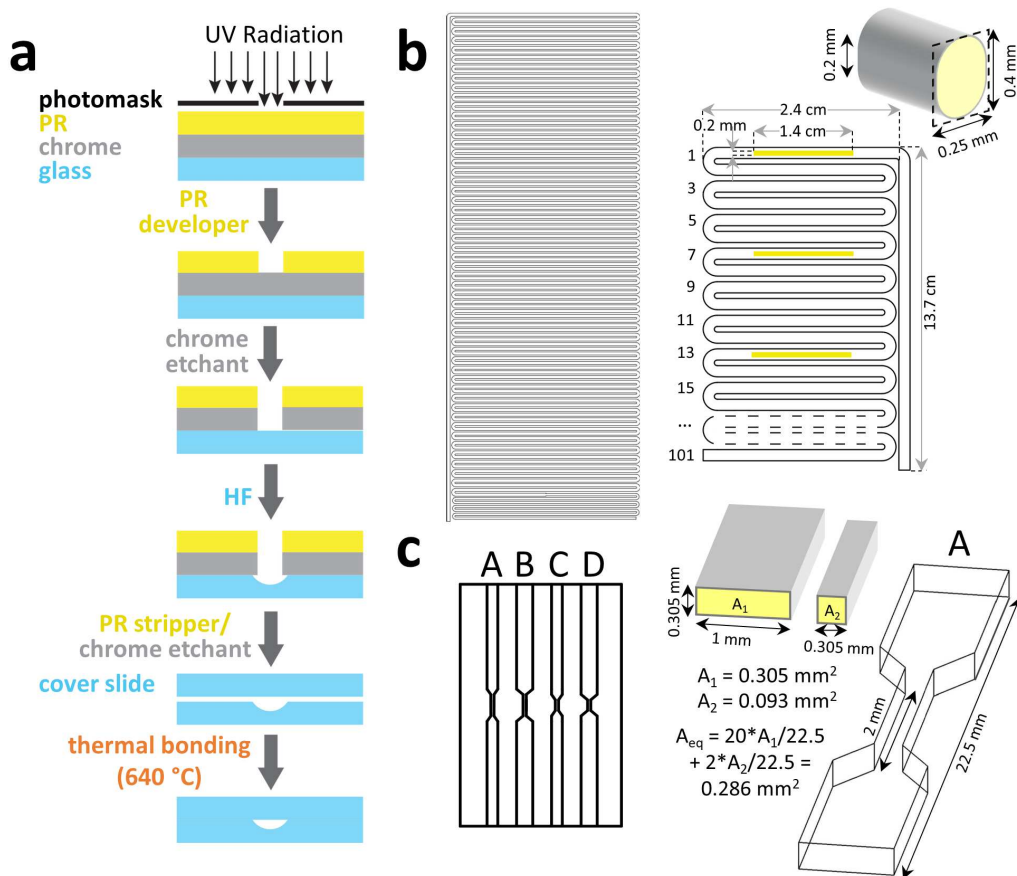


Figure 2.9: Chip manufacturing and design. a) Process of glass etching. Modified from [134] with permission; b) Serpentine microfluidic device and its dimensions c) Contraction-expansion custom made microfluidic device.

## 2.4.2 Microfluidic flow characterisation

This section introduces the microfluidic flow in the two chip designs used in this project. First, wall shear rates using Son's approach are estimated for the serpentine and contraction-expansion microfluidic device in expansion part of the microfluidic device and extension ratio quantified. Next, the pressure drop is calculated using Hagen-Poiseuille law to assess the operating limitations of each microfluidic device across range of relevant flow rates. Finally, 3D flow profiles are estimated in both microfluidic devices based on the dynamic

viscosity  $\eta$  of SDS/octanol/brine solution.

### Wall shear rate calculations

Wall shear rates were calculated to calibrate findings from this work in microfluidic devices to studies done in Couette flow geometries. In the serpentine channel geometry, the wall shear rate was calculated assuming pipe flow, where the hydraulic pipe radius (from diameter) was given by  $r_H = \frac{2A}{P}$  [135], where  $A$  is the cross-sectional area and  $P$  is the perimeter of the cross-section, giving  $r_H = 0.16$  mm. Wall shear rate in a pipe is then calculated by

$$\dot{\gamma} = \frac{4Q}{\pi r_H^3} \quad (2.26)$$

where  $Q$  is the volumetric flow rate. The wall shear rates in the contraction-expansion geometry were estimated based on Son's approach [136] for rectangular chip geometry.

$$\dot{\gamma} = \left( \frac{6Q}{WH^2} \right) \left( 1 + \frac{H}{W} \right) f^* \left( \frac{H}{W} \right) \quad (2.27)$$

where  $H$  is the height of the rectangular chip and  $W$  is the width of the rectangular chip and  $f^*$  is a geometric constant dependent on  $H/W$ , in the expansion part, 0.7297 and in the contraction part 0.5928.

Comparison between linear flow rates and wall shear rates in the linear and the contraction-expansion flow geometries (in the expansion part of the channel) are given in Fig. 2.10

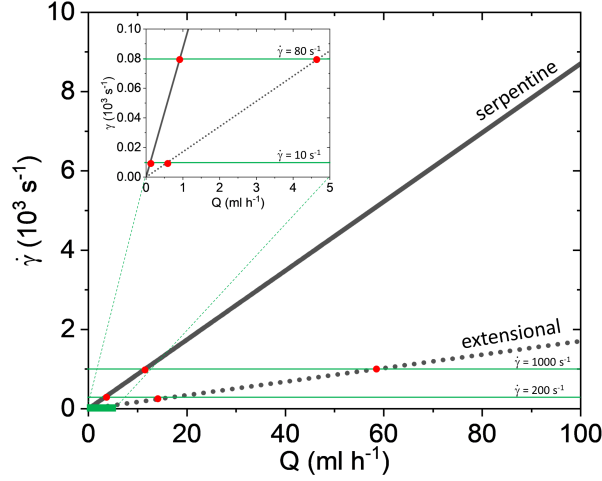


Figure 2.10:  $\dot{\gamma}$  estimates as a function of volumetric flow rates for serpentine (solid line) and contraction-expansion (dotted line) geometries.

### Pressure drop calculations

A flow in a straight channel at a constant flow rate  $Q$  will result in a constant pressure drop  $\Delta p$ . This is described by Hagen-Poiseuille law, which states,

$$\Delta p = R_{hyd}Q \quad (2.28)$$

where  $R_{hyd}$  is the hydraulic resistance. This is analogous to Ohm's law, where  $\Delta V = RI$ , which relates the electrical current  $I$  flowing through a wire with a resistance  $R$  resulting in  $\Delta V$  electrical potential [23].

The microchannel cross-sectional geometries are described in Fig. 2.9b, c. For pressure drop  $\Delta P$  calculations serpentine chip channel cross-section was assumed to be circular and for the contraction-expansion chip, expansion was assumed to be rectangular. The hydraulic resistances  $R_{hyd}$  used for each of the geometries are given in Table 2.4.

Following that, pressure drops were calculated for select flow rates and plotted along the channel dimensions. The flow rates chosen are relevant to the experiments carried out in this project, namely  $Q_s = 0.5 - 10 \text{ mL h}^{-1}$  for the serpentine and  $Q_{c-e} = 0.5 - 200 \text{ mL h}^{-1}$  for the contraction-expansion channel chips.

Since SDS/octanol/brine lamellar composition is non-Newtonian (shear thinning) [137],

Table 2.4: Hydraulic resistance  $R_{hyd}$  for straight channels with circular and rectangular cross-sections [23]. The yellow line area indicates the actual shape of the cross-section and the orange line shows the closest assumption.

| shape     | channel                                                                           | $R_{hyd}$                                      |
|-----------|-----------------------------------------------------------------------------------|------------------------------------------------|
| circle    |  | $\frac{8}{\pi} \eta L \frac{1}{r_H^4}$         |
| rectangle |  | $\frac{12\eta L}{1-0.63(H/W)} \frac{1}{H^3 W}$ |

the pressure drop along the serpentine and contraction-expansion channel for shear rates of 10, 80, 200 and 1000 corresponding to viscosity values  $\eta$  3, 1, 0.2 and 0.06 Pa has been calculated shown in Fig. 2.11. From wall shear rate calculations theses values correspond to volumetric flow rates  $Q$  of 0.1, 0.9, 2.8 and 11 mL h<sup>-1</sup> in linear channel geometry and 3, 1, 0.2 and 0.06 mL h<sup>-1</sup> in contraction-expansion channel geometry.

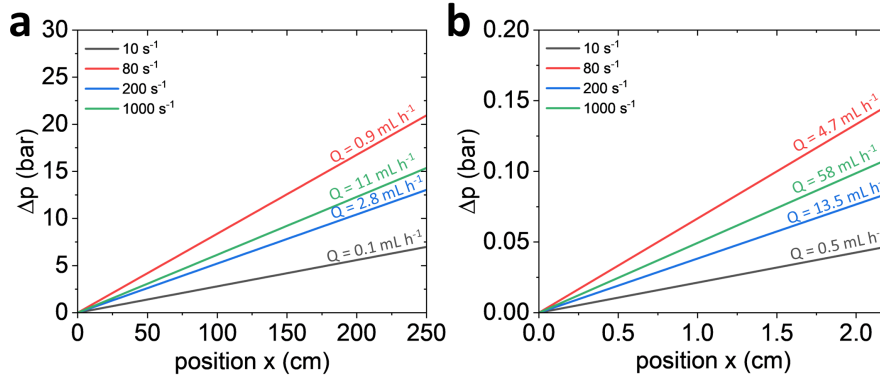


Figure 2.11: Pressure drop calculations based on Hagen-Poiseuille law. a) Linear serpentine chip; b) contraction-expansion chip

### Flow calculations for microfluidic channels

Poiseuille flow describes the flow between two stationary planes and its simplest case when the  $H/W$  ratio is sufficiently small,  $<0.1$  [23], considers the flow to be 2-dimensional.

In this case, the velocity along x-direction (direction of the flow), is given by

$$v_x(z) = \frac{\Delta p}{2\eta L}(h - z)z \quad (2.29)$$

where  $\Delta p$  is the pressure drop along z-axis (channel height  $h$ ),  $\eta$  is fluid viscosity,  $L$  is the section over which the pressure drop is measured and  $z$  is the position along the channel height (z-axis). Volumetric flow rate  $Q$  is calculated integrating Eq. 2.28:

$$Q = \frac{h^3 w}{12\eta L} \Delta p \quad (2.30)$$

However, in the channel geometries used in this work,  $H/W > 0.3$ , which is why the flow profile was calculated for a 3D case.

Here a steady Poiseuille flow in a rectangular channel for an incompressible fluid with a no-slip boundary condition was calculated using the following equation:

$$u_x(y, z) = \frac{4h^2 \Delta p}{\pi^3 \eta L} \sum_{n, \text{odd}} \frac{1}{n^3} \left[ 1 - \frac{\cosh(n\pi \frac{y}{h})}{\cosh(n\pi \frac{w}{2h})} \right] \sin \left( n\pi \frac{z}{h} \right) \quad (2.31)$$

where  $h$  is channel height (0.3 mm for contraction-expansion geometry, 0.25 mm for linear geometry),  $w$  is the half-width of the channel (0.3 mm in the wide part and 0.15 mm in the narrow part of the contraction-expansion geometry, 0.2 mm in the linear geometry) and  $n$  is the numbers in Fourier series ( $n = 1, 3, 5$ ). Integrating Eq. 2.31, the volumetric flow rate  $Q$  can be obtained:

$$Q = \frac{h^3 w \Delta p}{12\eta L} \left[ 1 - \sum_{n, \text{odd}} \frac{192h}{n^5 \pi w} \tanh \left( n\pi \frac{w}{2h} \right) \right] \quad (2.32)$$

The 3D plots were generated in Matlab software (The MathWorks, Inc., Natick, Massachusetts, United States). Fig. 2.12 shows velocity flow profiles  $u_x$  along the flow direction in linear and contraction-expansion microfluidic chip geometries, when estimated wall shear rate is  $10 \text{ s}^{-1}$  and  $\eta$  is 3 Pa s, corresponding to  $Q = 0.1 \text{ mL h}^{-1}$  and  $Q = 0.5 \text{ mL h}^{-1}$  respectively.

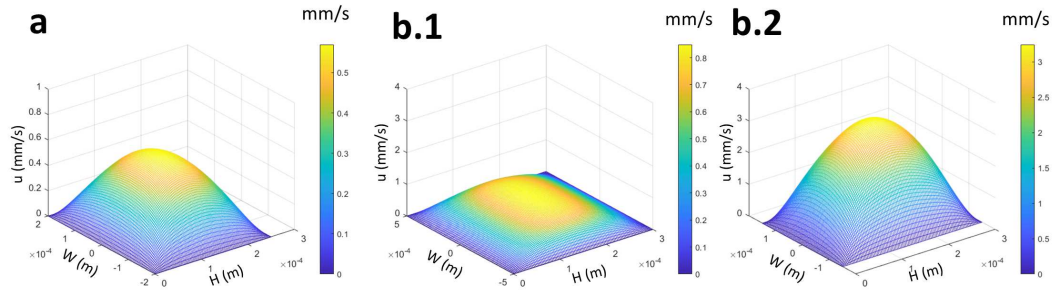


Figure 2.12: 3D flow profile for a) linear channel geometry; b1) wide part in contraction-expansion geometry; b2) narrow part in contraction-expansion geometry.

# Chapter 3

## Phase behaviour and solution structure of SDS/octanol/brine studied by SANS, NMR and microscopy

### 3.1 Introduction

Sodium dodecyl sulfate (SDS) is a common anionic surfactant, extensively employed in industry and academic research. The SDS/water phase diagram has been investigated in detail [13] and, in the liquid state, above Krafft temperature (15-17 °C) [138]–[140] and critical micelle concentration ( $\text{cmc} \simeq 6.9\text{--}8.2$  mM, or 0.19-0.24 w/w %) [140], [141], the system yields micellar ( $L_1$ ), hexagonal ( $H_\alpha$ ) and lamellar phases ( $L_\alpha$ ). However, to attain ordered  $H_\alpha$  and  $L_\alpha$  phases, relatively high SDS concentrations of 40 and 70% w/w and temperatures above 50 °C are required [13], [83]. The formation of liquid crystalline phases can be achieved at ambient temperatures and much lower surfactant concentrations (<10% w/w) by the addition of dopants, specifically mid-to-long chain alcohols, i.e. n-butanol to decanol, and by the addition of electrolytes, such as NaCl. In

general, the addition of alcohols modulates the interactions between surfactant molecules, for instance by reducing headgroup repulsions or altering packing efficiency, while salts impact electrostatic interactions between the headgroups, and in turn affect the formation of self-assembled structures [16].

Co-surfactants can be described as surfactants that, alone, are not able to form micelles, with alcohols forming an important class of co-surfactants [16]. The addition of alcohol has been well established in the phase diagram of SDS/n-alcohol/water systems, both experimentally and computationally [119]. The stability of mixed micelle systems is impacted by the relative matching of alkyl chain lengths [142]. For example, the addition of long chain alcohols ( $C_8$  to  $C_{16}$ ) has been found to lower the critical micelle concentration (cmc) and stabilise SDS micelles, arising from the ion-dipole interactions of the SDS sulfate group and octanol -OH group. This interaction increases packing efficiency and leads to micellar stabilisation below SDS concentrations of 150 mM [142]. However, at higher SDS and alcohol concentrations, with the exception of dodecanol, micelles are destabilised due to a mismatch in the hydrocarbon chain length, where the excess length and thermal motion lead to a decrease in packing efficiency [142], [143]. SANS studies on the effect of alcohols on SDS micellar phase have demonstrated that the addition of  $C_1$  to  $C_3$  alcohols lead to the formation of more spherical micelles while the addition of mid ( $C_4$  to  $C_6$ ) to long ( $C_7$  to  $C_{10}$ ) chain alcohols results in micelle elongation and the formation of wormlike micelles [144]–[146]. Increasing long chain ( $C_7$  to  $C_8$ ) alcohol to surfactant ratio has been found to further elongate micellar structures [144].

Addition of longer chain alcohols, above butanol  $C_4$ , has been found to promote the formation and stability of the  $L_\alpha$  phase, extending it to lower concentration ranges [16]. At constant surfactant concentration, alcohol addition has been reported to lead to rich lamellar phase behaviour, following the  $L_4$ - $L_\alpha$ - $L_3$  order [147]. In SDS  $L_\alpha$  systems, the length of the alcohol was reported to influence the bilayer thickness, with shorter chain alcohols ( $C_5$ - $C_7$ ) thinning the membrane; in turn this resulted in a 5-fold decrease in membrane bending rigidity  $k_C$ , as compared to longer chain alcohols  $C_8$ - $C_{12}$  [19].

The addition of electrolytes to ionic surfactants, such as SDS, generally increases the size of micellar aggregates due to electrostatic screening effects, by reducing headgroup repulsion, which is magnified in presence of alcohol co-surfactants [16]. The addition of  $\text{Na}^+$  salts generally favours the formation of ellipsoidal SDS micelles and, above 0.4 M, the formation of wormlike micelles has been reported [146], [148]. Similarly, salt addition generally reduces the membrane bending rigidity  $k_C$  of anionic surfactant lamellar phases, associated to charge screening of steric repulsions. It has also been demonstrated that the addition of NaCl to SDS/alcohol/water system extends the lamellar phase stability up to 95% water corner [149].

While the presence of mid- to long-chain ( $\text{C}_5$ - $\text{C}_{12}$ ) alcohols extends the lamellar phase of SDS aqueous solutions towards lower surfactant concentrations, the further addition of NaCl extends the narrow MLV  $L_4$  region, and opens a sponge phase  $L_3$ , alongside the  $L_\alpha$  phase, as shown in Fig. 3.1b. The SDS/octanol/brine system has been extensively employed to study  $L_\alpha$ -to-MLV flow-induced phase transformations, generally using a concentration of 6.5% SDS/7.9% octanol/85.6% brine w/w [33], [61]–[66], [150], exhibiting tightly and hexagonally packed vesicle formation, whose size can be modulated by temperature and shear. Extensive rheology, microscopy and light scattering studies have enabled a detailed phase map of SDS/octanol/brine (20 g/L NaCl) under quiescent conditions [17], [150], [151]. Work outlined in this chapter employed small angle neutron scattering (SANS) to elucidate the solution structures across this rich phase diagram, investigated as a function of composition and temperature. The neutron data gathered were complemented by optical microscopy and NMR to facilitate phase identification and benchmarking with previous work.

While the phase map of SDS/octanol/brine (20 g/L NaCl) has been published in literature and phases described with the aid of rheology and microscopy [17], [83], to our knowledge there has not been an in-depth structural SANS study of the system. This chapter looks at the effect of temperature and octanol concentration on the structure of phases in SDS/octanol/brine system with the aid of SANS, microscopy and NMR. Here, I investigate  $L_\alpha$  phases and with varying octanol:SDS ratios, one of them being the ratio between

octanol:SDS often cited in flow induced phase transformation studies, mixed MLV/ $L_1$  phase and pure  $L_1$  phase (dilution lines investigated shown in Fig. 3.1b).

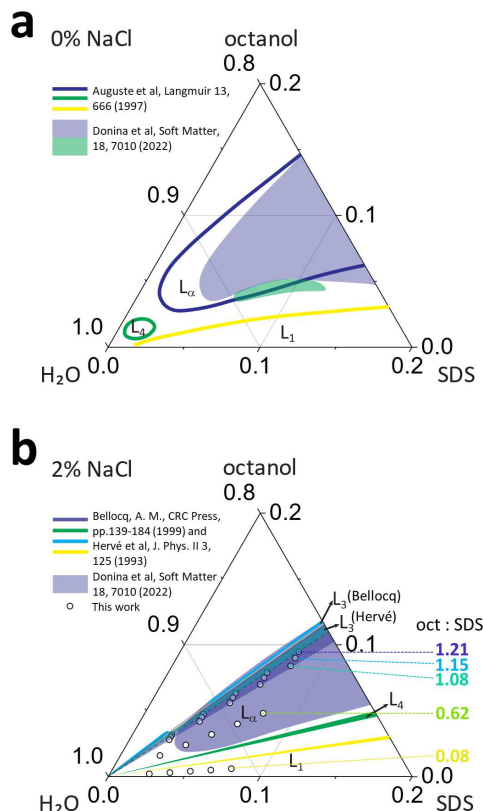


Figure 3.1: Phase maps for SDS/octanol/water with a) 0% salt and b) 2% NaCl (brine), compiled from literature [17], [83], [150] shown as solid lines, and optical microscopy data from previous work [152] (shaded regions), indicating micellar  $L_1$ , lamellar  $L_\alpha$ , sponge  $L_3$  and vesicle  $L_4$  phases. The data points in b) correspond to the compositions investigated in this work, with octanol:SDS ratios of 1.21, 1.15, 1.08, 0.62 and 0.08, employing SANS, microscopy and NMR, as a function of temperature (25-65 °C).

## 3.2 Methods

### Sample preparation

The experimental SDS/octanol/brine concentrations series were selected based on previously reported phase maps [17], [83] and our own optical and NMR measurements for this system. The samples were prepared by first dissolving 7.8 g of SDS (Sigma-Aldrich BioXtra,  $\geq 99.0\%$ ) each in  $D_2O$  brine (20 g/L, Sigma-Aldrich, 99.9 atom % D) of mass

18.39, 18.50, 18.63, 19.43 and 20.37 g. Dissolution was facilitated by heating the samples to 30 °C until full dissolution, and then allowed to cool to room temperature. Then, 1-octanol (Sigma-Aldrich, anhydrous,  $\geq 99\%$ ) was added in following amounts 9.48, 9.00, 8.4, 4.8 and 0.6 g, respectively, to each of the SDS/brine solutions above, resulting in oct:SDS ratios of 1.21, 1.15, 1.08, 0.62 and 0.08 respectively, and stirred for 2 min at 1000 rpm until fully incorporated. The solutions were allowed to equilibrate for 24 h at rest, to mitigate any inadvertent shear effects during sample preparation. From these concentrations, five isopleths were prepared by dilution, mixing 5, 4, 3 and 2 mL of the stock solution with 1, 2, 3 and 4 mL of D<sub>2</sub>O brine to make up 6 mL total solution. Each sample was then stirred for 1 min at 1000 rpm until fully incorporated, and allowed to rest for 24 hrs.

### Microscopy

Bright field and cross-polarised optical microscopy was carried out by placing 10  $\mu$ L of sample on a cavity slide, covered by a coverslip and mounted on Linkam THMS600 stage stage at 15 °C. The sample was then heated to the desired temperature (25, 35, 45 °C) at 10 °C/min and allowed to equilibrate for 5 min. Images were captured using Olympus BX41 reflection microscope equipped with a Basler acA2000-165um camera controlled with PylonViewer using 10x/0.25 Ach and 50x/0.50 MPlanFLN Olympus objectives with cross-polarised filters (U-AN-2 analyser and U-PO3 polariser), and bright-field (BF) and cross-polarised data were analysed with ImageJ.

### SANS

SANS experiments were carried out at the *Institut Laue Langevin*, Grenoble, using the D22 spectrometer, equipped with front and rear detectors, placing the latter at two distances 17.6 m and 5.6 m to the sample, and neutron wavelength  $\lambda = 6$  Å. The measured wavevector  $q$  range was 0.003 to 0.8 Å<sup>-1</sup>. The samples were loaded into ‘banjo’ Hellma cells of 1 mm path length with a needle (which induces preferred orientation in liquid

crystalline phases). Sample cells were mounted on a thermostated rack and measured at 25, 35 and 45 °C. Selected samples were measured from 25-65 °C in 5 °C steps. The data were reduced and calibrated with GRASP, and radially- or sector-averaged, as appropriate. Data fitting was carried out with SasView 5.0.5. In total, 24 samples and in excess of 100 spectra (at different temperatures) were measured and analysed.

Lamellar structures  $L_\alpha$  were fitted with the random head-tail sheet with Caillé structure factor model (SASView `lamellar_hg_stack_caillie`) [122], parameterised by the lamellar d-spacing and thickness  $\delta$ , the Caillé parameter  $\eta$  (characterising the membrane bending rigidity and compression modulus), and number of layers, as well as by the scattering length density profile; polydispersity  $p_D$  of d-spacing was also introduced. The sponge  $L_3$  phase was fitted with a model reported by Lei *et al.* [120], [121] coded into SASView, yielding estimates of the average sponge pore size,  $\xi$ , and membrane thickness,  $\delta$ , as a function of membrane volume fraction  $\phi_v \equiv (V_{octanol} + V_{SDS})/V_{total}$  and temperature. A sum of flexible cylinder and lamellar models ( $L_1+L_4$ ) was used to describe mixed micellar-vesicle phase (in SASView, `flexible_cylinder + lamellar_hg_stack_caillie`), yielding micelle shape and dimensions, and characteristic low- $q$  exponent. Finally and a core-shell cylinder model (SASView `core_shell_cylinder`) was employed to describe elongated micelles ( $L_1$ ). Details of scattering length density profiles, the models for analysis and interpretation are provided in Sections 2.3.1 and 2.3.2, 2.3.3, 2.3.4.

## <sup>1</sup>H NMR

Liquid state <sup>1</sup>H NMR spectra were acquired for 1.21, 1.15, 1.08, 0.62 and 0.08 oct:SDS w/w ratios made with D<sub>2</sub>O (Sigma-Aldrich, 99.9 atom % D) along the respective isopleths with a Jeol 400 MHz magnetic field strength NMR spectrometer. Each spectrum was collected using a relaxation delay of 4 s and one 45° RF-pulse followed by 4.37 s acquisition time (8 scans) at 25, 35 and 45 °C temperatures leaving each sample to rest for 5 min. Pure component spectra in solution, 6.5% w/w SDS/D<sub>2</sub>O and 7.9% w/w octanol/CD<sub>3</sub>Cl were collected for chemical shift identification in mixed systems (Fig. 3.2). Spectra were

analysed with the Mnova 14.3.0 software and calibrated using D<sub>2</sub>O residual solvent peak shift at 4.78 ppm (25 °C), 4.68 ppm (35 °C) and 4.58 ppm (45 °C).

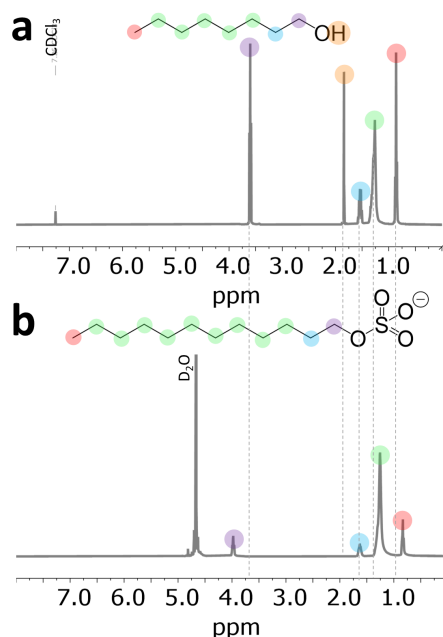


Figure 3.2: <sup>1</sup>H NMR of a) 7.9% w/v octanol in CDCl<sub>3</sub> and b) 6.5% w/v SDS in D<sub>2</sub>O.

## 3.3 Results

### 3.3.1 Effect of octanol concentration and temperature on the lamellar L<sub>α</sub> phase

First, this chapter considers the isopleths with oct:SDS ratio 1.21, within the L<sub>α</sub> phase, according to the phase diagram [17], [83], as shown in Fig. 3.3a. Composition II along the isopleth, 6.5%/7.9%/85.6% w/w SDS/oct/brine corresponds to the system employed in well-known L<sub>α</sub>-to-MLV flow induced phase transformation studies [33], [61]–[66]. <sup>1</sup>H NMR probes changes in local environment that are characteristic of molecular scale structures [153]. At 25 °C, composition I ( $\phi_v = 0.189$ ) displayed a peak broadening expected in anisotropic ordered phases, such as L<sub>α</sub>. At temperatures 35 and 45 °C, the emergence of an isotropic L<sub>3</sub> phase was indicated by the terminal -CH<sub>3</sub> triplet at  $\sim 0.7$ -0.8 ppm (positions 9 and 12\*) and hydrophobic chain -CH<sub>2</sub> multiplet at  $\sim 1.3$  ppm (4-8 and 3\*-11\*)

for octanol and SDS tails. Headgroup adjacent  $-\text{CH}_2$  (2 and 1\*) triplet peaks emerged further downfield at  $\sim 3.8$  ppm for octanol and  $\sim 4$  ppm for SDS. Cross-polarised optical images identified a birefringent  $L_\alpha$  phase at 25 °C, and the emergence of larger, more birefringent optical textures upon dilution (Fig. 3.3b). At 35 °C, the birefringence disappears as the system enters an isotropic phase, interpreted to be  $L_3$ , as previously reported for 6.5% SDS/7.9% octanol/86.5%  $\text{H}_2\text{O}$  w/w with  $L_\alpha/L_3$  coexistence between 30 to 38 °C [154]. At 45 °C the sample becomes fully isotropic, transitioning into the  $L_3$  phase.

SANS 2D spectra corroborate these observations, with samples at 25 °C displaying diffuse scattering closer to the beam center (Fig. 3.3b). Upon increasing the temperature to 35 °C, samples I and II show two scattering features, expected in phase coexistence, and further increasing temperature to 45 °C resulted in isotropic scattering, indicating the  $L_3$  phase. Analysis of normalised azimuthal intensity ( $\Delta I$ ) near the Bragg peak ( $q = 0.014 \text{ \AA}^{-1}$ ) showed 3-fold decrease in sample anisotropy upon dilution at 25 °C (Fig. 3.3c). Raising the temperature to 35 °C showed an increase in anisotropy for sample I, and disappearance of anisotropy for samples II-V. At 45 °C all samples had become isotropic. Sector averaged  $I(q)$  ( $0.003 \leq q \leq 0.08 \text{ \AA}^{-1}$ ) with  $\angle 30^\circ$  normal to Bragg peak orientation for  $L_\alpha$  at 25 °C indicated decrease of intensity and a linear shift to lower  $q$  values of the Bragg peak upon dilution indicating increase in polydispersity and membrane swelling (Fig. 3.3d). At 35 °C, the coexistence of two Bragg peaks for samples I and II was quantified in 2D SANS measurements: when  $L_\alpha/L_3$  coexist,  $L_\alpha$  Bragg peak is shifted to the higher  $q$  (0.050 to 0.055  $\text{\AA}^{-1}$  for sample I and 0.04 to 0.05  $\text{\AA}^{-1}$  for sample II) while  $L_3$  is shifted to lower  $q$  region 0.018 and 0.015  $\text{\AA}^{-1}$  for samples I and II respectively. At 45 °C all sample concentrations are in  $L_3$  phase and exhibit the same linear swelling upon dilution as the  $L_\alpha$  phases. The fitted radially averaged  $I(q)$  profiles are shown in Fig. 3.3e. Following the same procedure, analysis for  $L_\alpha$  phases with oct:SDS ratios of 1.15 and 1.08 are provided in Fig. 3.4 and Fig. 3.5 and do not exhibit phase transformation to  $L_3$  at 35 and 45 °C.

Quantification of scattering anisotropy  $\Delta I \equiv I - I_{\min}$  obtained from the azimuthal profile

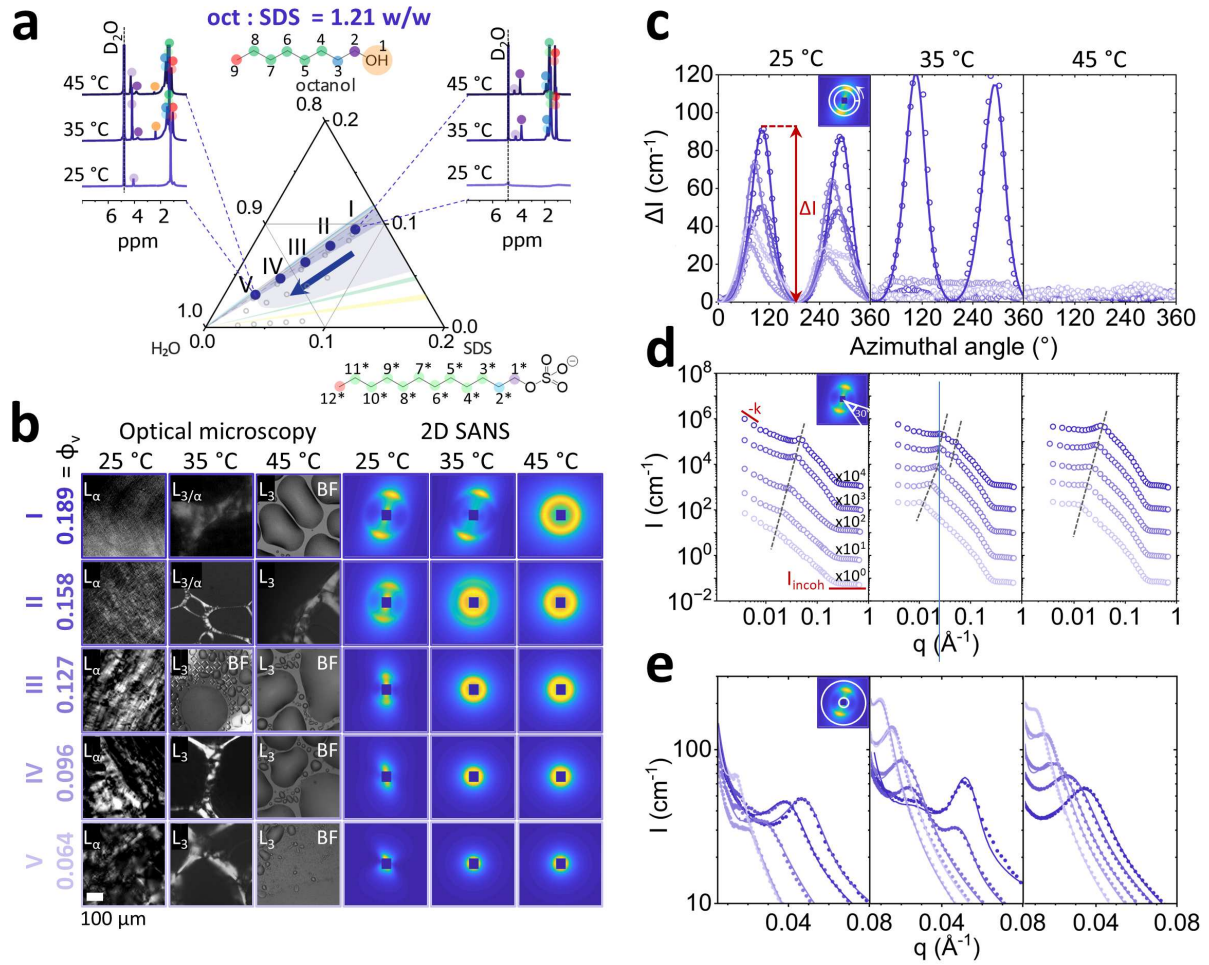


Figure 3.3: a) Overview of the experimentally measured compositions at octanol:SDS ratio 1.21, near the  $L_\alpha$  boundary with the  $L_3$  phase. Specifically, SDS/octanol/ $H_2O$  brine: I) 7.80/9.48/82.72, II) 6.5/7.9/85.6, III) 5.20/6.32/88.48, IV) 3.90/4.74/91.36, V) 2.60/3.16/94.24 (prepared from dilution of I); for SANS and NMR samples,  $D_2O$  was used instead. Representative NMR spectra are shown for I) and V) as a function of temperature. b) Corresponding birefringence and brightfield (BF) optical microscopy data at 25 °C and SANS at 25, 35 and 45 °C of samples I-V;  $\phi_v$  indicates the SDS+octanol volume fraction, i.e. total surfactant/co-surfactant content. c) Azimuthal profile of SANS data in b) around the respective Bragg peak for  $\Delta q = 0.014 \text{ \AA}^{-1}$ , subtracted by the respective  $I_{min}$  characterising scattering anisotropy. d) Sector average  $I(q)$  with a 30° angular range, normal pattern orientation; dashed lines indicate peak position(s). Data shifted vertically ( $\times 10$ ) for clarity. e) Radial average of SANS data near the peak; lines are fits to the lamellar and  $L_3$  models, described in the text.

at the peak, and  $q^n$  and fitted model parameters for  $L_\alpha$  phases are shown in figure 3.6 as a function of total octanol and SDS v/v fraction  $\phi_v$ , for temperatures 25, 35 and 45 °C. The  $\Delta$  profile indicates an increase in  $L_\alpha$  anisotropy with increasing octanol+SDS concentration at 35 and 45 °C for oct:SDS of 1.15 and 1.08 (Fig. 3.6a). After the  $L_\alpha$ -to- $L_3$

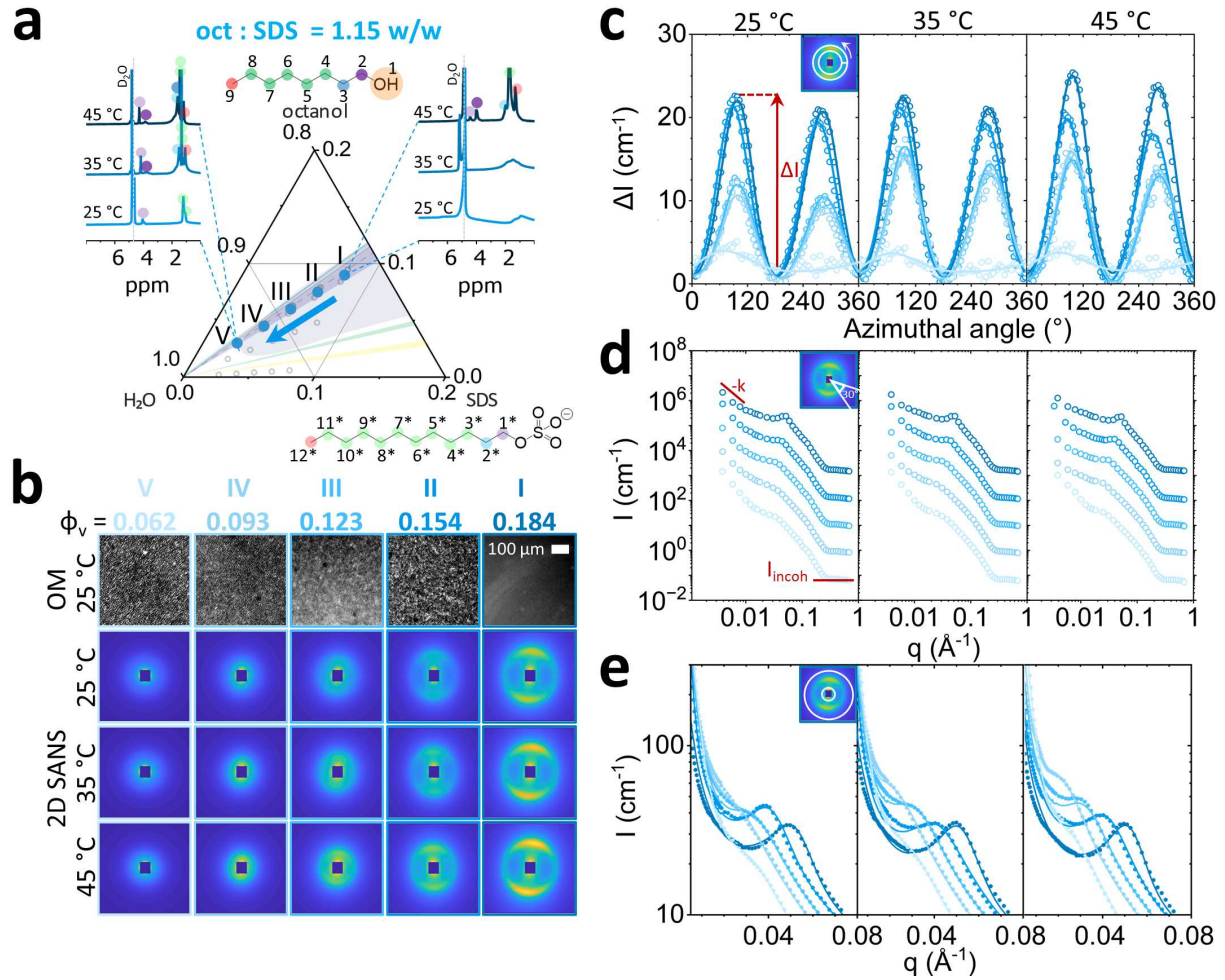


Figure 3.4: a) Overview of the experimentally measured compositions at octanol:SDS ratio 1.15,  $L_\alpha$  phase region. Specifically, SDS/octanol/H<sub>2</sub>O brine: I) 7.8/9.0/82.2, II) 6.5/7.5/86.0, III) 5.2/6.0/88.8, IV) 3.9/4.5/91.6, V) 2.60/3.0/94.4 (prepared from dilution of I); for SANS and NMR samples, D<sub>2</sub>O was used instead. Representative NMR spectra are shown for I) and V) as a function temperature. b) Corresponding birefringence and brightfield (BF) optical microscopy data at 25 °C and SANS at 25, 35 and 45 °C of samples I-V;  $\phi_v$  indicates the SDS+octanol volume fraction, i.e. total surfactant/co-surfactant content. c) Azimuthal profile of SANS data in b) around the respective Bragg peak for  $\Delta q = 0.014 \text{ \AA}^{-1}$ , subtracted by the respective  $I_{min}$  characterising scattering anisotropy. d) Sector average  $I(q)$  with a 30° angular range, normal pattern orientation; dashed lines indicate peak position(s). Data shifted vertically ( $\times 10$ ) for clarity. e) Radial average of SANS data near the peak; lines are fits to the lamellar model, described in the text.

phase transformation takes place for 1.21 membrane fraction at 35 and 45 °C no anisotropy was observed.

The power law exponent  $k$ ,  $I(q) = Aq^{-k}$  relates the scattering intensity  $I(q)$  to the scattering vector  $q$  and its magnitude relates to the shape of the scattering particles [115]. For example,  $q^{-4}$  suggests presence of uniformly sized spherical particles, power law

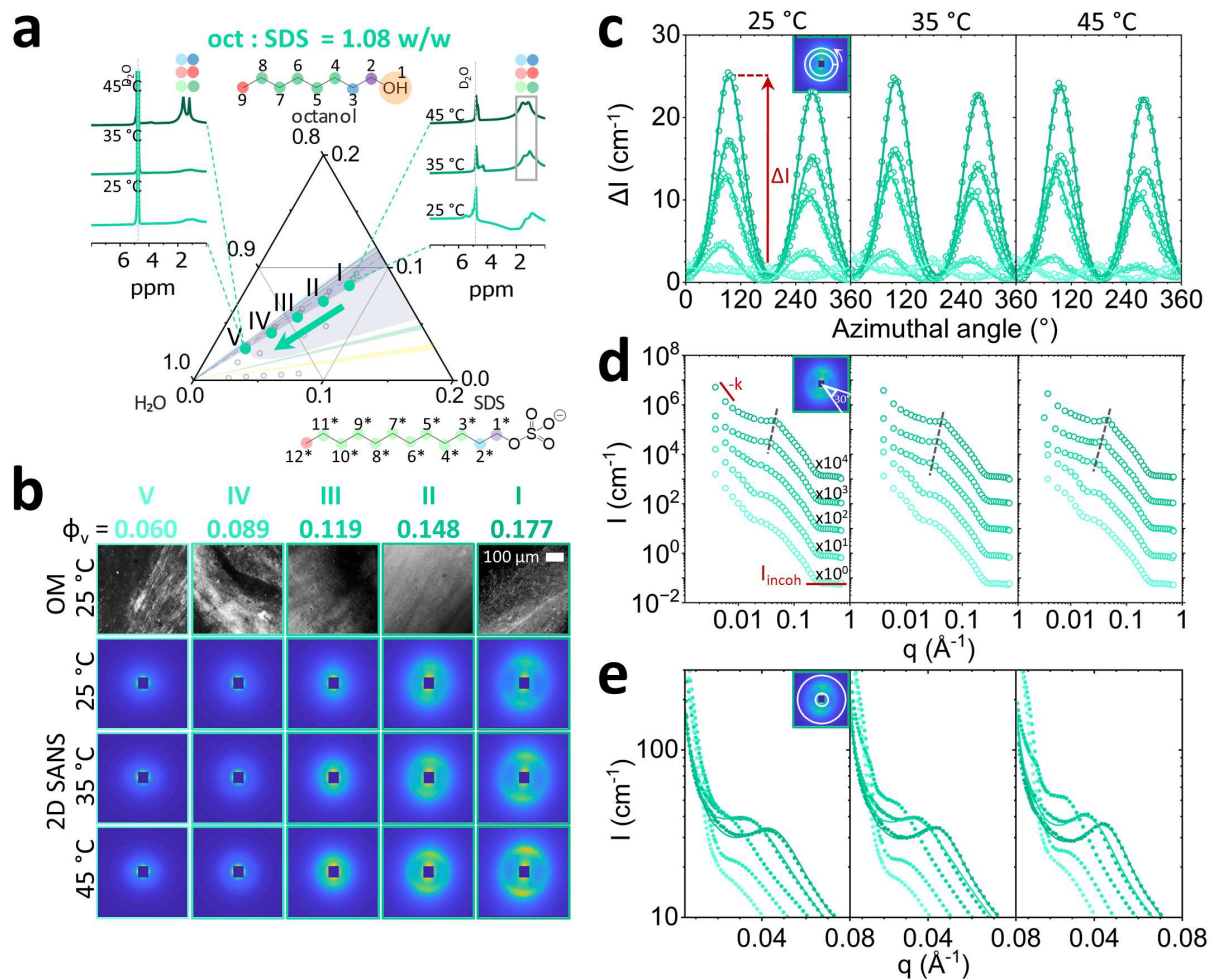


Figure 3.5: a) Overview of the experimentally measured compositions at octanol:SDS ratio 1.08,  $L_\alpha$  phase region close to the mixed phase  $L_\alpha/L_4$ . Specifically, SDS/octanol/H<sub>2</sub>O brine: I) 7.8/8.4/83.8, II) 6.5/7.0/86.5, III) 5.20/5.6/89.2, IV) 3.9/4.2/91.9, V) 2.6/2.8/94.6 (prepared from dilution of I); for SANS and NMR samples, D<sub>2</sub>O was used instead. Representative NMR spectra are shown for I) and V) as a function temperature. b) Corresponding birefringence and brightfield (BF) optical microscopy data and SANS of samples I-V at 25, 35 and 45 °C;  $\phi_v$  indicates the SDS+octanol volume fraction, i.e. total surfactant/co-surfactant content. c) Azimuthal profile of SANS data in b) around the respective Bragg peak for  $\Delta q = 0.014 \text{ \AA}^{-1}$ , subtracted by the respective  $I_{min}$  characterising scattering anisotropy. d) Sector average  $I(q)$  with a 30° angular range, normal pattern orientation; dashed lines indicate peak position(s). Data shifted vertically ( $\times 10$ ) for clarity. e) Radial average of SANS data near the peak; lines are fits to the lamellar, described in the text.

exponent between  $q^{-4}$  and  $q^{-2}$  will describe lamellar sheets where the degree of correlation between the sheets will determine the magnitude of power law,  $q^{-2}$  will describe thin discs,  $q^{-1}$  (Porod's law) will describe long rods and  $q^0$  (Guinier law) implies that the particle shape is independent from the scattering intensity  $I(q)$  and depends only on the

number density of the particles. Observed power law exponent  $-k$  was between 1.5 and 3 for  $L_\alpha$  phases with oct:SDS ratios of 1.08 and 1.15 with an upwards trend upon dilution (Fig. 3.6b) across 25, 35 and 45 °C with an overall decrease in power law upon increase in temperature. This would suggest decrease in  $L_\alpha$  order and correlation upon increasing concentrations and temperatures. Similar trend of decrease in  $L_\alpha$  power law exponent  $-k$  upon increase in oct+SDS concentration was observed for oct:SDS ratio of 1.21 at 25 °C with  $-k$  shifting from 1.5 to 1.0. When  $L_\alpha$ -to- $L_3$  phase transition occurred, drop in power law  $-k$  was observed to values between 0 to 0.5, suggesting that scattering intensity  $I(q)$  is  $q$ -independent, which is the case for complex isotropic structures, such as  $L_3$ . This was reflected in model fitting, where prefactor  $A$  describing the contributions from in-out correlations, was close to 0 [121].

$L_\alpha$  d-spacing and  $L_3$  pore size (denoted simply as d-spacing) is plotted as a function of  $\phi_v$  in Fig. 3.6c. d-spacing, calculated as  $d = 2\pi/q^*$  where  $q^*$  is the Bragg peak position of the repeat bilayer distance in  $L_\alpha$  or average pore size in  $L_3$ . Overall, at 25 °C the differences in d-spacing among isopleths 1.21, 1.15 and 1.08 were negligible and the only effect on the d-spacing was by dilution of  $L_\alpha$ . Upon dilution of an  $L_\alpha$  phase [155], the lamellar spacing is expected to follow:

$$d = A \frac{\delta}{\phi_v} \quad (3.1)$$

$\delta$  is  $L_\alpha$  membrane thickness,  $A$  is a multiplicative prefactor, which for  $L_\alpha$  is 1 and  $\phi_v$  is the volume fraction of membrane.  $\phi_v$  is calculated as  $(V_{oct} + V_{SDS})/V_{total}$ . From the expected d-spacing calculations, it can be observed that the  $L_\alpha$  isopleth follows the dilution law.  $\delta$ , membrane thickness used for these calculations was taken from the fitted data.

Sponge phases  $L_3$  followed the same dilution law, but the multiplicative prefactor  $A$  instead was 1.5. The data conformed to the sponge phase dilution law expect at the highest dilution when  $\phi_v$  is 0.063.

Caillé parameter  $\eta$  was lower, i.e. meaning membranes were more rigid when the membrane (SDS+octanol) concentration was higher (Fig. 3.6d). Intriguingly, a drop in  $\eta$  was observed

when the coexistence of  $L_\alpha$  and  $L_3$  take place, likely due to membrane compression reflected in a decrease in  $L_\alpha$  d-spacing. Other dilutions displayed  $\eta$  close to 1 which are the upper limit for Caillé model. d-spacing polydispersity  $p_D$  analysis (Fig. 3.6e) showed that dilution of  $L_\alpha$  sheets increased the variation of d-spacing.

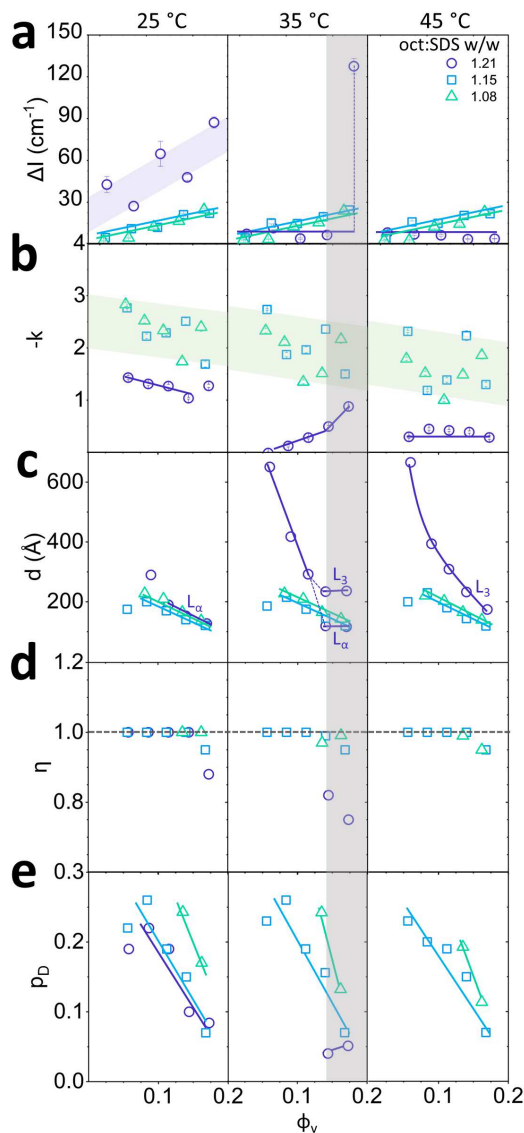


Figure 3.6: Parameters of  $L_\alpha$  phases with oct:SDS ratios of  $\circ$  1.21,  $\square$  1.15 and  $\triangle$  1.08. a) Normalised  $\Delta I$  measured around the Bragg peak, b) exponent fit at low- $q$  region ( $0.004 < q < 0.01 \text{ \AA}^{-1}$ ), c) d-spacing ( $L_\alpha$  or  $L_3$  as indicated), d) Caillé parameter  $\eta$ , e) polydispersity of  $L_\alpha$  d-spacing, as a function of  $\phi_v$  for 25, 35 and 45 °C. Anisotropy to isotropy shift observed for the 1.21 oct:SDS with increasing temperature, accompanied by a transition to  $L_3$ .

Next, the effect of increasing temperature in  $L_\alpha$  phases containing 6.5% SDS was investigated for temperatures from 25 to 65 °C in 5 °C each equilibrated for 20 minutes. Thermal

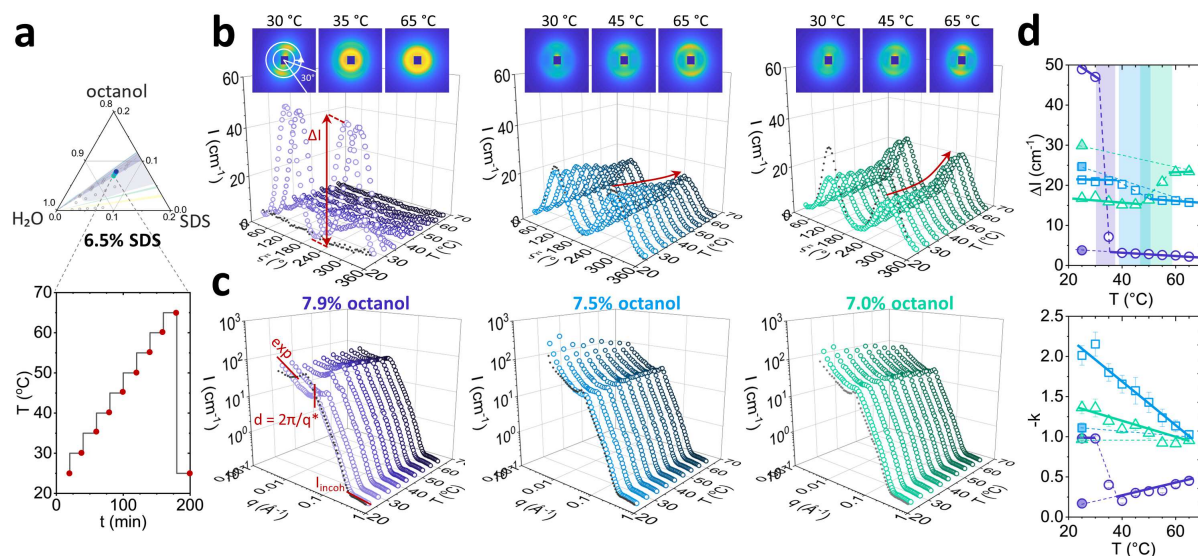


Figure 3.7: Temperature-induced changes of the 6.5% w/w SDS samples, with 7.9%; 7.5% and 7.0% w/w octanol, originating from the lamellar phase at room temperature. a) Composition and temperature profile used for SANS experiments, from 25 to 65 °C, in 5 °C increments in 20 min steps; b) Azimuthal profile and c) sector average (30° as shown) as a function of temperature. d) Scattering anisotropy  $\Delta I$  and low-q exponent as function of temperature, indicating a phase transition to  $L_3$  for 7.9% w/w octanol sample at  $\approx 35$  °C.

reversibility was tested following a temperature quench from 65 °C to 25 °C (Fig. 3.7a). Red points on the temperature ramp indicated the SANS measurements.

Azimuthal analysis of 2D SANS data reflected that the transition from  $L_\alpha$ -to- $L_3$  in the sample with 7.9% octanol took place between 30 and 40 °C as observed by [154]. This was reflected by a 10-fold drop (Fig. 3.7d top) in azimuthal intensity and the emergence of a distinct isotropic scattering ring in 2D SANS with virtually no anisotropy [154]. The sample showed thermal irreversibility upon temperature quench, meaning that the sample did not return to its equilibrium position which was supported by literature where a sample of similar concentration oct:SDS 1.36 did not show thermal reversibility even after several days [151].  $L_\alpha$  samples containing 7.5% and 7.0% octanol did not undergo transformation to  $L_3$  phase upon increase in temperature. However, azimuthal signal intensity dropped for 7.5% octanol sample and increased for 7.0% octanol sample. The quantification of the changes in azimuthal intensity  $\Delta I$  displayed a nonlinear trend (Fig. 3.7d top) in the azimuthal profile variation with temperature. In the case of the 7.5%

octanol decrease from 22 to 15 cm<sup>-1</sup> was observed between 40 to 50 °C while the 7.0% octanol sample showed an increase in  $\Delta I$  from 14 to 23 cm<sup>-1</sup> between 45 to 55 °C.

$I(q)$  sector averaging (30°) normal to the Bragg peak showed what previously was observed for  $L_\alpha$  at temperature above 35 °C, namely  $L_\alpha$ -to- $L_3$  transformation as evidenced by the apparent shift in peak position. Bragg peak in  $L_\alpha$  samples containing 7.5% and 7.0% octanol remained unchanged meaning no phase transition was observed. Changes in low- $q$  scattering were quantified by plotting power law  $q^{-n}$  as a function of temperature (Fig. 3.7d bottom). Power law fits for 7.9% octanol showed a drop from 1.0 to 0.2 in  $-n$  between 30 and 40 °C as expected for  $L_\alpha$ -to- $L_3$  phase transformation. Samples containing 7.5% and 7.0% octanol also showed decrease in  $-n$  from 2.0 to 1.0 and 1.4 to 1.0 respectively.

$L_\alpha$  phases were fitted with model described in Section 2.3.3 and  $L_3$  in Section 2.3.2 in Fig. 3.8a-c). Sample with 7.9% octanol showed a jump in d-spacing upon transition to  $L_3$  from 150 to 225 Å between 30 and 40 °C and a subsequent decrease in  $L_3$  pore dimensions  $\xi$  (equivalent to d-spacing) from 225 to 200 Å for temperatures between 40 and 65 °C. The decrease in sponge pore size  $\xi$  and increase in scattering intensity, with increasing temperature is associated with greater interfacial area accommodated at higher thermal energies.

On the contrary, lamellar d-spacing increase was observed for 1.15 and 1.08 oct:SDS samples (Fig. 3.8d). Lamellar  $L_\alpha$  dilution law ( $d = \frac{\delta}{\phi_v}$ ) assumes that all the water is located between the membranes [156], [157]. The value of  $\phi_v$  is affected by the decrease in D<sub>2</sub>O and octanol with temperature increase. When estimated based on literature density values [158], [159],  $\phi_v$  increases only by  $\approx 0.5\%$  from 25 to 65 °C whereas the increase in d-spacing was 7.7% and 2.7% for 1.15 oct:SDS (containing 7.5% octanol) and 1.08 oct:SDS (7.0% octanol) samples respectively. The discrepancy suggests that the thermal expansion alone does not account for the increase in d-spacing; there might be contributions from increase in membrane thickness  $\delta$  and/or that there is a presence of excess water outside the lamellar periodicity and dilution law does not apply [157]. In literature, increase of d-spacing with temperature measured by SAXS in the zwitterionic

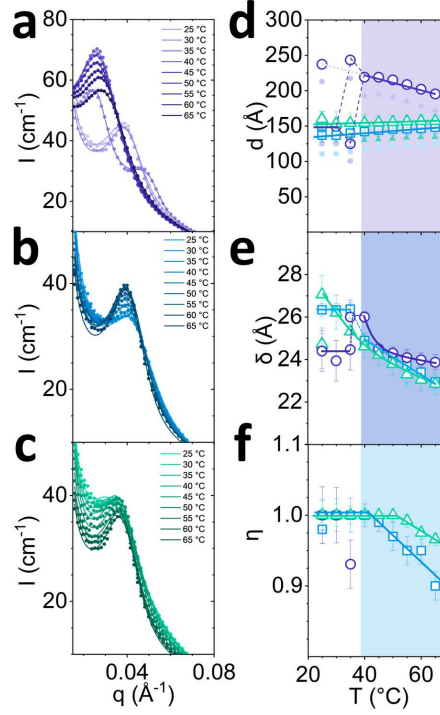


Figure 3.8: Analysis of data shown in Fig. 3.7 by fitting the radially-averaged SANS data near the scattering peak, as a function of temperature. Profiles for 6.5% w/w SDS and a) 7.9, b) 7.5 and c) 7.0% w/w octanol in  $\text{D}_2\text{O}$  brine. d) Fitted  $L_\alpha/L_3$  d-spacing with  $L_\alpha$  error bars corresponding to polydispersity,  $p_D$ ; filled smaller points correspond to  $\delta_w$  thickness after membrane thickness  $\delta$  has been subtracted; e) Fitted  $L_\alpha/L_3$  membrane thickness  $\delta$  and f) Caillé parameter  $\eta$  of  $L_\alpha$  phases as a function of temperature. Coloured panels indicate onset of non-monotonic shift in parameters.

3% w/w 1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC) bilayers has previously been reported and attributed to increase in membrane thermal undulations [156]. Additionally, from the  $P(q)$  fits, lamellar thickness  $\delta$  decreases by with temperature supported by studies done in similar charged lamellar systems [156], [160].

Caillé parameter  $\eta$  decrease was observed for 7.5% and 7.0% octanol  $L_\alpha$  samples at 45 and 50 °C respectively where  $\eta$  dropped to 0.9 and 0.95 respectively (Fig. 3.8e). A decrease in  $\eta$  suggests an increase in  $\kappa$  and  $\bar{B}$  product, which is an unexpected result since studies have shown decrease in both  $\kappa$  and  $\bar{B}$  in zwitterionic DOPC vesicles with increase in temperature and decrease in osmotic pressure [160], [161]. Addition of NaCl to charged surfactants has been shown to decrease the membrane bending rigidity via membrane screening effect [75], [152], [162]. Increase in temperature will disrupt the screening effect and facilitate the dissociation of  $\text{Na}^+$  ions from the lamellar membrane. This will lead

to an increase in SDS headgroup repulsions. Additionally, the increase in temperature will lead to changes of NaCl matrix electrostatic properties described by Bjerrum length  $\lambda_B$  calculated to correlate the structural changes observed in the lamellar  $L_\alpha$  phase upon increasing temperature and dilution. Bjerrum length  $\lambda_B$  is given by

$$\lambda_B = \frac{e^2}{4\pi\epsilon_w\epsilon_0k_BT} \quad (3.2)$$

where  $e$  is elementary charge,  $\epsilon_w$  is the dielectric constant of water,  $\epsilon_0$  is the vacuum permittivity,  $k_B$  is Boltzmann constant and  $T$  is temperature in K. The value for  $\epsilon_w$  in presence of 0.3 M NaCl (concentrations of NaCl in solutions used in our study) is 74.5 at 25 °C [163], lower than that of 78.3 in DI water. Empirically, the effect of  $T$  on  $\epsilon_w$  is given by  $\epsilon_w(T) = 87.740 - 0.4008T + 9.398 \times 10^{-4}T^2 - 1.410 \times 10^{-6}T^3$  [164].  $\lambda_B$  for 0 M and 0.3 M NaCl concentrations as a function of  $T$  is given in Figure 3.9.

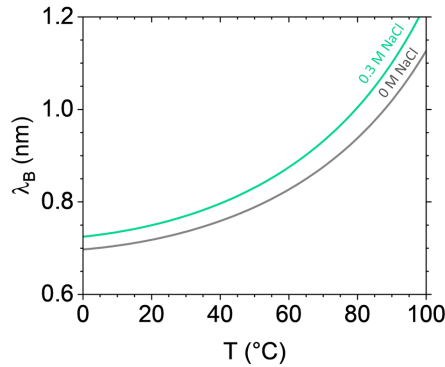


Figure 3.9: Bjerrum length  $\lambda_B$  temperature dependence for 0 M and 0.3 M NaCl solutions.

### 3.3.2 Effect of temperature and octanol concentration on the mixed $L_4/L_1$ phase

At lower octanol concentrations mixed phase consisting of wormlike micelles and vesicles was formed. This section describes the concentration isopleths where oct:SDS ratio is 0.62 corresponding to mixed  $L_4/L_1$  phase and 0.08 ratio corresponding to  $L_1$  phase.

The mixed  $L_4/L_1$  phases were analysed following the same experimental protocol as for

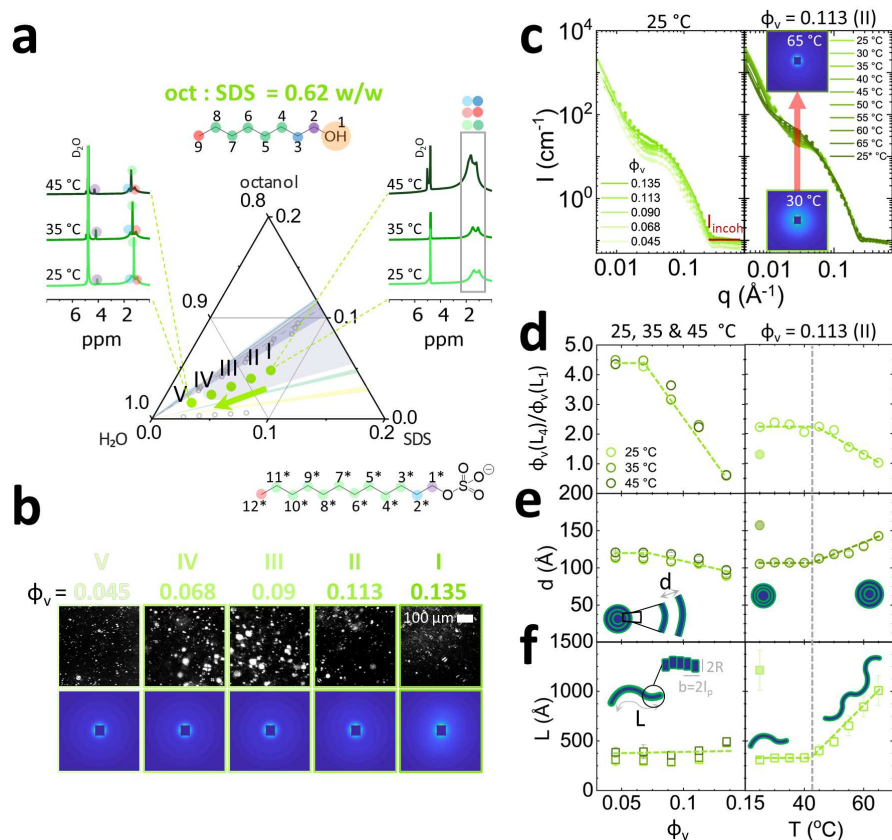


Figure 3.10: Coexistence of micellar  $L_1$  and vesicle  $L_4$  phases, along SDS I) 7.8% SDS/4.8% octanol, II) 6.5% SDS/4.0% octanol, III) 5.2% SDS/3.2% octanol, IV) 3.9% SDS/2.4% octanol, V) 2.6% SDS/1.6% octanol, corresponding to a fixed oct:SDS = 0.62 w/w ratio. a) Experimentally investigated compositions and illustrative NMR data at varying temperature. b) Corresponding optical birefringence and SANS data at 25 °C. c) Sector-averaged scattering profiles for compositions I-V at 25 °C (left) and temperature evolution of the scattering data for composition II, i.e. with  $\phi_v(\text{SDS}+\text{octanol})=0.113$  v/v (right) d) Fitted vesicle to micellar ratio  $\phi_v(L_4)/\phi_v(L_1)$  dependence on  $\phi_v$  for 25-45 °C temperature range (left), and temperature 25-65 °C for composition II, with  $\phi_v=0.113$ . e) Fitted dimensions of combined lamellar Caillé and flexible cylinder model, characterised by d-spacing  $d$  and f) wormlike micelle contour length  $L$ , measured at temperatures within 25-45 °C (left); temperature dependence of lamellar and micellar dimensions for composition II (right). Kuhn length  $b$  and cylinder radius  $R$  was fixed at 14 Å.

the  $L_\alpha$ . From  $^1\text{H}$  NMR analysis, an increase in peak resolution is observed upon dilution around  $\sim 1$  ppm corresponding to hydrocarbon tails (3-9 and 3\*-12\*) of octanol and SDS, indicating the formation of more spherical structures ascribed to vesicles  $L_4$  (Fig. 3.10a, left). The emergence of the peak at  $\sim 4$  ppm (1\* Hs next to SDS  $\text{SO}_4^-$ ) suggests that the SDS headgroups are more deshielded, compatible with an increase in surface curvature, expected for formation of vesicles. The absence of  $-\text{CH}_2$  (1) shift at 3.5 ppm implies that

octanol headgroups are electrostatically and/or sterically shielded and are thus embedded within the bilayer membrane and/or micelles. Upon heating the concentrated sample containing 7.8 % SDS (0.135 SDS+octanol volume fraction), a hydrocarbon peak growth was observed at  $\sim 1$  ppm suggesting a shift towards micellar structures. Crosspolarised optical microscopy (Fig. 3.10b) indicates the presence of vesicles as evidenced by Maltese crosses in microscopy across the isopleth. The SANS spectra are isotropic and exhibit pronounced forward scattering, along with a characteristic micellar profile. The radially averaged  $I(q)$  spectra, are shown in Fig. 3.10c (left). The SANS profiles were thus fitted with a sum of lamellar and flexible cylinder models (SASView `lamellar_hg_stack_caille + flexible_cylinder`). Data fits indicate a decrease in lamellar to micelle ratio  $L_4/L_1$  at higher concentrations (Fig. 3.10d, left) from 4.5 to 0.5 and temperatures 45 °C and above from 2.0 to 1.0 (Fig. 3.10d, right). This effect with increasing temperatures has been previously reported in NaLAS/Na<sub>2</sub>SO<sub>4</sub> system where, at similar salt concentrations ( $\sim 0.2$  M), a shift towards wormlike micelles was observed at temperatures above 30 °C [165]. The lamellar d-spacing  $d$  increases with dilution from 100 to 130 Å and increase with temperatures above 40 °C from 110 to 140 Å. The length of wormlike micelles decreases only slightly with dilution, from 500 to 400 Å but rapidly grows with temperature, above 45 °C, from 400 Å to 1200 Å. The data fits were compatible with fixed micellar radius  $R$  and Kuhn length  $b$  at  $\simeq 14$  Å. Such micellar elongation with temperature has been previously reported in C<sub>12</sub>E<sub>3</sub> surfactants [166].

### 3.3.3 Effect of temperature and octanol concentration on the micellar $L_1$ phase

Finally, the effect of dilution and temperature in SDS/octanol/brine was characterised for micellar  $L_1$  region following 0.08 oct:SDS dilution line (Fig. 3.11a). From literature, the addition of salt NaCl and mid-to-long chain 1-alcohol such as 1-octanol favours the formation of wormlike micelles.

<sup>1</sup>H NMR analysis revealed well resolved peaks in the hydrocarbon region between 1-2

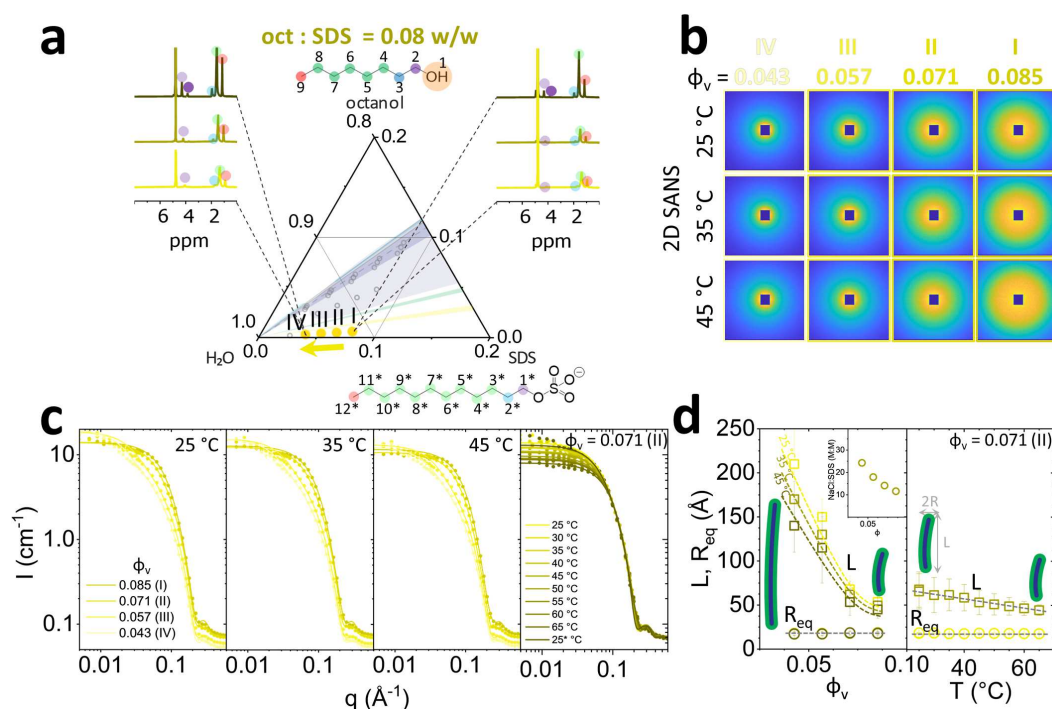


Figure 3.11: Characterisation of the micellar phase  $L_1$ , illustrated along the isopleth defined by I) 7.8% SDS/0.6% octanol, II) 6.5% SDS/0.5% octanol, III) 5.2% SDS/0.4% octanol, IV) 3.9% SDS/0.3% octanol in brine. a) Experimentally investigated compositions and illustrative NMR data at varying temperature. b) Corresponding SANS patterns at 25, 35, and 45 °C. c) Radially-averaged scattering profiles, and a fine temperature scan for composition II,  $\phi_v=0.07$ . d) Micellar dimensions obtained by fitting a core-shell cylinder model, indicated the equatorial radius  $R_{eq}$  and length  $L$ , as a function of composition  $\phi_v$  and temperature. The inset highlights that salt content (and salt:surfactant ratio) increases upon dilution with brine in these experiments, leading to micellar elongation.

ppm (Fig. 3.11a). Increase in temperature resulted in growth of headgroup H peaks in 4 ppm region, implying the headgroups are more de-shielded and as a result more spherical.

2D SANS scattering showed an isotropic scattering as expected for  $L_1$  that was higher in intensity for higher SDS/octanol concentrations (Fig. 3.11b).

Reduced sector analysis  $I(q)$  (Fig. 3.11c) of diluted phases and temperature scans for of was fitted with core shell cylinder model [123] described in Section 2.3.4.  $I(q)$  data fitting revealed an increase in cylinder (wormlike micelle) growth from 50 Å to 200 Å upon dilution with brine as a consequence of increased brine:SDS ratio (Fig. 3.11d, left). Higher ratio of brine:SDS (Fig. 3.11d, left inset) leads to screening of SDS headgroup charge promoting wormlike micelle formation.  $R_{eq}$  remained unchanged, at 18 Å. Increase in temperature from 25 to 65 °C lead to linear decrease in cylinder length from 55 Å to

45 Å for the sample with  $\phi_v=0.071$  (6.5% w/w SDS) membrane volume fraction.

### 3.4 Summary

This chapter investigated the solution structure of SDS/octanol/brine, a model surfactant/alcohol/water system whose phase diagram has been previously reported [17], [83], alongside extensive rheology and flow-induced transformation studies. In particular, the composition 6.5% SDS/7.9% octanol/85.6% brine (20 g/L NaCl) w/w mass fraction has been employed in the elucidation of the lamellar  $L_\alpha$  to MLV transformations, including the formation of ordered onion phases under specific flow and temperature conditions [33], [48], [66], and so-called ‘flow phase maps’. While the phase diagram of the system and the transformations associated with this specific composition have been well-characterised, the solution structures of the ternary system in the vicinity of the lamellar  $L_\alpha$  had not been mapped, which work described in this chapter sought to address. Here, I have employed a combination of optical microscopy,  $^1\text{H}$  NMR and SANS to determine the nanostructure of lamellar  $L_\alpha$ , sponge  $L_3$ , vesicle  $L_4$  and micellar  $L_1$  phases by following a series of dilution isopleths at oct:SDS ratios of 1.21, 1.15, 1.08, 0.62 and 0.08, and SDS 2.6-7.8% SDS mass fractions, and varying temperature from 25-45 °C. Given the significance of the 6.5% SDS isopleth (and all aforementioned oct:SDS ratios), a finer temperature scan or 25 to 65 °C, at 5 °C increments, was carried out. This extensive experimental survey centred on the dilute  $L_\alpha$  phase quantifies the nanoscale changes leading up to the phase transformations, which are illustrated in Fig. 3.12.

$L_\alpha$  structures oct:SDS 1.21 ratio are found to undergo a phase transition to  $L_3$  between 30 to 40 °C, accompanied by loss of birefringence in microscopy, loss of higher order microstructure as evidenced by the emergence of chemical shifts corresponding to hydrocarbon chain around 1-2 ppm region in  $^1\text{H}$  NMR, and isotropic SANS patterns with the Bragg peak shifted to lower  $q$  (higher  $d$ -spacing). Significantly, this means that such  $L_\alpha$  systems, such as the 6.5% SDS/7.9% octanol/85.6% brine system frequently investigated in  $L_\alpha$ -to-MLV flow-induced transformation studies [33], [61]–[66], [150], are located in

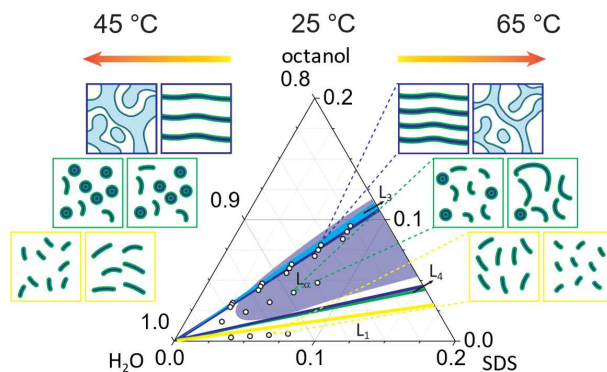


Figure 3.12: Overview of the solution structure observed in SDS/octanol/brine as a function of composition and temperature. The accompanying sketches indicate the key transformations observed: top) membrane swelling upon dilution in all lamellar phases and  $L_\alpha$  to  $L_3$  transformation upon increasing temperature for oct:SDS of 1.21; middle) dilution of mixed phase promotes the formation of more isotropic phase, in this case vesicles while temperature increase results in micellar elongation; bottom) dilution of  $L_1$  phase with brine promotes the formation of wormlike micelles while increase in temperature favours less elongated micelles.

the immediate vicinity of the  $L_3$  phase and are thus prone to phase change upon modest heating. However, this transition was not observed for  $L_\alpha$  with oct:SDS ratios of 1.15 and 1.08 even at 65 °C, with  $L_\alpha$  Bragg peak becoming sharper with increasing temperature, indicating an increase in membrane stiffness. Under isothermal conditions, within the investigated temperature range, both  $L_\alpha$  and  $L_3$  were stable upon dilution up to 95% brine (the maximum investigated) and the intermembrane spacing  $d$  and  $\xi$  followed the corresponding dilution laws characteristic of these phases.

At lower octanol:SDS ratios (0.62), mixed micellar and vesicle phases were found at 25 °C. Here, dilution results a greater fraction of vesicles  $L_4$ , while the  $d$  spacing increases slightly, and the length of wormlike micelles remains broadly unchanged. Temperature increase above 45 °C leads to a decrease in vesicle  $L_4$  fraction, accompanied by an increases in  $d$  spacing, and a significant (linear) elongation of wormlike micelles. Finally, at 0.08 oct:SDS ratio, the  $L_1$  phase is characterised by elongated micelles at room temperature, which grow linearly upon dilution with brine as a consequence of decreased electrostatic repulsion between the charged SDS sulfate headgroups; increasing temperature causes the micelles to become progressively more spherical. Overall, our results elucidate the rich behaviour of SDS ternary systems in presence of long chain alcohol octanol, which

aids structure-formation at low surfactant content, as a function of concentration and temperature, relevant to a range of academic and industrial contexts.

# Chapter 4

## Effect of membrane elastic properties on the textural transformations in SDS/octanol/brine $L_\alpha$ phase

This chapter is based on published work in [152].

### 4.1 Introduction

Amphiphilic membranes are formed via the noncovalent self-assembly of amphiphilic molecules, such as lipids, surfactants, or block-copolymers, into broadly planar monomolecular arrays of one or two layers, characteristic of cell membrane bilayers, and liquid crystalline surfactant lamellar  $L_\alpha$  phases. The elastic properties of  $L_\alpha$  membranes, namely their low compressibility and low membrane bending rigidity [167], largely govern their physical behaviour [168], [169] and flow response [79].

Generally, membrane bending rigidity is estimated by either measuring the associated thermal undulation spectrum, or by deforming the membrane and measuring its response, thus involving distinct experimental techniques and data analysis models [170]. Experiments probing individual membranes are generally based on giant unilamellar vesicles ( $\sim 100 \mu\text{m}$ ),

observable by light microscopy, employing fluctuation spectroscopy [171] or micropipette aspiration [172]. Scattering and NMR techniques generally probe concentrated membrane ensembles, or stacks, where neighbouring interactions are important [167]. The membrane bending rigidity is reflected on the line shape of the lamellar Bragg peak measured by small angle neutron or X-ray scattering (SANS, SAXS) which, in a  $L_\alpha$  system can be described by the Caillé structure factor  $S(q)$  model [122], [173], [174],

$$S(q) \sim (q - q_h)^{1+\eta} \quad (4.1)$$

where  $q_h$  denotes the peak position in reciprocal space, and the Caillé parameter  $\eta$  reads

$$\eta = \frac{\pi k_B T}{2\sqrt{\kappa \bar{B}} d^3} \quad (4.2)$$

where  $\kappa$  is membrane bending modulus,  $\bar{B}$  is membrane compressibility modulus and  $d$  corresponds to the  $L_\alpha$  repeat distance (d-spacing),  $k_B$  is Boltzmann constant and  $T$  is temperature. Neutron or X-ray scattering, in conjunction with osmotic stress measurements [175] or dynamic light scattering [176] can determine both  $\kappa$ , and  $\bar{B}$ . If  $\bar{B}$  cannot be measured by ancillary techniques, model estimations can be made, assuming electrostatic or steric interactions between adjacent membranes [77], [175]. The inter-membrane potential for charged planes can be obtained from the one-dimensional Poisson-Boltzmann equation, as [77]

$$\bar{B}_{PB} = \frac{\pi k_B T d}{2l_B (d - \delta)^3} \quad (4.3)$$

where  $l_B = e^2/(4\pi\epsilon_0\epsilon_r k_B T)$  is the Bjerrum length of the solvent and corresponds to  $\simeq 0.7$  nm for water at room temperature and  $\delta$  is membrane thickness. This theory applies to weakly screened electrostatic repulsions and  $\bar{B}_{PB}$  can be decreased by attractive contributions of counterions near the membrane [177]. Steric repulsions can also contribute

to the overall  $\overline{B}$ , as described by Helfrich equation [178]:

$$\overline{B}_{und} = \frac{9\pi^2(k_B T)^2}{64\kappa} \frac{d}{(d - \delta)^4} \quad (4.4)$$

where  $\kappa$  is membrane bending rigidity and will be relevant for adjacent undulating flexible membranes relevant for d-spacing values below  $\simeq 10$  nm [177].

Experimentally, Neutron Spin Echo (NSE) can measure shape fluctuations in  $L_\alpha$  membranes via the intermediate scattering function  $I(q, t)$  from which  $\kappa$  can be directly estimated [77], [179], although measurements are long ( $\sim$ days), require large sample volumes ( $\sim$  several mL), and experimental access is somewhat limited [167].

The elastic properties of membranes can be modulated by the addition of dopants that embed within the bilayer (e.g., polymers, surfactants, alcohols, nanoparticles) or by addition of salt, thereby impacting  $\kappa$ . As an example, Meklesh and Kekicheff reported that addition of polyethylene glycol (PEG) to sodium dodecyl sulfate(SDS)/octanol/brine system increases membrane bending rigidity once the polymer concentration crossover from dilute to semidilute regimes is reached [177]. The addition of charged surfactants has been found to both increase and decrease  $L_\alpha$  membrane bending rigidity [180], [181]. Similarly, addition of salt will impact membrane bending rigidity  $\kappa$  in a manner that will depend on the initial membrane charge. In the case of non-ionic surfactant  $L_\alpha$  phases, addition of salt will lead to increase in  $\kappa$ . For example, NaCl addition to nonionic dioleoylphosphatidylcholine (DOPC)  $L_\alpha$  phase was reported to increase bending rigidity [76]. In a different study, nonionic  $C_{15}E_5$ , upon addition of antagonistic  $RbBPh_4$  salt, was also found to increase membrane bending rigidity [77]. However, other studies have indicated a decrease in  $\kappa$  with salt addition; for instance, the addition of NaCl to anionic dipalmitoylphosphatidyl glycerol (DDPG) surfactant has been shown to decrease membrane bending rigidity  $\kappa$ , caused by charge screening of steric repulsions [75].

In this chapter, I consider the impact of salt addition, and thus varying membrane bending rigidity, on the flow-induced transformation of a model  $L_\alpha$  surfactant phase into multilamellar vesicles (MLVs). This  $L_\alpha$  to MLV transformation [30] has been extensively

studied using different shear fields, stress and rates, using various model systems (non-ionic [43], [49], [58], cationic [182], [183] and anionic [66], [184]) alongside the effect of added co-surfactants [181], [185] and salt [76], [77]. Zilman and Granek [79] have proposed a theoretical model that estimates the critical shear required for the transformation in terms of the membrane properties ( $d$  and  $\kappa$ ) and flow geometry, although experimental evidence appears unclear, with increasing membrane bending rigidity resulting in both higher [77], [186] or lower critical shear rates [187].

To date, only a few studies have examined the coupling between  $L_\alpha$  membrane elastic properties and their flow response [77], [186], [187]. This chapter considers the effect of *varying* NaCl content on the model anionic SDS/octanol/water system in the  $L_\alpha$  phase, building upon previous work on the flow-induced MLV phase transformation of the 2% NaCl system investigated by rheometry [33], [61], [65], [66] and microfluidics [98], [188]. First, the effect of NaCl under quiescent conditions is established using SANS, viscometry and electrophoretic measurements (conductivity and zeta potential) to quantify and distinguish the effect of charge to the membrane elastic properties. Following that the spatiotemporal evolution of the fluid structure is investigated both varying NaCl at a constant flow rate, and the effect of varying flow rate for a select NaCl concentration by employing microfluidic-SANS [132], crosspolarised optical microscopy and  $^2\text{H}$  NMR, and seek to rationalise the behaviour in terms of the  $L_\alpha$  membrane properties.

## 4.2 Methods

### Sample preparation

Following phase mapping by optical microscopy (Fig. 4.1), the selected  $L_\alpha$  concentration, namely 6.5% SDS, 7.9% octanol and 85.6% brine, denoted with a red star in Fig. 4.2, was prepared with varying salt content. First, brine solutions with concentrations of 0, 1, 5, 10, 15, 18, 20, 22 and 25 g/L NaCl (ACS Reagent,  $\geq 99.0\%$ ) in  $\text{D}_2\text{O}$  (Sigma-Aldrich, 99.9 atom % D) corresponding to 0, 17, 86, 171, 257, 308, 342, 376 mM and 427 mM

were prepared. These concentrations will be denoted as 0, 0.1, 0.5, 1, 1.5, 1.8, 2.0, 2.2, 2.5% w/w NaCl in the paper referring to amount of NaCl in brine solution. Following that, 0.65 g (2.25 mmol) of Sodium Dodecyl Sulphate, SDS (Sigma-Aldrich BioXtra,  $\geq 99.0$  %) were dissolved in 9.52 g (427 mmol) of  $D_2O$  brine solution made of 0, 1, 5, 10, 15, 18, 20, 22 and 25 g/L NaCl. Dissolution was aided by heating to 30 °C until SDS had dissolved and allowed to cool to room temperature. Then, 0.790 g (6.07 mmol) of 1-octanol (Sigma-Aldrich, anhydrous,  $\geq 99$  %) was added to each of the SDS/brine mixture and stirred for 2 min at 1000 rpm until fully incorporated. The resulting solutions were left to equilibrate for 48 h to mitigate any inadvertent shear effects during sample preparation. The same procedure was employed to prepare samples made for microfluidic experiments but only 1.5 %, 1.8%, 2.0 % and 2.2 % samples were prepared, given their relatively lower viscosity (Fig. 4.7, 5-10 Pa s) and thus suitability for microfluidic flow.

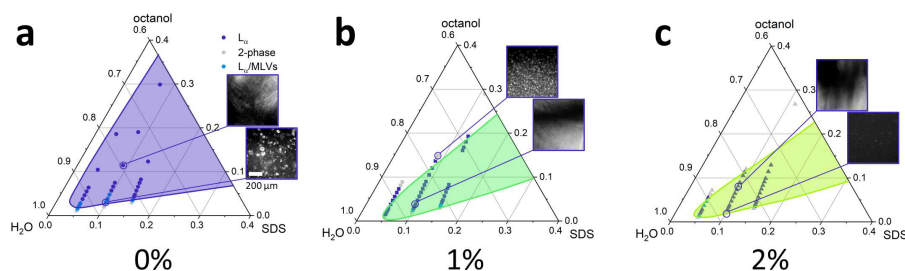


Figure 4.1: Phase maps and corresponding optical microscopy of SDS/octanol/water system with different salt concentrations. a) 0% NaCl; b) 1% NaCl; c) 2% NaCl.

### Static SANS and data fitting

SANS experiments were performed on the D22 spectrometer at the *Institut Laue Langevin*, Grenoble. Static measurements used ‘banjo’ Hellma cells (1 mm path length) with first detector and collimator distance of 5.6 m, second detector distance at 1.4 m and neutron wavelength  $\lambda = 6$  Å. The measured wavevector  $q$  range was 0.01 to 0.8 Å<sup>-1</sup> and the transmission of the samples was relatively high ( $>0.8$ ) with low background values of  $\sim 0.2$  cm<sup>-1</sup>. The sample rack was kept at room temperature, 25 °C. The data were reduced with GRASP software and data fitting (of radially- and sector-averaged spectra) was performed with SasView 5.0.2, employing the random head-tail sheet with Caillé structure

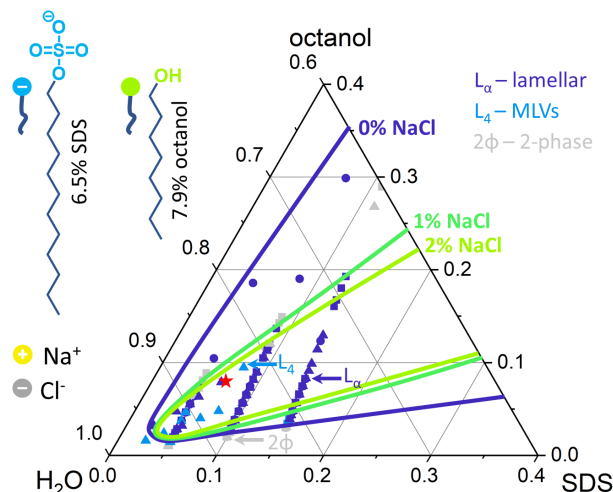


Figure 4.2: Ternary phase diagram of SDS/octanol/water system in the presence of NaCl. The (anionic) SDS surfactant molecule is shown in blue, and octanol in green. The coloured lines indicate the phase boundary between the micellar  $L_1$  region and the enclosed  $L_\alpha$  regions at selected NaCl concentrations ( $\circ$ ) 0, ( $\blacksquare$ ) 1%, and ( $\triangle$ ) 2% w/w; selected  $L_4$  (MLV) and two-phase ( $2\phi_v$ ) concentrations are also indicated. The red  $\star$  symbol shows the selected  $L_\alpha$  concentration for our study.

factor model [122] the fitted parameters compared for the different NaCl concentrations.

### Viscosity measurements

Viscosity shear sweep measurements were performed using an Anton Paar MCR 302 rheometer equipped with cone plate cell (part no. 79040). Samples investigated were with 0, 0.5, 1.0, 1.5 and 2.0% NaCl concentrations. Each sample was kept at 25 °C, with the gap between the cone-plate set to 0.2 mm and shear sweep performed from 0.1 to 2000  $s^{-1}$  with 20 points/decade, maintaining each shear rate for 20 seconds. The viscosity was measured at low 0.1  $s^{-1}$  shear rate value and high 1000  $s^{-1}$  shear rate.

### Zeta potential and conductivity

Zeta potential and conductivity measurements for micellar SDS/water solutions, and lamellar SDS/octanol/water, were collected using a Litesizer 500 and a Omega cuvette (225288) by injecting 1 mL of sample for every NaCl concentration and rinsing the cuvette in-between runs with DI water. The temperature of the cell was set to 25 °C and

the sample was equilibrated for 1 min, after which 3 measurements with 20 runs were performed. The Zeta potential  $\zeta$  was estimated via the Helmholtz-Smoluchowski equation [189]  $\zeta = \frac{\mu\eta}{\epsilon_r\epsilon_0}$  where  $\mu$  is the electrophoretic mobility measured experimentally,  $\eta$  is the viscosity of the solution with dielectric constant  $\epsilon_r$  and  $\epsilon_0$  is the vacuum permittivity. Conductivity of DI water with various NaCl concentrations was measured with a Hanna instruments multimeter (HI-2020) equipped with conductivity probe (HI-763100).

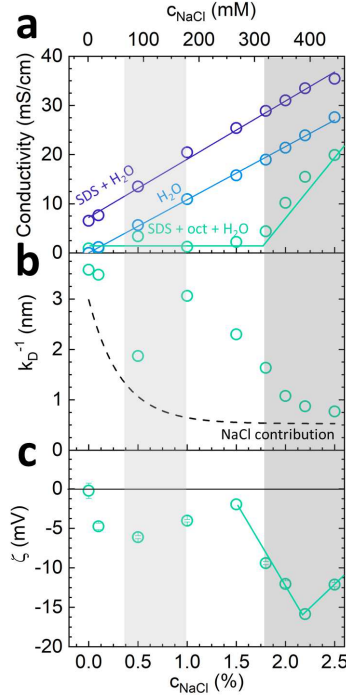


Figure 4.3: Conductivity and zeta potential  $\zeta$  measurements. a) Conductivity measurements for water, 6.5% SDS/water micellar solution, and 6.5% SDS/7.9% octanol/ 85.6 % water, as a function of NaCl content; b) Debye length  $k_D^{-1}$  estimated by assuming only salt ions contributing to the ionic strength (dashed line) and  $k_D^{-1}$  calculated from the experimental conductivity data of SDS/octanol/water/NaCl (circles); The light shaded area indicates a dip in  $k_D^{-1}$ , near the 1:1 molar ratio of SDS and NaCl ( $\sim 0.8\%$  NaCl). c) Zeta potential  $\zeta$  measurements for SDS/octanol/water system with varying NaCl concentrations estimated from electrophoretic mobility  $\mu_{mob}$  by the Helmholtz–Smoluchowski equation. The darker shaded area corresponds to the onset of the linear conductivity dependence for the lamellar system with salt addition.

The conductivity of micellar SDS/water and water increases linearly with NaCl at all concentrations investigated, as shown in Fig. 4.3a. By contrast, the conductivity of the lamellar SDS/octanol/water system remains largely unchanged up to  $\sim 1.8\text{--}2\%$  NaCl, indicating charge condensation at the membrane surface, and then increasing linearly

beyond this threshold, in agreement with the onset of demixing (Fig. 4.2). This behaviour is qualitatively in line with expectations from Manning theory for counterions condensation on spherical and planar geometries [190]. The Debye length  $k_D^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{2ne^2}}$ , where  $n$  is the number charge density and  $e$  is the electric unit charge, was first estimated with the assumption that only  $\text{Na}^+$  and  $\text{Cl}^-$  ions contribute to number charge density [77], yielding values between 2.32 and 0.46 nm with increasing NaCl concentration, as shown by the dashed line in Fig. 4.3b. A more accurate estimate utilises conductivity  $K_c$  measurements, as  $k_D^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 D}{K_c}}$ , where  $D$  is diffusion constant for  $\text{Na}^+$  and  $\text{Cl}^-$  ions,  $D = 1.7 \mu\text{m}^2 \text{ms}^{-1}$  [191], shown as markers. The dip around 0.5-1 % NaCl (shaded) coincides with the isoelectric point for this system. Zeta potential measurements are shown in Fig. 4.3c, approximately following the results of Fig. 4.3a, b. Specifically,  $\zeta$  decreases around 1.8-2% NaCl, beyond which the system demixes.

### Serpentine channel microfluidic setup

A commercially available serpentine,  $\sim 3$  m long, tubular microfluidic device etched in high optical and neutron transmittance crown glass [98], [192], [193] (Dolomite Microfluidics, ref. 3000281) was selected for these experiments. The device was fitted with a 30 cm long inlet and outlet polytetrafluoroethylene (PTFE) tubing (Cole Parmer, ref. WZ-06406-60, i.d.= 0.79 mm). The sample was slowly poured onto the barrel of a 20 mL stainless steel syringe, and mounted on a high-pressure PHD ULTRA 4400 syringe pump (both Harvard Apparatus). The extremity of the long serpentine channel outlet was connected to the syringe (input); two of three access ports were closed and the remaining one was used as outlet and connected to a waste container. The sample was infused for 60 min to reach a steady state at  $0.5\text{-}5 \text{ mL h}^{-1}$  equivalent to  $1.6\text{-}16 \text{ mm s}^{-1}$  and wall shear rates of  $\sim 40\text{-}400 \text{ s}^{-1}$  (estimated following [136] as  $\dot{\gamma} = (4Q/\pi R_{eq}^3)$ , where  $Q$  is volumetric flow rate and  $R_{eq}$  is the equivalent radius of an ellipsoid calculated as  $2A/P$  with  $A$  is the cross-sectional area,  $0.086 \text{ mm}^2$ , and  $P$  the perimeter,  $1.08 \text{ mm}$ ). Oscillatory rheology data for the 2% NaCl reference system [137] indicate a  $G'$  and  $G''$  crossover at  $\sim 0.45 \text{ s}^{-1}$  corresponding to characteristic timescales of  $\sim 2 \text{ s}$ . The flow conditions examined can thus be considered

‘strong’, and well within the shear regime expected for MLV formation [33]. Measurements were recorded for every channel section with optical microscopy and every 7th channel section for SANS. The position of the fluid on the microfluidic chip was calculated as the sum of inlet length + serpentine channel section number  $\times$  24 mm (i.e., the length of each section). Flow profiles obtained by PIV of the fluid in the serpentine channel are given in Fig. 4.4 and showed plug-like flow.

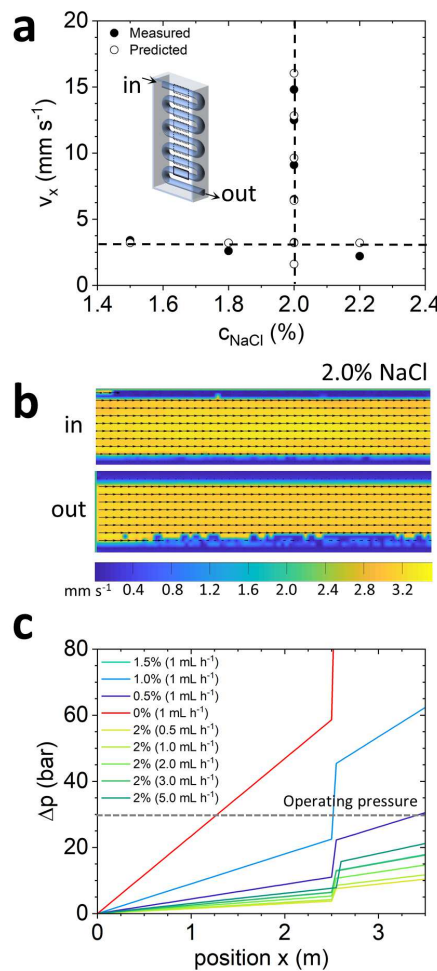


Figure 4.4: Overview of flow conditions. a) Imposed vs measured flow rate  $v_x$ ; b) PIV of 2.0% NaCl condition at the start and end of the chip showing plug-like flow profile. PIVs were obtained using PIVLab software inputting 20 consecutive images and ensemble correlation with 2 passes with 64 x 64 and 32 x 32 pixel by pixel interrogation window sizes (1 pixel = 1.54  $\mu$ m), and selecting a Gauss 2 x 3-point sub-pixel estimator and ‘standard’ correlation quality; c) Pressure drop calculations along the microfluidic chip for various flow and NaCl conditions estimated using Hagen–Poiseuille equation. A maximum safe operating pressure for this microfluidic system is estimated to be approximately 30 bar.

## Microscopy

Following 60 min infusion of the sample onto the chip, the flow was stopped and microscopy images were then acquired with Olympus BX41 reflection microscope equipped with cross-polarised filters (U-AN-2 analyser and U-PO3 polariser). Image capture was done with a Basler acA2000-165um camera controlled with PylonViewer using 10x/0.25 Ach and 50x/0.50 MPlanFLN Olympus objectives under 10000  $\mu s$  and 200000  $\mu s$  exposure time respectively. Data were analysed with ImageJ by measuring the average light intensity and FFT for images acquired along the serpentine channel.

## Microfluidic-SANS

The microfluidic chip was mounted on a micromachined aluminium frame, thermalised to 25 °C, on the D22 spectrometer configured as described above.

A neutron beam slit mask with dimensions 1.4 cm  $\times$  200  $\mu m$  was used to define the beam footprint, within the bounds of the microdevice dimensions, resulting in a scattering volume of 0.7  $\mu L$  (given the 0.25 mm sample pathlength, i.e. channel depth). The device was illuminated in the neutral flow direction ( $z$  in Fig. 4.5a), probing the  $xy$  plane. The channel was aligned with the neutron beam by iteratively scanning the empty chip and tracking the scattering and transmission signals along  $x$  and  $y$  directions until a microchannel map is resolved. Continuous microfluidic experiment was performed for 4 different NaCl concentrations (1.5, 1.8, 2.0 and 2.2%) scanning every 7<sup>th</sup> channel section, as shown in Fig. 4.5b. As above, the data were reduced with GRASP, sector averaged, and fitted with SasView 5.0.2 employing the random head-tail sheet with Caillé structure factor model.

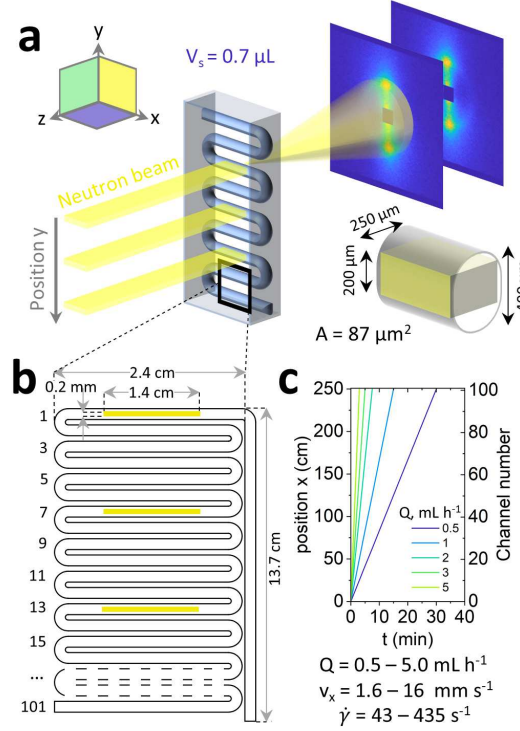


Figure 4.5: SANS microfluidic setup and experimental parameters. a) Serpentine microchannel device illuminated, channel by channel, along the  $y$ -direction, under steady state flow conditions ( $0.5\text{--}5.0\text{ mL h}^{-1}$ ). The channel dimensions are indicated, and the neutron beam slit is illustrated in yellow. b) Microchannel dimensions and arrangement; the beam slit defines a horizontal length and vertical height of  $1.4\text{ cm} \times 200\text{ }\mu\text{m}$  and, for a channel depth of  $250\text{ }\mu\text{m}$ , resulting in an illuminated volume  $V_s \simeq 0.7\text{ }\mu\text{L}$ . c) Sample position, and corresponding serpentine channel number, as a function of time for  $0.5, 1.0, 2.0, 3.0$  and  $5.0\text{ mL h}^{-1}$  flow rates indicated in legend, corresponding to average linear velocity  $v_x$  range of  $1.6\text{--}16\text{ mm s}^{-1}$  and wall shear rate range  $43\text{--}435\text{ s}^{-1}$ .

## 4.3 Results

### 4.3.1 Effect of salt on the $L_\alpha$ equilibrium phase structure

The effect of salt on the  $L_\alpha$  phase was initially investigated under quiescent conditions with optical microscopy (Fig. 4.1 and Fig. 4.2) and SANS. 2D scattering images (Fig. 4.6a, for front and rear detectors) show higher order diffraction orders for  $0\%$  NaCl that gradually disappear with increasing NaCl concentrations.

The radially-averaged scattering profiles  $I(q)$  exhibit equidistant Bragg peaks ( $q^* \simeq 0.04\text{ }\text{\AA}^{-1}$ ,  $2q^* \simeq 0.08\text{ }\text{\AA}^{-1}$ ,  $3q^* \simeq 0.12\text{ }\text{\AA}^{-1}$  and  $4q^* \simeq 0.16\text{ }\text{\AA}^{-1}$ ) indicating the presence of bilayer structures characteristic of  $L_\alpha$  phases (Fig. 4.6b). The higher order features [194] can be

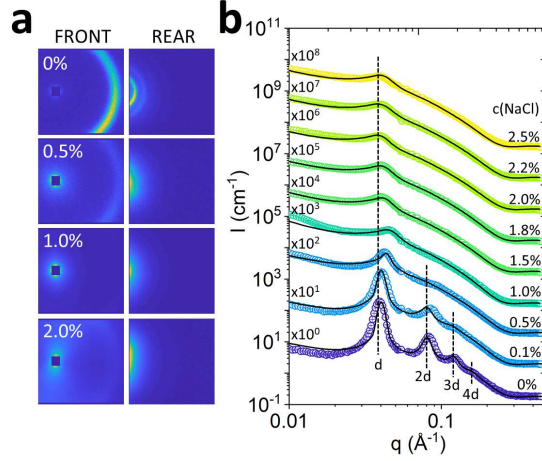


Figure 4.6: SANS data at quiescent conditions. a) 2D scattering profiles for selected NaCl concentrations (0%, 0.5%, 1.0%, 2.0% w/w) acquired simultaneously in two detectors, indicated as 'front' (distance 5.6 m) and 'rear' (distance 1.3 m) detectors. b) Radially-averaged  $I(q)$  profiles for SDS/octanol/brine 6.5%/7.9%/85.6% with NaCl concentrations in brine ranging from 0 - 2.5% w/w. The dashed vertical lines indicate peak positions corresponding to  $d$ ,  $2d$ ,  $3d$  and  $4d$  ( $q^* \simeq 0.04, 0.08, 0.12, 0.16 \text{ \AA}^{-1}$ ), denoting the primary, secondary, tertiary and quaternary Bragg peaks, whose equidistant spacing between indicates  $L_\alpha$  stacks. Deviation from the dashed line are discussed in the text. The profiles are shifted vertically for clarity by the multiplicative factors shown.

disturbed by fluctuations of the  $L_\alpha$  sheets [138], [195]. Indeed, membrane order decreased, indicated by the disappearance of secondary, tertiary and quaternary Bragg peaks upon the addition of NaCl (Fig. 4.6b). The decrease in  $L_\alpha$  ordering was accompanied by a decrease in low shear rate ( $0.1 \text{ s}^{-1}$ ) viscosity, which follows a linear trend up to 1.0% NaCl addition, and then largely remains unchanged at higher salt (detailed in Fig. 4.7).

The  $I(q)$  profiles were fitted with the Caillé structure factor model, shown by the solid lines in Fig. 4.6b. Scattering length density,  $SLD$  values used for fitting are detailed in Section 2.3.1. The Caillé parameter  $\eta$  was found to increase rapidly with the addition of NaCl, as shown in Fig. 4.8a, reaching a plateau of 1, which is the limit of the model assumptions. The solid line is an exponential rise to maximum, employed as a guide to the eye. An approximate d-spacing of  $150 \text{ \AA}$  was observed across all NaCl concentrations, although varying from  $156 \text{ \AA}$  at 0% NaCl, and dropping to  $135 \text{ nm}$  at 1%, near the 1:1 molar ratio of SDS:NaCl. The bilayer thickness  $\delta$  was calculated as  $2(l_{tail} + l_{head})$  remains largely unchanged upon the addition of NaCl (fig. 4.8a) indicating no appreciable swelling.

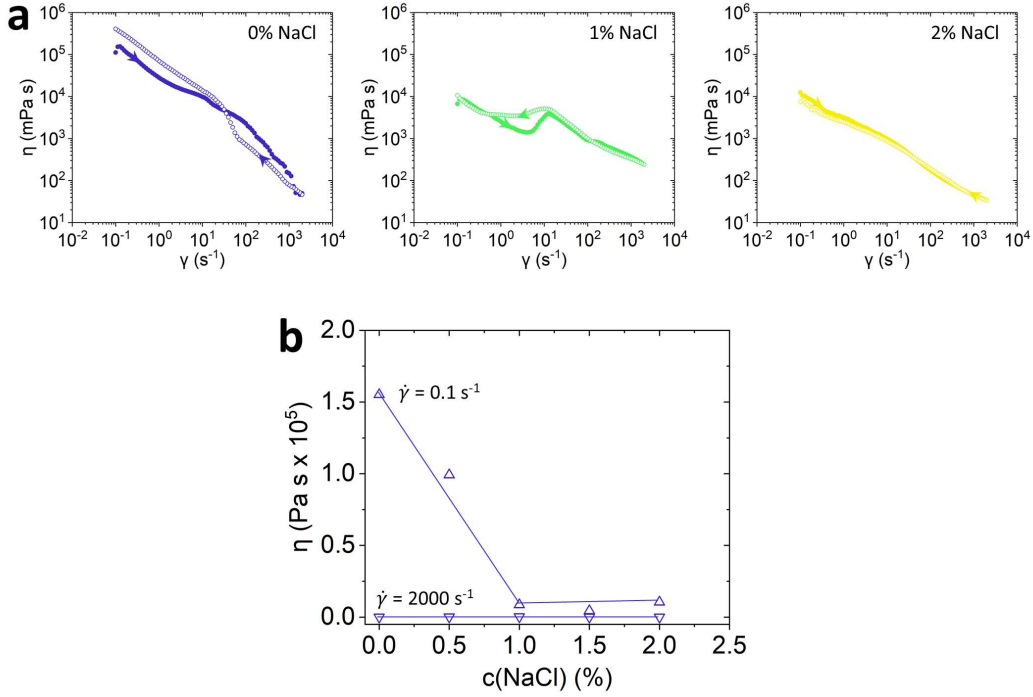


Figure 4.7: Rheological characterisation of SDS/octanol/water system with different salt concentrations. a) Rheological shear sweeps from 0.1 to 2000 s $^{-1}$  for selected salt concentrations for 0%, 1% and 2% NaCl; b) Viscosity  $\eta$  dependence on NaCl concentrations.

From the fitted  $\eta$  values and Eq. 4.2,  $\overline{B}\kappa$  was estimated and found to decrease monotonically with increasing NaCl concentration, as shown in Fig. 4.8b. Theoretical  $\overline{B}$  estimates were obtained by Eq. 4.3 assuming only electrostatic contributions, and are plotted in Fig. 4.8c. These indicate a non-monotonic behaviour upon addition of NaCl with a highest value of 95 kPa when SDS:NaCl molar ratio is 1:1 ( $c(\text{NaCl})=1\%$ ) and subsequent drop in value until phase transition boundary conditions are reached around 2% NaCl (Fig. 4.8c). The membrane sheet schematics illustrate the decrease in stiffness and long range order induced by the salt addition. Parameter  $\kappa$  was estimated from model fitting results and theoretical  $\overline{B}$  calculations indicating an overall decrease in membrane bending rigidity (Fig. 4.8c) from  $3.2 k_B T$  to  $0.04 k_B T$ . This decreasing trend is consistent with that of the Debye length  $k_D^{-1}$  (shown in Fig. 4.3b) indicating  $k_D^{-1} \simeq 3.58$  nm at low NaCl concentrations, decreasing to  $\simeq 0.78$  nm at high NaCl, thus corresponding to approximately 1/4 to 1/20 of the lamellar  $d$ -spacing. A previous study of salt addition to dipalmitoylphosphatidylglycerol (DPPG) [75] also reported a decrease in  $k_D^{-1}$  with decreasing  $\kappa$ , as expected for reduced electrostatic repulsions.

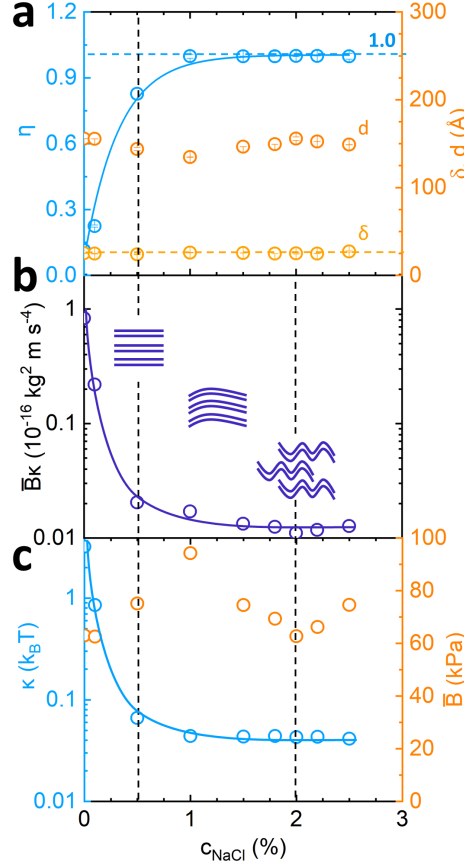


Figure 4.8: Fitted parameters from Fig. 2 according to the Caillé structure factor model. a) Caillé parameter  $\eta$  and  $L_\alpha$  spacing  $d$  dependence on NaCl concentration; b) Estimated  $\overline{B}\kappa$  value dependence on NaCl concentration, where  $\overline{B}$  is the compressibility modulus and  $\kappa$  is membrane bending rigidity, and accompanying schematics; c) Calculated  $\overline{B}$  values from  $\overline{B}_{el} = \frac{\pi k_B T d}{2l_B(d-\delta)^3}$  and corresponding  $\kappa$  from  $\overline{B}\kappa$  model fit estimates.

Membrane compressibility modulus  $\overline{B}$  dependence on d-spacing with steric contributions shown in Fig. 4.9.

### 4.3.2 Effect of NaCl on the lamellar phase under continuous microfluidic flow (fixed flow rate)

The effect of NaCl addition on the flow response of the  $L_\alpha$  phase under continuous microfluidic flow was examined by a combination of crosspolarised optical microscopy,  $^2\text{H}$  NMR and SANS. At a fixed flow rate of  $1 \text{ mL h}^{-1}$ , the residence time of the fluid within the microchannel length probed was  $\sim 12 \text{ min}$ . In general, the correspondence between position, channel section, and residence time for different flow rates is illustrated in Fig.

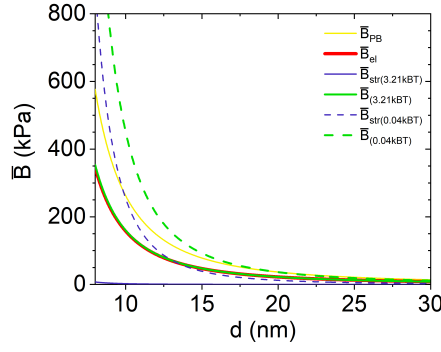


Figure 4.9: Membrane compressibility modulus  $\bar{B}$  dependence on d-spacing  $d$ .  $\bar{B}_{el}$  (red solid line), value adjusted when accounting for spatial correlation of counterions adjacent to membrane and  $\bar{B}_{str}$  are summed to obtain  $\bar{B}$  values for low and high membrane bending rigidity conditions shown in dashed and solid green colours respectively.  $\bar{B}_{PB}$  is the value of membrane compressibility modulus only considering electrostatic contributions without counterion interactions.

4.5c. Given the higher viscosities of low NaCl systems, the following concentrations were selected for microfluidic experiments at a *fixed* flow rate of  $1 \text{ mL h}^{-1}$ : 1.5, 1.8, 2.0 and 2.2 % NaCl, in order to ensure the safe operation of the microdevice within a pressure operating range below 30 bar. Pressure drop estimations are shown Fig. 4.4c, based on the Hagen–Poiseuille equation  $\Delta p = 8\pi\eta LQ/A^2$  where  $L$  is the channel length,  $Q$  is the volumetric flow rate,  $\eta$  is dynamic viscosity and  $A$  the cross-sectional area of the channel. The system was allowed to equilibrate for  $\sim 1 \text{ h}$ , greatly exceeding the residence time of  $\sim 12 \text{ min}$  (at  $1 \text{ mL h}^{-1}$ ), at an average flow velocity  $\sim 3.21 \text{ mm s}^{-1}$ . The corresponding wall shear rate is estimated [136] at  $\simeq 87 \text{ s}^{-1}$ , within the regime in which  $L_\alpha$ -to-MLV transformation was previously observed [33], [41], [48].

Optical birefringence measurements at the centre of each serpentine channel section (2.4 cm length) showed a decrease in (crosspolarised) light intensity along microchannel position, as shown in Fig. 4.10a, for NaCl concentrations between 1.5-2%, beyond which (2.2% NaCl) the trend is reversed. Given that light intensity scales approximately with feature size, the results suggest a size decrease and ordering of the characteristic fluid structures. Complementary  $^2\text{H}$  NMR data were acquired at reference start (\*) and end (\*\*) positions, illustrated for 1.8% and 2.2% NaCl in Fig. 4.10b. The single peak observed at 1.8% is characteristic of an isotropic fluid, contrasting with the dual peaks of 2.2%,

expected for an anisotropic fluid. Thus the former corresponds to MLVs and the latter to an oriented lamellar sheet structure. Further the end-channel (\*\*) data of 1.8% NaCl shows a narrowing of the peak upon microflow, expected for increasing uniformity in MLV size.

Optical images acquired at the channel entrance and at position 210 cm are indicated with \* and \*\* in Fig. 4.10c, corroborating a varying degree of ordering amongst the 1.5-2.2% NaCl samples. A fine, regular texture is observed for the resulting fluid structure (\*\*) for 1.8 and 2.0% NaCl, accompanied by FFTs exhibiting a cloverleaf pattern. Structures observed at the bends of the serpentine channel sections, shown in Fig. 4.10d, were of higher overall average light intensity, reflecting the additional rotational component of the shear flow. Overall, while the light intensity and MLV texture dimensions decrease along the microchannel position, these do not reach a plateau, indicating that a morphology of regularly packed onions is not attained within the experimental timescales. Employing oscillatory flow and contraction-expansion flows, enabling longer residence times of  $\sim 2$  h, we have previously observed an asymptotic optical characteristics after approximately 60 min shearing times at similar shear rate regime [188].

In order to resolve the nanoscale arrangement of the  $L_\alpha$  structure, we employed microfluidic-SANS and a narrow, rectangular, beam slit ( $1.4 \text{ cm} \times 200 \text{ }\mu\text{m}$ ) precisely aligned along the horizontal channel sections, as shown in Fig. 4.5b), illuminating a  $0.7 \text{ }\mu\text{L}$  sample volume. Given the low illuminated volume ( $0.7 \text{ }\mu\text{L}$ ), each SANS spectrum was recorded for 20 min to acquire adequate statistics. The centre of every 7<sup>th</sup> channel section, along the y direction, was sampled, corresponding to 17 channel positions along the serpentine channel, illustrated in Fig. 4.5b).

The scattering data at the start of the microchannel are generally anisotropic, as expected for aligned  $L_\alpha$  sheets for all NaCl concentrations. Sector analysis of  $I(q)$  reveals greater alignment along the normal ( $xz$ ) direction to flow, than along the flow direction, illustrated in Fig. 4.11a for channel position 15 cm. The scattering varies non-monotonically with NaCl content and is lowest, and least anisotropic for 1.8% NaCl; at the highest NaCl

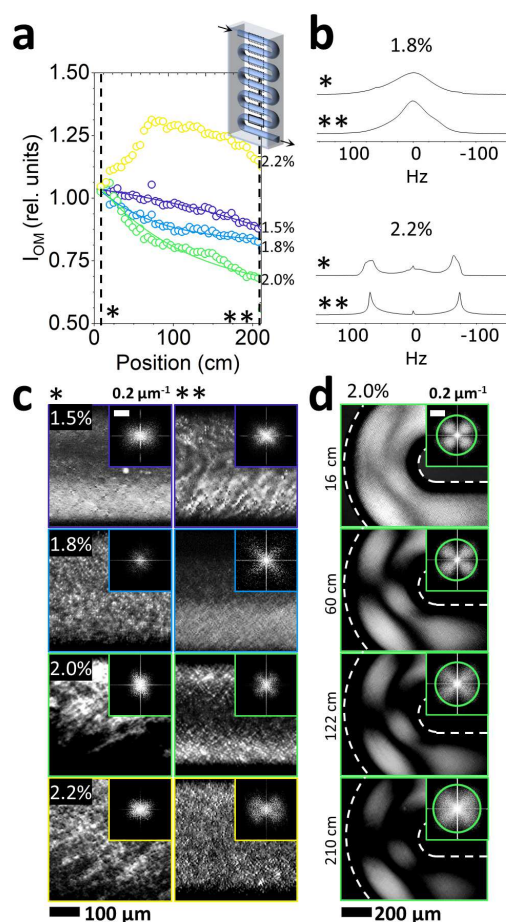


Figure 4.10: Measured polarised optical microscopy light intensity and texture evolution as a function of channel position. a) Relative intensity (referenced to the start position) for NaCl concentrations of 1.5, 1.8, 2.0 and 2.2% w/w; b)  $^2\text{H}$  NMR of 1.8 and 2.2% NaCl showing the sample before (top) and after (bottom) being subjected to microfluidic flow; c) Optical textures and FFTs at ‘start’ (14.9 cm) and (‘end’) position 211 cm, corresponding to 11 min shear time; d) Optical texture and FFTs at bends along the channel at positions of 16, 60, 122, 210 cm for 2.0% NaCl.

concentration investigated, 2.2%, the anisotropy is greatest and no scattering peak is visible along the flow direction ( $xz$ ). This behaviour is expected for MLVs at 1.8% and sheets a 2.2% NaCl.

Further analysis of the evolution of the alignment along the chip was carried out by integrating the scattering intensity under the Bragg peak (within  $0.025 \leq q \leq 0.05 \text{ \AA}^{-1}$ ) as a function of channel position, as shown in Fig. 4.11b for 1.8% and 2.0% NaCl. The integrated intensity along the flow  $xz$ , and perpendicularly to the flow  $yz$ , is shown by  $\circ$  and  $\triangle$  markers respectively. The relative fraction of sheets on  $xy$  plane cannot be measured directly, but its evolution along channel position was estimated by subtracting

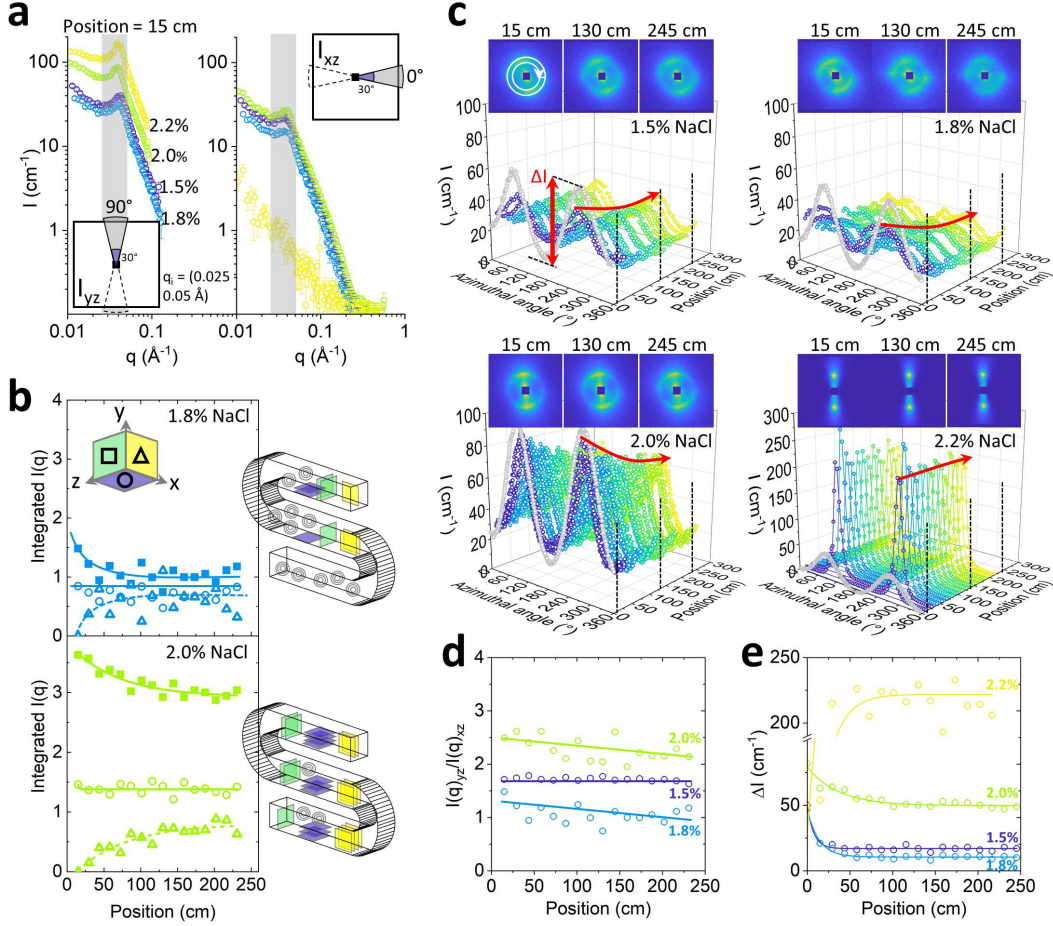


Figure 4.11: Effect of salt on the SANS flow evolution of the lamellar phase on serpentine microfluidic chip at fixed flow rate of  $1 \text{ mL h}^{-1}$ . a) Sector analysis at  $90^\circ$  and  $0^\circ$  (with  $30^\circ$  angular integration range) probing lamellar sheets aligned, respectively, with the flow (along the  $xz$  plane) and perpendicularly to the flow (along the  $yz$  plane); b) Integrated scattering intensity at the Bragg peak ( $0.025 \leq q \leq 0.05 \text{ \AA}^{-1}$ ) as a function of channel position for  $yz$  (■),  $xz$  planes (○) and inferred for  $xy$  plane (△), shown as dashed line, for 1.8 % NaCl (top) and 2.0 % NaCl (bottom). Schematics illustrate the transformations inferred; c) Azimuthal averages of 2D SANS scattering patterns as a function of channel position, computed within  $0.035 \leq q \leq 0.045 \text{ \AA}^{-1}$ , for 1.5, 1.8, 2.0 and 2.2% NaCl. Selected 2D patterns at channel positions 15 cm, 130 cm and 245 cm are indicated on the left, and by the vertical dashed lines. A degree of anisotropy  $\Delta I$  is computed from  $I_{max} - I_{min}$  in the azimuthal plots, hence  $\Delta I \rightarrow 0$  corresponding to an isotropic pattern; d) Comparison between populations of lamellar sheets aligned with the flow and perpendicular to the flow; e) SANS  $\Delta I$  computed as a function of the serpentine channel position for the various NaCl concentrations; Lines are guides to the eye.

the sum of intensities on the  $yz$  and  $xz$  planes and subtracting their initial value, i.e. at the start of the channel. In this way, assuming that the overall scattering integral remains approximately constant within this  $q$ -range, the intensity in the ‘missing plane’ corresponding to the fraction of sheets exchanged into  $xy$  plane can be inferred, indicated

by  $\Delta I_{xy}$  in terms of intensity. In the case of 1.8%, the relative sheet alignment approaches a similar end point, implying that the populations of the sheets in all principal directions are approximately equal, and this isotropic structure supports the formation of MLVs. The alignment observed for 2.0% NaCl is evidently not equal at this channel position, but gradually evolves to become more isotropic along the channel, compatible with partial MLV formation.

The evolution of the orientational order under flow for each NaCl concentration was further examined by the azimuthal analysis of the 2D scattering spectra, integrated within a narrow  $q$  range 0.035 - 0.045  $\text{\AA}^{-1}$  (Fig. 4.11c). In the case of 1.5% and 1.8% NaCl, anisotropy decreased rapidly along the channel position, while for 2.0% NaCl, the anisotropy decreases modestly and the lamellar sheets remain largely aligned within the microchannel length (up to  $\sim 250$  cm) and flow time ( $\sim 12$  min). By contrast, the system with 2.2% NaCl content remains highly aligned throughout, as expected for lamellar sheets under shear flow. This concentration corresponds to the onset of demixing evidenced the optical phase mapping data.

These results corroborate the sector analysis provided in Fig. 4.11b, in terms of the absolute peak intensity evolution towards more isotropic structures, in particular for the 1.8% NaCl system. Fig. 4.11b and c show the ratio between  $I(q)_{yz}$  and  $I(q)_{xz}$  populations (Fig. 4.11d) and the maximum amplitude of the azimuthal intensity variation, termed  $\Delta I$  (Fig. 4.11e), as a function of channel position. The results are consistent to those reported by optical microscopy in Fig. 4.10a, albeit the SANS data readily reach a plateau value within relatively short channel travel distances ( $\sim 25$ -100 cm). In terms of NaCl content, the systems can be readily ranked from iso- to anisotropic, as 1.8%, 1.5%, 2.0% and finally 2.2% NaCl. The fact that the SANS data exhibit asymptotic behaviour within short channel distances (and thus times) is expected given the nanoscale dimensions probed, while the larger, micronscale regular arrangements probed by optical microscopy evolve subsequently and refine over much longer times [188].

### 4.3.3 Effect of varying microfluidic flow rate on the lamellar phase (fixed salt content)

Next, I describe the effect of *varying* flow magnitude on the  $L_\alpha$ -to-MLV transformation by investigating flow rates 0.5, 1.0, 2.0, 3.0 and 5.0 mL h<sup>-1</sup> with microflow-SANS at a *fixed* 2.0% NaCl concentration, for consistency with previous work on this system. These flow rates yield wall shear rates estimates of 40-400 s<sup>-1</sup>, in the range expected for MLV formation for this system (10-1000 s<sup>-1</sup>) [33], [66]. Comparing the integrated area of radially averaged  $I(q)$  sectors parallel ( $xz$ ) and orthogonal ( $yz$ ) to the flow, shown in Fig. 4.12a, follows that increasing flow rate has the dual effect of (i) inducing a greater *initial* lamellar sheet alignment, while also (ii) causing a more rapid decrease in anisotropy *subsequently*, as shown in Fig. 4.12b and 4.12c. The latter plots the ratio of the integrated sector intensities  $I(q)_{yz}/I(q)_{xz}$ , which increases approximately linearly with flow rate, and decreases with microchannel position. Direct observation of 2D scattering images, in Fig. 4.12d, shows that the anisotropic profiles evolve gradually along channel position, and the azimuthal analyses for 0.5, 1.0 and 5.0 mL h<sup>-1</sup> quantify the decrease in anisotropy at the higher flow rates (1.0 and 5.0 mL h<sup>-1</sup> shown) but exhibits virtually no change at the lowest rates of 0.5 mL h<sup>-1</sup> (see Fig. S8 for 2.0 and 3.0 mL h<sup>-1</sup>).

While the flow alignment of the  $L_\alpha$  phase is expected and widely reported [54], [98], the subsequent decrease in anisotropy under microfluidic flow indicates a gradual evolution towards MLVs, within the accessible residence time windows. Previous mechanistic studies of MLV formation suggest that lamellar sheets first align with the flow and experience a suppression of membrane undulations [79], [80], eventually resulting in vesicle formation at sufficiently high shear rates and longer times.

By contrast, oscillatory flows can potentially facilitate MLV-formation by selecting a different pathway [43]. From a practical viewpoint, oscillatory flow fields also permit a decoupling between flow rate and residence time (which are otherwise constrained as illustrated in Fig. 3c), and thus the investigation of arbitrarily long shearing times. Fig. 4.13 contrasts the effect of continuous (this chapter) and oscillatory [188] flows on the  $L_\alpha$ -

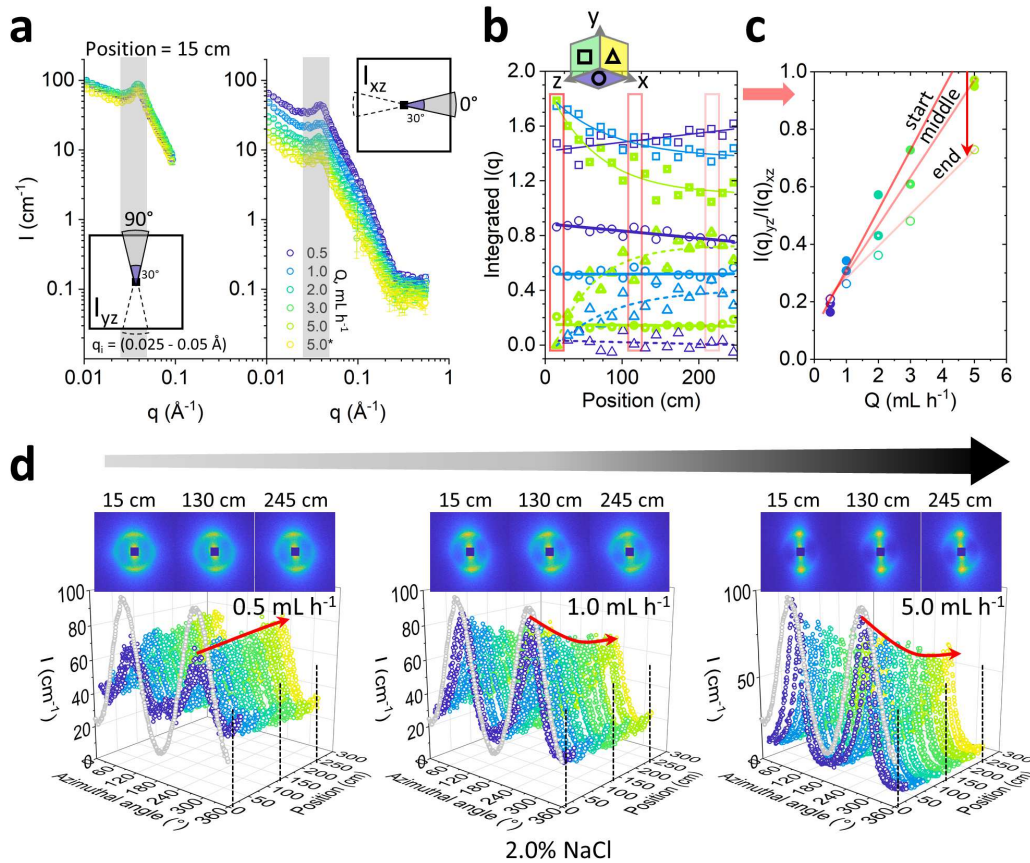


Figure 4.12: Effect of flow rate on the lamellar phase at fixed 2.0% NaCl measured by SANS. a) SANS sector analysis at 90° and 0° (with 30° angular integration range) probing, respectively, lamellae sheets aligned with the flow (along the  $xz$  plane), and perpendicularly to the flow (along the  $yz$  plane); b) Integrated scattering intensity at the Bragg peak ( $0.025 \leq q \leq 0.05 \text{ Å}^{-1}$ ) as a function of channel position for  $yz$  (■),  $xz$  (○) and inferred  $xy$  (△) planes for flow rates of 0.5, 1 and 5 mL h<sup>-1</sup>; c) Ratio  $I(q)_{yz}/I(q)_{xz}$  of integrated populations reflecting the effect of flow rate ( $Q = 0.5-5 \text{ mL h}^{-1}$ ) on the anisotropy (higher value indicating higher anisotropy) for illustrative channel positions 15, 130 and 245 cm denoted as 'start', 'middle' and 'end' respectively; d) azimuthal averages of 2D SANS scattering patterns as a function of channel position, computed within  $0.035 \leq q \leq 0.045 \text{ Å}^{-1}$ , for 0.5, 1 and 5 mL h<sup>-1</sup>. Selected 2D patterns at illustrative channel positions indicated by the vertical dashed lines.

to-MLV transformation on the same system. Overall, we find that the transformation rate is greater for oscillatory flow under comparable velocity and wall shear rate conditions (Fig. 4.13), highlighting the role of rotational flow components and acceleration/deceleration often found in practical flow nozzles used in MLV generation by flow processing.

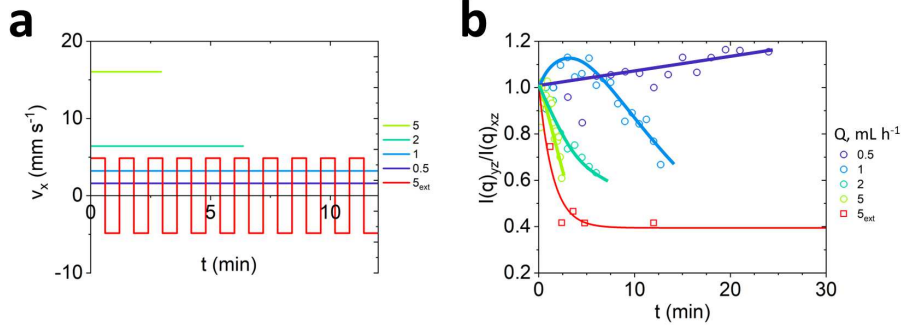


Figure 4.13: Comparison of the flow effects induced by serpentine and extensional/oscillatory microfluidic chip geometries. a) Imposed average flow velocity as the corresponding volumetric flow rates: horizontal lines correspond to the serpentine channel (0.5, 1.0, 2.0 and 5.0  $\text{mL h}^{-1}$ ), while the square wave indicates the velocity (wide cross-section) within the extensional/oscillatory field at 5  $\text{mL h}^{-1}$ ; b) Normalised  $I(q)_{yz}/I(q)_{xz}$  evolution comparison between extensional geometry at 5  $\text{mL h}^{-1}$  and linear serpentine geometry at 0.5, 1.0, 2.0 and 5.0  $\text{mL h}^{-1}$ .

## 4.4 Summary

This chapter has considered the effect of salt addition (0-2.5% NaCl) on the phase behaviour and microstructure of a model  $L_\alpha$  system, namely 6.5% SDS/7.9% octanol/85.6% brine, known to undergo a lamellar-to-MLV transition under flow. Salt addition was found to decrease  $L_\alpha$  ordering, increase the Caillé parameter, and correspondingly decrease  $\overline{B}\kappa$ , the product of membrane compressibility modulus and bending rigidity, while the membrane thickness remained largely unchanged, and the  $d$ -spacing varied non-monotonically. The effect of flow was examined using a serpentine microfluidic device, consisting of a  $\sim 3$  m long tubular microchannel, operated in continuous flow, using polarised optical microscopy and SANS. Owing to operating pressure limits of the microdevice, and the high viscosity of the  $L_\alpha$  system, NaCl content  $>1.5\%$  were investigated under flow. Salt addition was found to promote MLV formation up to a crossover point between 1.8 and 2.0% NaCl.

Figure 4.14 provides an overview of the findings, in terms of the scattering observables, fitted membrane properties and accompanying lamellar schematics. Figure 4.14a shows the terminal (minimum) value  $I_{min}$  of the cross-polarised light intensity (top), and the azimuthal intensity amplitude at Bragg peak,  $\Delta I_{min}$ , measured at the end position measured along the serpentine channel (bottom), as a function of NaCl concentration.

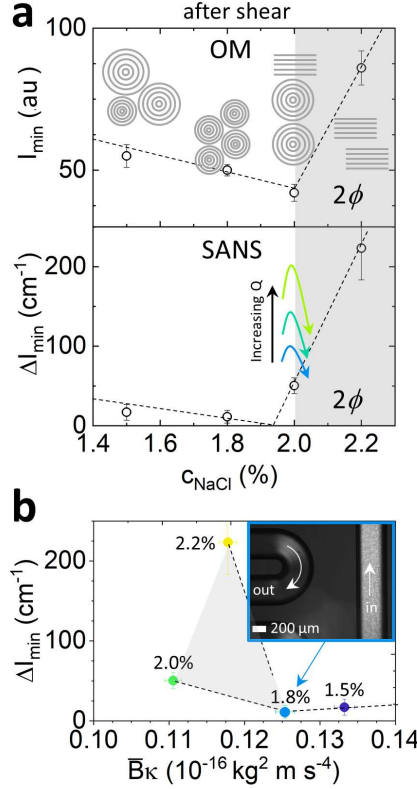


Figure 4.14: Optical and SANS intensity dependence on NaCl concentration at a fixed ‘end’ channel position 245 cm. a) Optical (top) and SANS azimuthal (bottom) intensity dependence on NaCl concentration and flow rate, with accompanying schematics. The dashed lines are guides to the eye. Qualitative effect of flow rate at a reference 2% NaCl concentration is indicated with arrows; b) SANS azimuthal intensity  $\Delta I_{min}$  as a function of  $\overline{B}\kappa$  computed from the quiescent data in Fig. 4.8b.

The effect of increasing flow rate examined at a fixed 2% NaCl addition increased the *initial* alignment of the  $L_\alpha$  phase, and thus increase flow anisotropy, but also subsequently cause a faster decrease in anisotropy as a function of time, toward MLV formation. Figure 4.14b then correlates  $\Delta I_{min}$  with the fitted  $\overline{B}\kappa$  parameter obtained from quiescent SANS data, exhibiting a minimum value corresponding to the 1.8% NaCl concentration with  $\overline{B}\kappa \simeq 0.125 \times 10^{-16} \text{ kg}^2 \text{ m s}^{-4}$ ; for this system, further decreasing  $\overline{B}\kappa$  leads to the onset of demixing, and therefore does not facilitate MLV formation. The apparent inversion of the trend between 2.0 and 2.2% NaCl is likely due to the fact that the latter is within the biphasic region. An optical image taken near the channel inlet and outlet for the 1.8% NaCl concentration is included as inset, illustrating the change in optical texture and intensity effected by the microchannel flow. Combined microfluidic SANS and optical

approach is thus able to relate  $L_\alpha$  membrane properties to continuous flow behaviour in a tubular geometry, relevant to most practical flow processing of such fluids, relating MLV formation to the effect of salt, and establishing 1.8% NaCl as an ‘optimal’ condition for this system.

## Chapter 5

# Effect of microfluidic flow on the lamellar-to-MLV phase transformation

Findings describe in this chapter are based on the work published in [188].

### 5.1 Introduction

Surfactants in solution can self-assemble into ordered mesophases, known as lyotropic liquid crystalline phases [2], which are generally responsive to flow, changing macro- and microscale properties upon application of shear. In the lamellar  $L_\alpha$  phase, surfactant molecules assemble to form a bilayer structure with a thickness  $\delta$  and interlayer distance  $d$  (Fig. 5.1a). Under shear flow, for instance in a Couette geometry, lamellar phases can be aligned along any of three principal directions termed neutral, velocity and velocity-gradient alignment [196]. Further,  $L_\alpha$  lamellae can also be transformed into multilamellar vesicles (MLVs), or “onions” [33], [37], [43] which is the focus of this work. Vesicles find numerous applications, ranging from drug molecule carriers [197], [198] and nano/microparticle encapsulants (“stuffed onions”) [199] to microreactors [200] and can

be formed by electrolyte addition [201], [202], via extrusion [203] under shear [33], [34], [43], or less commonly, spontaneously [32].

The formation of vesicles under shear is particularly appealing for its size control and spatial ordering [33], [34]. In the pioneering work of Roux and co-workers, over two decades ago, the formation of vesicles (“onion”) phase in di(2-ethylhexyl) sulfosuccinate (AOT)/brine was established by polarised optical microscopy and small angle light scattering (SALS) [30]. A critical shear rate required for MLV formation ( $\dot{\gamma}_c \sim 10 \text{ s}^{-1}$ ) was identified, and the resulting vesicle radii  $R$  was found to depend on the applied shear rate  $\dot{\gamma}$  as

$$R \propto \dot{\gamma}^{-\frac{1}{2}} \quad (5.1)$$

Subsequent studies with Sodium Dodecyl Sulphate (SDS)/pentanol/dodecane/water proposed a ‘flow phase map’ with three distinct regions comprising defective  $L_\alpha$ , packed MLVs and aligned  $L_\alpha$  phases as a function of shear rate, established with the aid 2D small angle neutron scattering (SANS)[34]. Further, the MLV radius was found to be proportional to the square-root of lamellar  $d$ -spacing and square of the lamellar membrane fraction  $\phi_v$ , following [34],

$$R \propto d^{-2} \propto \phi_v^2 \quad (5.2)$$

Once formed, MLVs can undergo a further ordering transition, identified by Sierro and Roux [33] using the SDS/octanol/brine (20 g  $L^{-1}$  of NaCl in  $H_2O$ )  $L_\alpha$  pseudoquaternary system. At higher shear rates ( $\dot{\gamma} \approx 80 \text{ s}^{-1}$ ) MLVs can form a hexagonally packed structure accompanied by jump in vesicle size (from  $\sim 1 \text{ }\mu\text{m}$  to  $\sim 10 \text{ }\mu\text{m}$ ). The (dis)continuous nature of the transition appears, in part, to be controlled by temperature, with higher temperatures favouring continuous transitions from MLVs into a packed structure [33].

Several mechanisms have been proposed to describe MLV formation under flow, generally in terms of a balance between the curvature energy and compression energy [15]. Zilman and Granek [79] considered that flow acts to reduce the membrane excess area via suppression

of thermal membrane undulations; in turn, this induces buckling of the lamellar sheets and, above certain critical pressure (or shear rate), MLVs form. Theoretical predictions deviate considerably from experiment, which was rationalised as due to defects in lamellar phase which cause the ‘local’ shear rate to be higher than the imposed shear rate. A different model suggests that the undulations are introduced via non-uniformities in the applied shear [37], [78]. Experimentally, the formation of MLVs has been described by the emergence of intermediate multilamellar cylinder (MLC) phase [41], [49], [54] in continuous shear flow or a direct emergence of MLVs with oscillatory flows [43].

Numerous experimental reports have considered the effect of shear field, stress and rate, on various model systems (non-ionic [43], [49], [58], [204], cationic [182], [183] and anionic [66], [184]), the effect of added co-surfactants [19], [181] and salt [76], [77], and the effect of oscillatory shear flows [3], [43], [46]. Predominant analytical techniques include rheology [48], [205], scattering [41], [48], [49], [206], optical microscopy [206], [207] and  $^2\text{H}$  NMR [43], [45], [50], [208], [209].

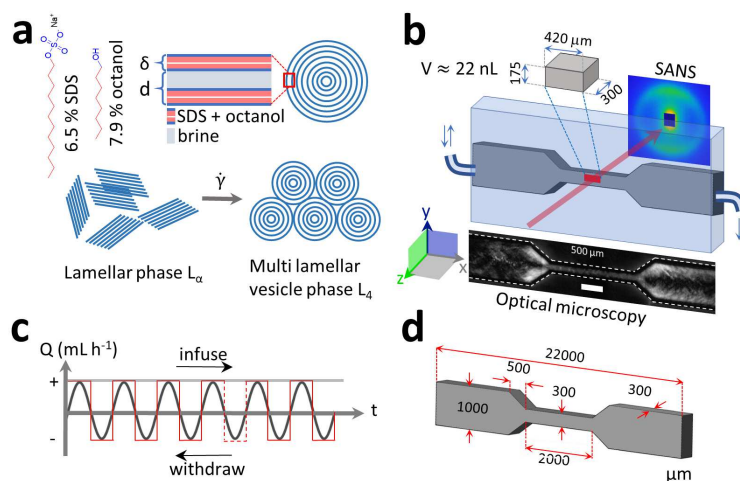


Figure 5.1: a) SDS/octanol/brine lamellar system and illustration of the shear-induced lamellar to MLV transformation; b) Schematic of the high-pressure contraction-expansion microfluidic device platform coupled to SANS and cross-polarised optical microscopy. A SANS beam footprint of  $175 \times 420 \mu\text{m}^2$  yields a scattering volume of 22 nL, and allows the mapping of the chip at different positions; c) Square-wave oscillatory shear profile imposed, shown by the red trace; d) Contraction-expansion microdevice dimensions.

This chapter looks at tubular flow, in continuous and oscillatory modes, and both wall

shear and extensional (*viz.* contraction-expansion) flows, motivated by their industrial relevance in complex fluid processing (e.g., through nozzles and continuous flow reactors) and academic importance. In order to precisely control flow type, magnitude and enable the spatiotemporal investigation of flow-induced transformations, bespoke microfluidic device coupled with SANS and polarised optical microscopy was employed (and ancillary characterisation approaches). Flow induced self-assembly in microfluidics has been employed to investigate, for example, the formation of wormlike micelles from micellar solutions under extensional flows [101], [104], [105] and the formation of non-spherical block copolymer nanostructure [210]; The coupling of microfluidics with a range of analytical techniques such as rheology [85], SANS/SAXS [88], [98], [192] and NMR [7] has enabled the precise, in situ characterisation of minute ( $< 0.1 \mu\text{L}$ ) samples in exceptionally well defined environments. While the effect of microflow on  $L_\alpha$  phases has been previously investigated by SANS/SAXS (and shown to undergo orientational flips upon exiting constrictions) [5], [6], [98], this work focused on the lamellar to MLV transformation in model microdevice geometries. Here the well-known SDS/octanol/brine system was selected, illustrated in Fig. 5.1 was subjected to continuous and oscillatory shear flows on a bespoke contraction-expansion microdevice, depicted in Fig. 5.1d, compatible with both crosspolarised optical microscopy and SANS (Fig 5.1b), as illustrated in Fig. 5.1c. This work demonstrated that a single contraction-expansion device can induce flow transformations on a short timescale, with lamellar phase reorientation orthogonal to the flow direction, and over longer time periods, achieve size control in an isotropic MLV phase.

## 5.2 Methods

### SDS/octanol/brine solution sample preparation

Fresh samples were prepared prior to each series of measurements, as follows: 6.50 g (22.5 mM) of Sodium Dodecyl Sulphate, SDS (Sigma-Aldrich BioXtra,  $\geq 99.0\%$ ) was dissolved in 85.6 g of brine solution made of 20 g/L NaCl (ACS Reagent,  $\geq 99.0\%$ ) in  $\text{D}_2\text{O}$

(Sigma-Aldrich, 99.9 atom % D). Dissolution was aided by heating to 30 °C until clear and allowed to cool to room temperature; then 7.90 g (60.7 mM) of 1-octanol (Sigma-Aldrich, anhydrous,  $\geq 99\%$ ) was added to the SDS/brine mixture and stirred for 2 min at 1000 rpm until fully incorporated. The solution was then left to equilibrate for 48 h to relax inadvertent shear effects induced during sample preparation.

### Sample characterisation in tubular geometry

Preliminary characterisation was carried out on samples loaded on 1 mL plastic syringe and sheared with a long (150 cm) capillary FEP tubing (inner diameter = 0.79 mm) assembly, subjected to oscillatory flow (1 mL sample volume displaced at a flow rate of 5 mL h<sup>-1</sup> with a Harvard 33 DDS pump in infuse/withdraw mode) for 5h. The sample was then placed between glass coverslips with a 120  $\mu$ m thick spacer and imaged by cross-polarised microscopy (Olympus BX41) with 50x/0.50 magnification MPlanFLN objective. Additionally, <sup>2</sup>H NMR spectra were acquired before and after shear with a Jeol 400 MHz NMR spectrometer.

### Microscopy-microfluidic set-up

A custom-designed, boron-free, crown glass contraction-expansion microfluidic device (fabricated by Dolomite Microfluidics) was fitted with 20 cm long inlet and outlet polytetrafluoroethylene (PTFE) tubing (inner diameter = 0.79 mm) and mounted on Linkam THMS600 temperature control stage set at 24.3 °C. The sample was slowly loaded on 20 mL plastic syringe, mounted on a LabVIEW-controlled Harvard PHD ULTRA 4400 pump, and connected to the device; the outlet was connected to a glass vessel containing an unsheared sample. The sample was first infused at 0.5 mL h<sup>-1</sup> and allowed to stabilise for 10 min. Continuous and oscillatory shear experiments were then recorded with an Olympus BX41 reflection microscope equipped with a Basler acA2000-165um camera controlled with PylonViewer using 5x/0.10 MPlan, 10x/0.25 Ach and 50x/0.50 MPlanFLN Olympus objectives with cross-polarised filters (U-AN-2 analyser and U-PO3 polariser),

and data were analysed with ImageJ. Volumetric velocities used in microscopy experiments ranged from 0.5 to 100 mL h<sup>-1</sup> corresponding to linear velocities between 0.5 to 90 mm s<sup>-1</sup> assuming plug flow and wall shear rates between 8.5 to 1700 s<sup>-1</sup> in the expansion and between 35 to 7000 s<sup>-1</sup> in the constriction. Wall shear rates estimated based on Son's[136] approach  $\dot{\gamma} = (6Q/WH^2)(1 + H/W)f * (H/W)$ , where  $Q$  is volumetric flow rate and  $f * H/W$  is a geometric function calculated based on aspect ratio between  $H$  (height) and  $W$  (width). In this instance the  $f * H/W$  for expansion is 0.7297 and for the constriction 0.5928 for shear rate as a function of flow rate linear plots). The extension rate along the channel centreline was approximately between 2 to 430 s<sup>-1</sup> at the flow rates stated above.

### Velocity flow profile

The flow velocity profile in the microchannel was measured by cross-polarised microscopy with a 10x objective and 10 ms frame rate with 2000  $\mu$ s exposure time. Matlab based PIVLab software employed 20 consecutive images and ensemble correlation with 2 passes with 64x64 and 32x32 pixel by pixel interrogation window sizes (1 pixel = 1.54  $\mu$ m), and selecting a Gauss 2x3-point sub-pixel estimator and 'standard' correlation quality. The velocity profiles largely followed plug flow, and thus the flow velocity in the wide and narrow sections of the channel could be approximated by 0.46, 4.55, 45.5 mm s<sup>-1</sup> and 1.49, 14.9, 149 mm s<sup>-1</sup> corresponding to the (representative) 0.5, 5, 50 mL h<sup>-1</sup> volumetric flow rates.

### SANS-microfluidic set-up

SANS experiments were performed on the D22 spectrometer at the *Institut Laue Langevin*, Grenoble. For reference, static sample measurements were collected using 'banjo' Hellma cells (1 mm path length) with collimator distance of 8 m, sample to detector distances of 2, 8 and 17.6 m and neutron wavelength of 6 Å. Microfluidic experiments were acquired at the mid- $q$  (8 m) configuration. The microfluidic chip was mounted on a 3D printed frame (Fig. 5.2) and the temperature was set to 24.3 °C. A neutron beam mask (or

diaphragm) with dimensions of  $420\ \mu\text{m}$  by  $175\ \mu\text{m}$  was used to define the beam footprint, commensurate with microdevice dimensions, resulting in an scattering volume of only 22 nL (given the  $300\ \mu\text{m}$  sample pathlength, i.e. channel depth).

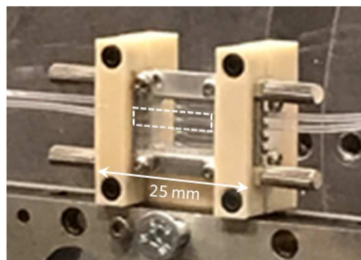


Figure 5.2: A custom 3D printed holder was fabricated to firmly mount the chip to ensure position stability and repeatability during xy scans. The location of the microchannel is highlighted by the dashed rectangle.

The device was illuminated in the neutral flow direction ( $z$  in Fig. 5.1b), probing the  $xy$  plane. The channel was aligned with the neutron beam by iteratively scanning the empty chip and tracking the scattering and transmission signals along  $x$  and  $y$  directions until a microchannel map is resolved (this ‘battleship’ exercise requires spatial precision, and the microdevice assembly must be stable and drift-free, to ensure repeatability of the data over time). Continuous microfluidic flow spectra were collected for flow rates  $0.5$  and  $5\ \text{mL h}^{-1}$  at the inlet, contraction and exit of the chip with acquisition time of 10 min. Oscillatory shear flow experiments were performed after at  $0.5$ - $50\ \text{mL h}^{-1}$  flow rates, and data acquired after cycles 1, 2, 3, 4, 10 and 30, for 10 min, at the outlet position, under stopped flow conditions (needed as the acquisition time exceeded the flow oscillation frequency). Microstructural stability was monitored by acquiring spectra for 10 min after complete cessation of shear at 0, 4 and 20 h. The data were reduced with GRASP software by subtracting the empty beam, sample transmission and blocked beam and calibrated with direct beam. Data fitting of the radially and sector-averaged spectra was performed with SasView 5.0.2, employing the random head-tail sheet with Caillé structure factor model [122].

## 5.3 Results

### 5.3.1 Fluid structure before and after shear in a tubular geometry

The system was first characterised by  $^2\text{H}$  NMR, optical microscopy and SANS, prior and following the application of shear in a long capillary to emulate the conditions of a microdevice, as shown in Fig. 5.3. The ‘quiescent’ sample was allowed to equilibrate for 48 h prior to measurement, to minimise effects of sample preparation. Upon application of shear lamellar sheets aligned with the flow based on crosspolarised optical microscopy (Fig. 5.3).

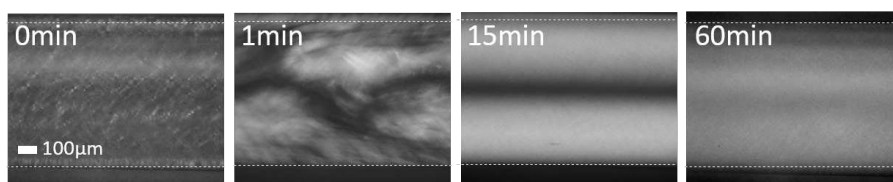


Figure 5.3: Optical texture evolution observed in a tubular geometry (FEP tubing, diameter  $d = 0.79$  mm, length  $l = 1.5$  m) at  $5 \text{ mL h}^{-1}$ .

An average flow velocity of  $4.55 \text{ mm s}^{-1}$  (estimated from the volumetric flow rate  $5 \text{ mL h}^{-1}$  and cross-sectional area  $0.495 \text{ mm}^2$ ) and shear rate of  $58.5 \text{ s}^{-1}$  is expected to be well above the critical shear rate for MLV formation [33]. The  $^2\text{H}$  NMR (Fig. 5.4a) and cross-polarised microscopy data (Fig. 5.4b) shows characteristic features of anisotropic (prior to shearing) and isotropic (after shearing for 5 h) lamellar structure.  $^2\text{H}$  NMR indicates a doublet indicative of an anisotropic lamellar phase and a broad singlet peak after shearing, expected for the isotropic phase with either non uniform distribution of MLVs or coexistence between lamellar sheets and MLV phase [208], [209], [211]. The transformation of doublet peak into singlet peak in  $^2\text{H}$  NMR indicates that the transformation is continuous rather than discontinuous [45] under these experimental conditions.

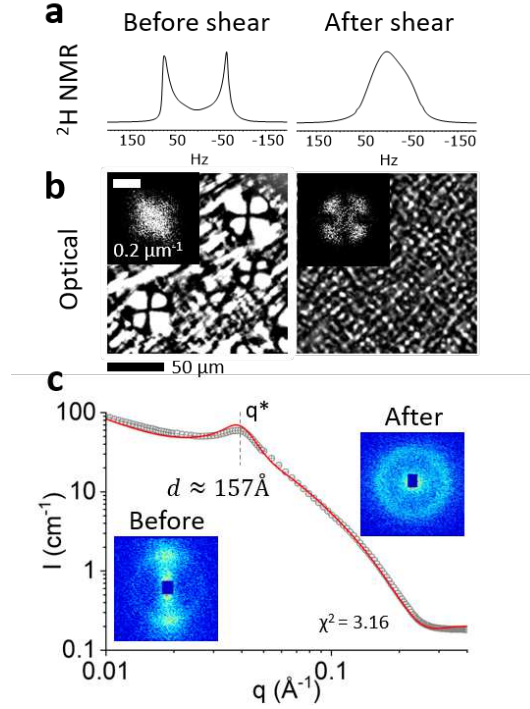


Figure 5.4: SDS/octanol/brine sample characteristics measured by a)  $^2\text{H}$  NMR of sample in bulk before and after shear (in a 3 m long, 1/32" diameter capillary, for 5 h and flow rate of  $5 \text{ mL h}^{-1}$ ); b) corresponding cross-polarised optical microscopy images and FFT inset; c) 2D SANS scattering images and radially-averaged scattering profile (before shear) measured at detector distances 17.6, 8 and 2 m, and  $\lambda = 6 \text{ \AA}$  neutron wavelength with fitted with random head-tail sheet with Caillé structure factor model.

Similarly, cross-polarised optical microscopy indicates the presence of disordered lamellar sheets before shear and an ordered isotropic phase indicated by the change in optical texture [206], [207]. This was corroborated by fast Fourier transform (FFT) analysis after shearing, displaying the characteristic cloverleaf pattern indicative of formation of spherical objects [43], [48], [206], [207]. The size of the vesicles was estimated to be  $3 \mu\text{m}$ . Microscopy images recorded over the duration of the experiment indicated that the onset of cloverleaf pattern development was around 20 min into the experiment (Fig. 5.4). The birefringence intensity along the channel cross-section dropped in the middle of the channel likely due to shear being close to 0 and lamellar sheet alignment on both sides of the tubing being orthogonal to each other. The  $L_\alpha$  d-spacing was measured to be 15.7 nm, in agreement with the previous literature for this sample composition [63] and with the octanol to SDS molar fraction ratio  $\sim 2.7$  and the membrane volume fraction  $\phi_v$  around 0.15 this value close to pure SDS/octanol/water d-spacing value 15 nm [176].

Generally, the addition of long chain alcohol will aid the swelling of  $L_\alpha$  since the phase boundary for  $L_\alpha$  formation is lowered. Typical values for such systems are between 4 to 40 nm [18], [67]. The SANS scattering profile was unchanged by flow, with  $d$  spacing remaining at  $\simeq 15.7$  nm. 2D scattering orientational change reflects the expected lamellar (anisotropic) to MLV (isotropic) transformation, as shown in Fig. 5.4c. The scattering data could be well described by a random head-tail sheet with Caillé structure factor model (*lamellar\_hg\_stack* in SASView [122], as detailed in Section 2.3.3. In general, the shear threshold and transformation timescales are expected to vary with the composition of the lamellar phase, and depend on the bending rigidity  $\kappa$  of the membrane. The latter can be modulated by addition of dopants, such as polymers [181], co-surfactants [77] or electrolytes [76], [77], as described in Chapter 4.

### 5.3.2 Continuous microfluidic flow

Since one of the most effective ways to form MLVs is via extrusion [203], the fluid structure at the nano and mesoscale was studied in continuous flow over a short timescale ( $<72$  s through a *single* constriction).

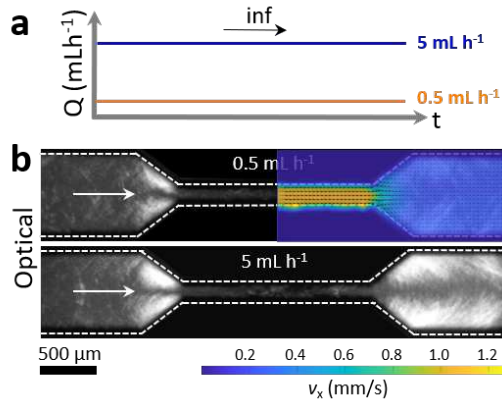


Figure 5.5: Continuous flow. a) Constant volumetric flow rate over time, illustrated here for  $0.5$  and  $5 \text{ mL h}^{-1}$ , corresponding to an average velocity within the constriction of  $\simeq 1.49$  and  $14.9 \text{ mm s}^{-1}$ , respectively; b) Cross-polarised microscopy images of the fluid flow at the two flow rates with PIV for  $0.5 \text{ mL h}^{-1}$  indicating plug-like flow.

Figure 5.5 shows cross-polarised microscopy data for two representative flow rates ( $0.5$  and  $5 \text{ mL h}^{-1}$ , Fig. 5.4a), with accompanying PIV map.

The residence time of the fluid within the chip was 72 and 7.2 s for 0.5 and 5 mL h<sup>-1</sup> respectively. The linear flow rates in the expansion were 0.455 mm s<sup>-1</sup> and 4.55 mm s<sup>-1</sup> and 1.49 mm s<sup>-1</sup> and 14.9 mm s<sup>-1</sup> in the constriction for 0.5 and 5 mL h<sup>-1</sup> respectively with corresponding wall shear rate values roughly representative of shear rates below and above the MLV transformation region [33]. Cross-polarised optical microscopy revealed a large scale orientation and qualitatively showing alignment along the flow before and upon entering the constriction, and normal to the flow upon exiting. The birefringence intensity and the relative alignment with the flow is greater for 5 mL h<sup>-1</sup> (bottom image Fig. 5.4b) than for 0.5 mL h<sup>-1</sup> (top image Fig. 5.5b). PIV of fluid at 0.5 mL h<sup>-1</sup> volumetric flow rate shows plug-like flow for which the linear velocity component roughly corresponds to the estimated velocity obtained dividing volumetric flow rate by crosssectional area, namely 0.43 mm s<sup>-1</sup> and 1.46 mm s<sup>-1</sup>.

SANS confirmed that the lamellar sheets undergo an orientational 90° flip upon exiting the constriction, as shown in Fig. 5.6a. Quantitative population analysis from the scattering intensity of the lamellar sheet orientation shown by the colours (blue, grey, orange) can be obtained from data fitting and azimuthal intensity  $I(q)$  analysis. Orientational lamellar phase realignments are well documented in the literature for microfluidic constriction-expansion devices alongside with the decrease in the scattering intensity [5], [6], [98], [106].

Further analysis of the continuous flow SANS images showed that the radially averaged structure factor profile does not change with the flow and the position along the channel, Fig. 5.6b and more detail in Fig. 5.15a,b and Fig. 5.16a,b. However, the scattering intensity and orientation of the pattern did change, Fig. 5.6c with more detail in Fig 5.15d,e and Fig. 5.16d,e, reflecting the number density of lamellar sheets contributing to the scattering orientation probed and the ratio of lamellar sheets as a function of direction subjected to the contraction-expansion flow. A drop in intensity could be caused by the sheets changing plane (aligning in the grey plane indicated in Fig. 5.6a) or by changing phase (e.g. entering a micellar phase). The latter is ruled out by the fact that  $S(q)$  does not show the characteristic micellar profile at low  $q$ , and thus the drop in intensity is

ascribed to a change in orientation of polycrystalline grains of lamellar sheets or the formation of regular MLVs.

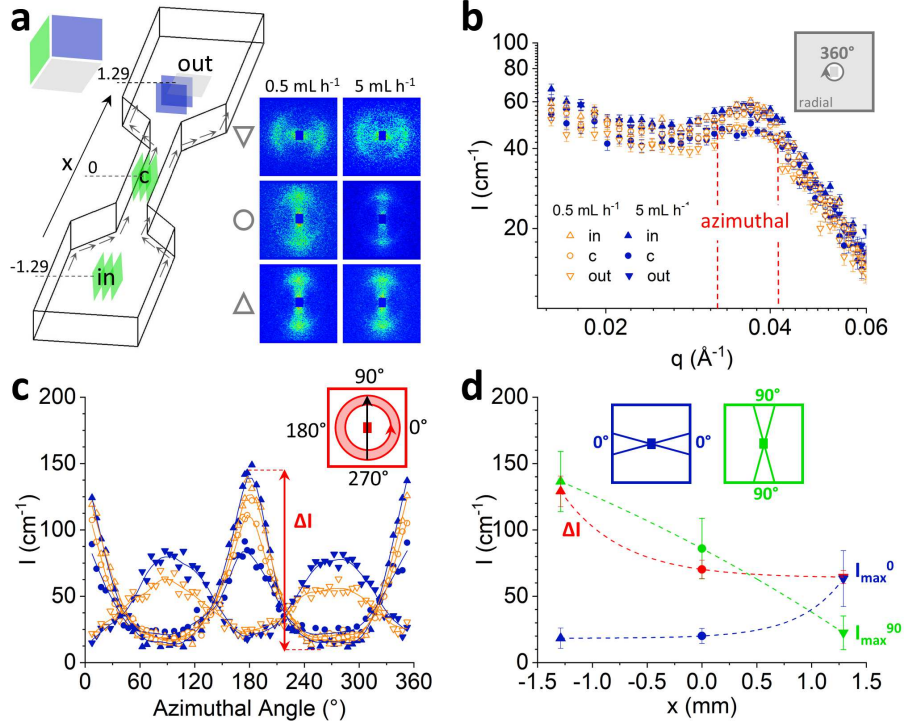


Figure 5.6: Continuous flow SANS analysis. a) Microfluidic SANS 2D scattering images of oscillatory shear cycles (measured at 8 m and  $\lambda = 6 \text{ \AA}$ ); b) Radially-averaged 2D SANS intensity acquired at the entrance (*in*), constriction (*c*), and exit (*out*) of the contraction-expansion geometry, at flow rates of 0.5 and 5  $\text{mL h}^{-1}$ ; the dashed lines around the lamellar peak indicate the integration limit selected for the azimuthal average; c) Azimuthal average within  $0.035 \leq q \leq 0.045 \text{ \AA}^{-1}$  computed from the 2D data shown in panel a), from where an orientation parameter  $\Delta I$  is estimated from the difference between the maximum and minimum intensities as a function of azimuthal angle; d) Summary of the parameters extracted,  $\Delta I$  (red), and  $I_{\max}$  at  $0^\circ$  (blue) and  $90^\circ$  (green), at the the constriction entrance (*in*), centre (*c*) and exit (*out*), measured at 0.5  $\text{mL h}^{-1}$ . The x axis coordinate refers to the distance from the center of the channel.

From the azimuthal average of the SANS 2D spectra (within  $0.035 \leq q \leq 0.045 \text{ \AA}^{-1}$ ), the orientational parameter defined as  $\Delta I$  (from the difference between the maximum and minimum intensity) is plotted as a function of azimuthal angle. In addition, the maximum intensities at  $0^\circ$ , along the flow direction, and  $90^\circ$ , perpendicular to the flow direction are shown in blue and green traces in Fig. 5.6. These were computed at three representative channel locations, namely at the the constriction entrance (*in*), centre (*c*) and exit (*out*). The overall anisotropy was found to decrease as shown by  $\Delta I$  (Fig. 5.6d) and the fact

that  $I_{max_0}$  and  $I_{max_{90}}$  profiles are not mirrored upon the orientational flip (Fig. 5.6c, d) caused by the contraction-expansion. While a scaling relation might be expected between orientation parameters (e.g.,  $\Delta I$ ) and flow descriptors (e.g., extension gradient or a particular derivative of the shear field, sampled over the illuminated scattering volume), the two flow rates and single contraction-expansion ratio investigated did not enable a sufficiently precise quantification. Nonetheless, given the reduction in anisotropy with one-pass constriction, I hypothesise that oscillatory microfluidic flow can be effective at inducing a lamellar-to-MLV transformation and seek to quantify its requirements.

### 5.3.3 Oscillatory flow: effects of flow rate, volume and time of oscillation

Oscillatory flows have been previously shown to be a successful approach to study and quantify lamellar-MLV phase transformations [43], [66], [212]. Oscillatory shear rheology is a dynamic approach that allows to characterise non-linear properties of the material and relies on selecting two variables oscillatory shear amplitude  $\gamma_0 \ll 1$  and frequency  $\omega$  [213]. Depending on the value  $\gamma_0$  the viscoelastic response of the material will either be linear or non-linear. In the case of  $\gamma_0 \ll 1$  the shear stress response will have a linear relationship to shear amplitude  $\gamma_0 \ll 1$  while with increasing  $\gamma_0$  values above a certain point the material will respond non-linearly with respect to  $\gamma_0$ . These experiments are classed as small or large amplitude oscillatory shear (SAOS or LAOS) respectively [213]. The non-linear viscoelastic response induced by LAOS allows to control the formation kinetics of MLVs with increase in  $\gamma_0$  and/or decrease in  $\omega$  accelerating the formation [43], [212]. Inspired by this, LAOS-on-a-chip type experiment was emulated with oscillatory microfluidic flows where  $\gamma_0$  is controlled by the flow rate ( $Q$ ) and  $\omega$  is determined by volume oscillated ( $V$ ).

Thus the effect of flow cycling was investigated to quantify the cumulative effect of sequential contraction expansion flows (Fig. 5.7).

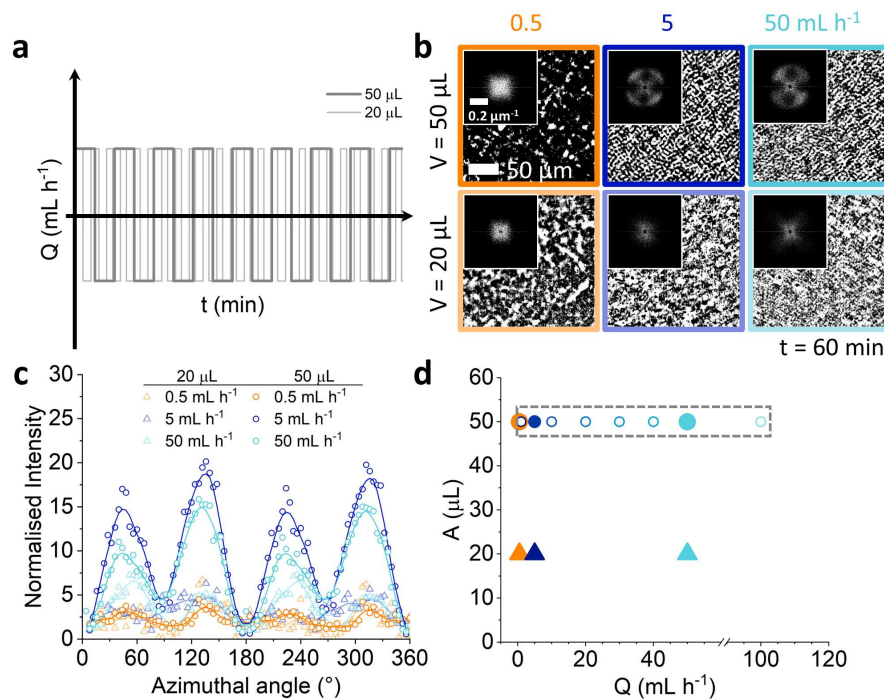


Figure 5.7: Oscillatory shear amplitude volume ( $V$ ) and volumetric flow rate ( $Q$ ) effect on flow induced structure formation. a) Schematic of square-wave applied oscillatory flow profiles for 0.5, 5 and 50  $\text{mL h}^{-1}$ , for  $V = 20 \mu\text{L}$  (dashed) and  $V = 50 \mu\text{L}$  (solid); b) Cross-polarised optical microscopy images with corresponding FFT images for samples sheared at 0.5, 5 and 50  $\text{mL h}^{-1}$  and displaced volume  $V = 50$  and  $20 \mu\text{L}$ , sheared for 3600 s; c) Azimuthal average of FFT computed around the intensity maximum ( $0.12\text{--}0.18 \mu\text{m}^{-1}$  for 5  $\text{mL h}^{-1}$  and  $0.18\text{--}0.23 \mu\text{m}^{-1}$  for 50  $\text{mL h}^{-1}$ ) normalised by dividing each curve by its minimum value; d) Morphology map indicating the sheared volume and flow rate conditions investigated; after 3600 s (1 h) the conditions marked with the box resulted in a regular MLV arrangement.

Here three different flow rates were selected of 0.5, 5 and 50  $\text{mL h}^{-1}$  (Fig. 5.7a) with wall shear rates in the expansion ranging from 8.5 to 850  $\text{s}^{-1}$  [136]. The shear rates correspond to the literature values for the shear diagram regions of no MLV, disordered MLVs and hexagonally packed MLVs [33]. Volumes of 20 and 50  $\mu\text{L}$  were selected based on an iterative approach to ensure the reliability of the displaced volume by the syringe pump, given the compressibility and capacitance of the flow system [214]. The overall time of oscillation was kept constant (1 h). Crosspolarised optical microscopy images (Fig. 5.7b) taken after the constriction across the middle of the channel show increased long range ordering with increasing flow rates and oscillatory volumes with the emergence of cloverleaf pattern indicative of spherical objects [43], [48], [206], [207]. This is further quantified by normalised intensity analysis (obtained by dividing each curve by its baseline

intensity value) of FFTs as a function of azimuthal angle (Fig. 5.7d), which shows an increase in anisotropy over repeat oscillatory shear cycles. The FFTs indicated spherical object size of  $2\ \mu\text{m}$  for  $5\ \text{mL h}^{-1}$  flow rate and  $1.5\ \mu\text{m}$  for  $50\ \text{mL h}^{-1}$  ( $50\ \mu\text{L}$  volume amplitude). The values were calculated by measuring the intensity profile across the microfluidic channel and further verified by measuring repeat distance from the center to one of the lobes of the cloverleaf in FFT. Empirically, the relationship between the shear rate and radius corresponds roughly to scaling law of  $-1/4$ . This follows the general trend of radius of MLVs decreasing with increase of  $\dot{\gamma}$ . However, it deviates from the value of  $-1/2$  reported by and Roux [33]. An explanation for the difference could be down to applied shear rate deviating from the effective shear rate due to wall slip [64].

From this sparse flow phase map, sufficient conditions for the formation of ordered structures from  $L_\alpha$  phase were established as  $50\ \mu\text{L}$  amplitude and  $5$  and  $50\ \text{mL h}^{-1}$  flow rate. These are within the wall shear rate range previously reported for the formation of MLVs in SDS/octanol/brine system [33]. I next investigate the development of the ordered structures under oscillatory shear with flow rates between  $1$  to  $100\ \text{mL h}^{-1}$ , corresponding to wall shear rate between  $20$  to  $1700\ \text{s}^{-1}$ .

To examine MLV formation, the polarised light intensity was monitored (integrated over the image size) as a function of oscillatory shear cycle and time. MLV dimensions were estimated from FFT of optical birefringence data, from the outer  $q$  value of the clover-leaf patterns, and validated using the intensity profile across several MLVs on the real-space optical images. Further, since the intensity is related to particle size, intensity plateau is associated with completion on the transition. Therefore, the formation of the vesicles is time-dependent rather than oscillatory shear cycle dependent (Fig. 5.8a).

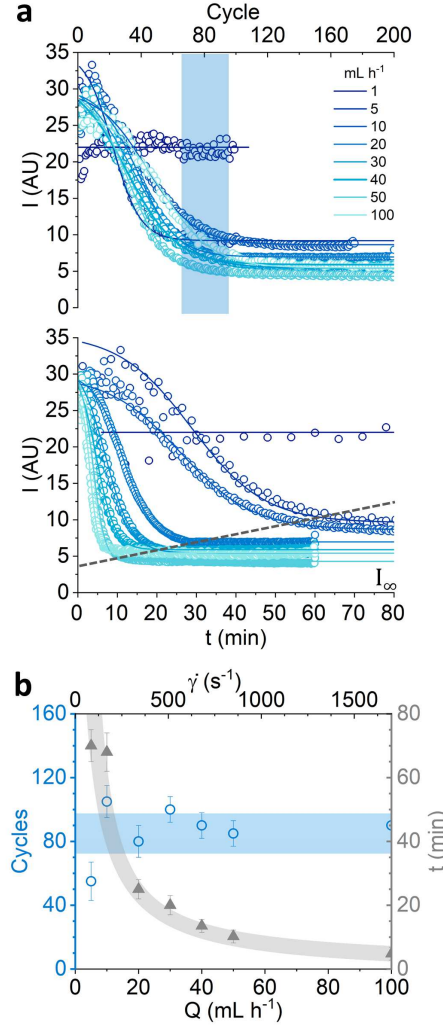


Figure 5.8: Effect of flow rate on MLV formation. a) Average light intensity of cross-polarised optical images as a function of oscillatory shear cycle (top) and time (bottom), at flow rates 1-100 mL h<sup>-1</sup> and  $V = 50 \mu\text{L}$ . The blue area (top) indicates the oscillatory shear cycle range at which the data reach a plateau, while the grey dotted line (bottom) indicates the completion time for MLV formation. Lines are fits to a logistic function; b) Cycle number and associated time for MLV formation as a function of flow rate, obtained from a). Generally, MLVs form after the same approximate number of cycles, and thus the associated time decreases with increasing flow rate.

Except for lowest flow rate of 1 mL h<sup>-1</sup>, possibly affected by finite compressibility and flow non-linearity, the light intensity starts leveling off after cycle 80. Evidently, different flow rates will reach cycle 80 at different time, and thus the corresponding time dependence for vesicle formation are extracted. This can be rationalised in terms of a total shear  $\gamma$  required for the sample to undergo the transformation, computed from  $t \times \dot{\gamma}$ , where the associated time is shown in Fig. 5.8b.

Next, I investigate the effect of shear rate on vesicle size scanning from 1 to 100  $\text{mL h}^{-1}$  after fluid had been subjected to 80 cycles of shearing, as illustrated by the microscopy images and FFTs in Fig. 5.9. The vesicle size estimated by the light intensity profile variation (Fig. 5.9b shaded circles) and verified by the  $I_\infty$  intensity plateau (Fig. 5.9b hollow triangles) value. The optical textures and accompanying FFTs display a decrease in vesicle size with increasing shear rate (Fig. 5.9a). The increase in size above 200  $\text{s}^{-1}$  (corresponding to 20  $\text{mL h}^{-1}$  flow rate) did not show a size jump as observed by Roux [33]. The size dependence of vesicles on shear rate followed a more gradual trend with the power law of  $1/4$  rather than  $1/2$  as previously reported [33] until the wall shear rate reaches 200  $\text{s}^{-1}$  (20  $\text{mL h}^{-1}$ ) This could be due to overestimation of the actual shear rate experienced by the bulk fluid since as it is the maximum shear rate experienced.

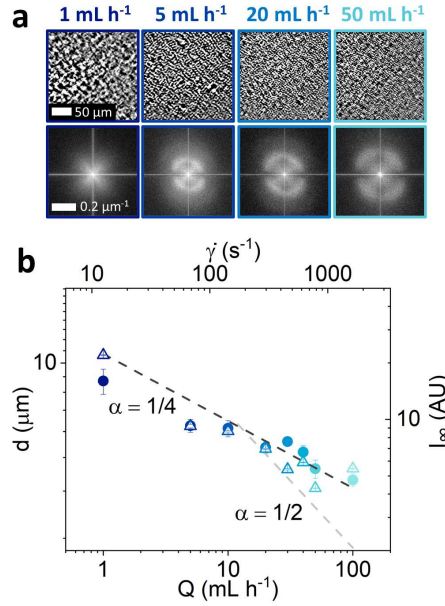


Figure 5.9: MLV size dependence on flow rate. a) Cross-polarised optical images and their corresponding FFTs at selected flow rates 1-50  $\text{mL h}^{-1}$ . b) Vesicle size ( $\circ$ ) and the asymptotic average optical image intensity ( $\triangle$ ) dependence on flow rate. Data are generally described by a  $1/4$  power with wall shear rate; given the data scatter, the  $1/2$  power (observed by Roux [33]) can not be ruled out above 20  $\text{s}^{-1}$  shear rate.

The emergence of the isotropic phase upon oscillatory shear cycles was examined at 5  $\text{h}^{-1}$  50  $\mu\text{L}$  amplitude condition. Shear-induced effects on the optical texture at the wall and centre of the channel were indiscernible for flow rate 5  $\text{mL h}^{-1}$ , hence measurements only

at the centre of the channel were collected (Fig. 5.10).

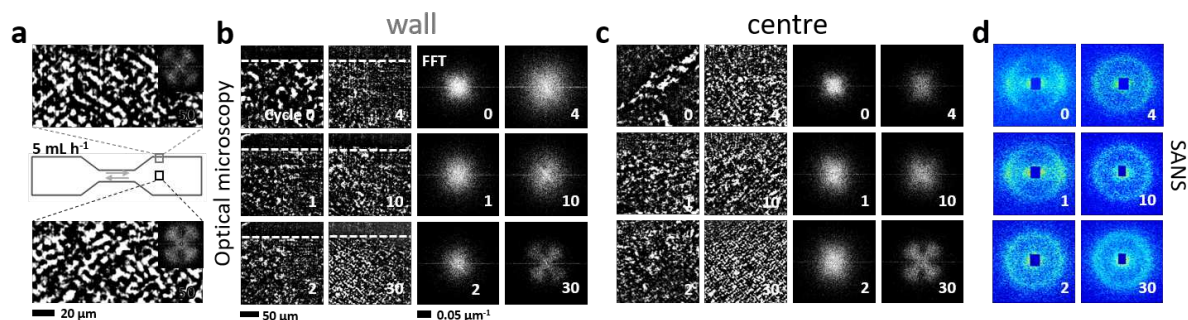


Figure 5.10: Optical texture changes near the wall and in the middle of the channel for an oscillatory shear experiment performed at  $5 \text{ mL h}^{-1}$ ; a) Sheared sample after 1 h of shearing at the wall vs. centre. The size of the squares is to the scale of image analysed; b) Evolution of the optical pattern and the corresponding FFTs measured near the wall; c) Evolution of the optical pattern and the corresponding FFTs in the middle of the channel; d) Corresponding 2D SANS patterns.

This was further elucidated by the corresponding FFTs with the emergence of the characteristic cloverleaf pattern (Fig. 5.11a). The gradual evolution of peaks indicates that the transformation from lamellar to MLV phase is continuous under these experimental conditions. Further azimuthal analysis showed emergence of four peaks (Fig. 5.11b) whose intensity evolution was fitted to an exponential and leveled out around cycle 30 (Fig. 5.11c), earlier than the overall intensity drop had taken place (cycle 80).

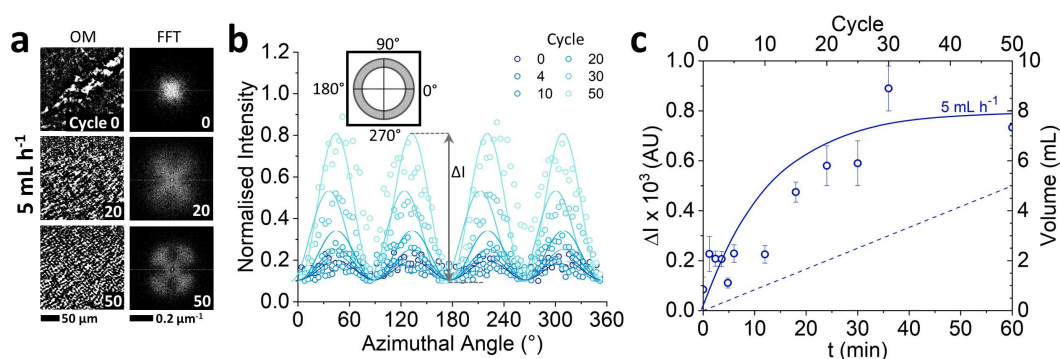


Figure 5.11: Effect of oscillatory flow at  $5 \text{ mL h}^{-1}$  on  $L_\alpha$  phase over multiples cycles from 0-50. a) Morphology evolution observed by cross-polarised optical microscopy at the channel wall and corresponding FFTs, associated with MLV formation; b) Oscillatory shear cycle azimuthal average of FFTs (computed within  $0.12-0.18 \mu\text{m}^{-1}$ ); c) FFT  $\Delta I_{az}$  for oscillatory shear cycles at  $5 \text{ mL h}^{-1}$  on  $L_\alpha$  phase over multiples cycles from 0-30.

This is likely due to the initial formation of vesicles and subsequent reduction in size since

the FFT analysis is expected to capture the emergence of ordered structures, while overall light intensity correlates favourably with the size of the scattering objects. No further long range ordering as reported by Sierro and Roux [33] was observed.

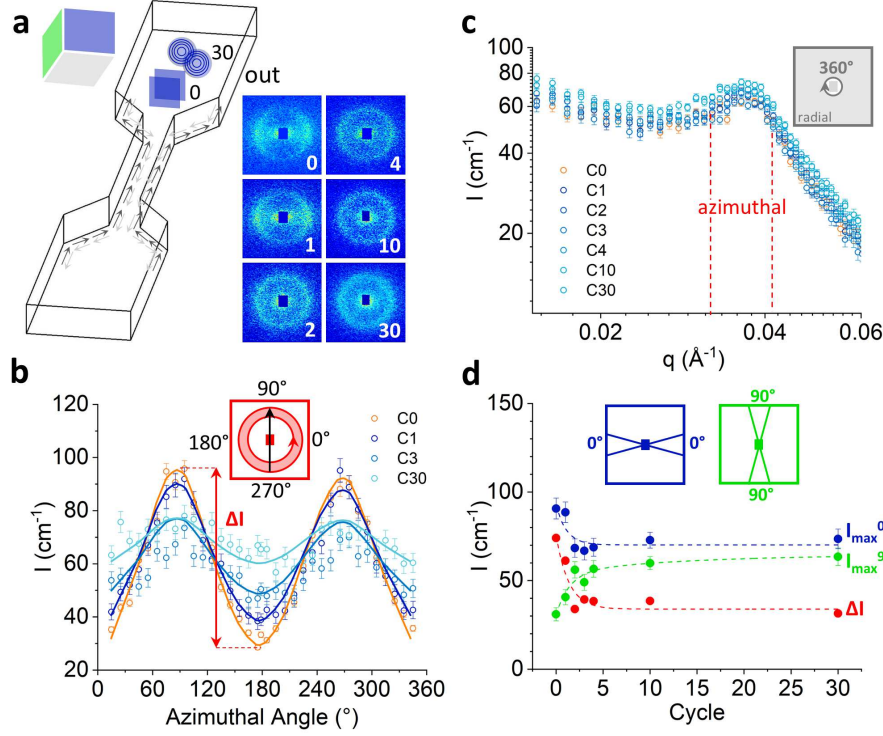


Figure 5.12: Oscillatory flow SANS analysis. a) Microfluidic SANS 2D scattering images of oscillatory shear cycles (measured at 8 m and  $\lambda = 6 \text{ \AA}$ ); b) Azimuthal average for selected cycles 0, 1, 3 and 30 within  $0.035 \leq q \leq 0.045 \text{ \AA}^{-1}$  computed from the 2D data shown in panel (a), from where an orientation parameter  $\Delta I$  is estimated from the difference between the maximum and minimum intensities as a function of azimuthal angle.

Since the formation of the isotropic phase appeared to be uniform across the channel (Fig. 5.10, SANS data were acquired only at the centre of the channel after the constriction. 2D SANS indicated a formation of isotropic phase already after the second oscillatory cycle (Fig. 5.12a) in contrast to the formation of ordered phase observed by optical microscopy appeared to form around cycle 30. This is somewhat expected given the smaller lengthscales probed by SANS, compared to those of optical microscopy. Employing SANS, I probe the evolution of nanoscale orientation of the system (measured at the exit) subjected to  $5 \text{ mL h}^{-1}$  flow rate and  $50 \text{ \mu L}$  amplitude. Upon a few cycles ( $\sim 5$ ), the anisotropy decreases significantly shown by azimuthal intensity  $\Delta I$  value decreasing

(Fig. 5.12b), while the overall  $I(q)$  profile remains unchanged (Fig. 5.12c). Simultaneously,  $0^\circ$  intensity drops and  $90^\circ$  increases until the pattern is (nearly) centrosymmetric (Fig. 5.12b). Finally,  $\Delta I$ ,  $I_{max}^{90^\circ}$ ,  $I_{max}^{0^\circ}$  and  $I_{max}^{360^\circ}$  all plateau around  $5^{th}$  cycle suggesting that the formation of an isotropic MLV phase takes place early on (Fig. 5.12d). The timescales for MLV formations observed with microscopy were approximately the same as timescales observed by rheo-SALS in literature [206].

### 5.3.4 Stability of MLVs after the cessation of shear

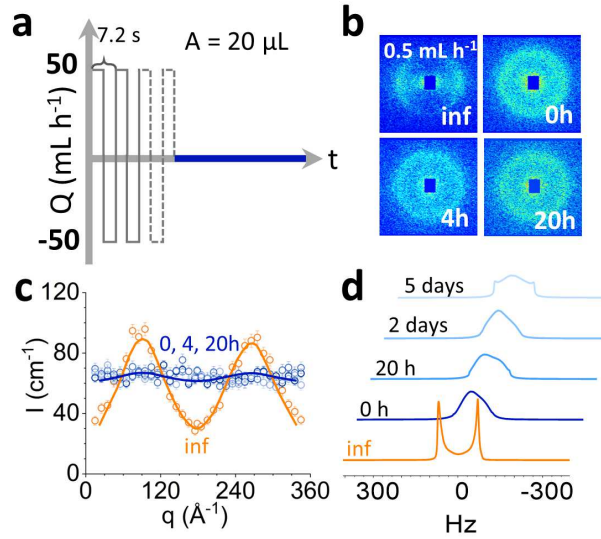


Figure 5.13: MLV stability after shearing. a) Oscillatory shear profile with flow rate of  $50 \text{ mL h}^{-1}$  and  $50 \mu\text{L}$  volume amplitude applied for 500 cycles; b) 2D SANS scattering images collected before and 0, 4 and 20 h after cessation of shear; c) Azimuthal average within  $0.035 \leq q \leq 0.045 \text{ \AA}^{-1}$  computed from the 2D data shown in panel b). d)  $^2\text{H}$  NMR relaxation over several days. Vesicles remain stable for up to 2 days.

Once MLVs have been formed they remain stable after cessation of shear (Fig. 5.13). In this experiment, the samples were sheared for consecutive 500 cycles with flow rate of  $50 \text{ mL h}^{-1}$  and amplitude of  $50 \mu\text{L}$  which corresponded to the plateau region where MLVs have been already formed. The resulting 2D SANS images showed emergence of isotropic phase that remained virtually unchanged for 20h (Fig. 5.13b,c). This was further corroborated by  $^2\text{H}$  NMR showing the stability of isotropic MLV phase to extend over a period of few (2 days). After 5 days, the appearance of two shoulder peaks at the position

and distance (150 Hz) can be observed pointing to re-emergence of lamellar phase. These stability timescales correspond to the values often reported in literature, where MLVs would stay stable over period of several days [33].

## 5.4 Summary

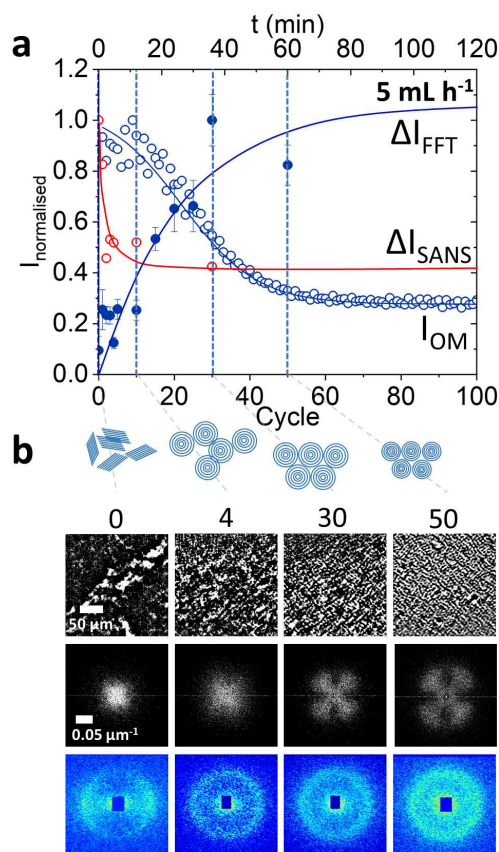


Figure 5.14: Overview of MLV formation under oscillatory shear flow. a) Normalised azimuthal intensities of cross-polarised microscopy images and SANS for flow rate of  $5 \text{ mL h}^{-1}$ . A drop in SANS intensity  $\Delta I_{SANS}$  around cycle 4 indicates MLV formation (isotropic) while the drop in optical intensity  $I_{OM}$  and increase in azimuthal optical parameter  $\Delta I_{FFT}$ , plateau at cycle  $\sim 60$ , indicates the progressive ordering of packed vesicles. b) corresponding SANS and microscopy images.

This chapter investigated a flow-responsive surfactant model system, namely SDS/octanol/brine in the lamellar  $L_\alpha$  phase, subjected to microfluidic contraction-expansion flows by a combination of SANS, optical and NMR experiments. While the shear induced  $L_\alpha$  to MLV transformation of SDS/octanol/brine has been previously documented [33],

[37], herewith the focus was on tubular microflow, the role of frequency and amplitude of oscillation (analogous to LAOS), and both wall shear and extensional flow. This system exhibits low membrane bending rigidity (near 1, based on the Caillé model fit) and is thus prone to forming vesicles. Owing to its highly scattering nature and large SANS beam flux, sample volumes down to  $\sim$ nL could be interrogated (with  $\sim$ min acquisition times) enabling the spatiotemporal mapping by SANS, employing a custom designed, high-transmission microdevice capable of withstanding considerable pressures ( $\sim$ 100 mbar), and demonstrated here with fluid velocities up to  $\sim$ 0.3 m s<sup>-1</sup>.

Under continuous flow, lamellae aligned along the flow direction upon entering a constriction, and in the normal orientation upon exiting, although the short residence time of the fluid within the microchip (typically, a few to tens of seconds) was not found to induce MLV formation. However, a reduction in anisotropy and overall scattering intensity is observed following one single constriction pass, leading us to examine their cumulative effect in oscillatory flow, thus extending the fluid residence time up to multiple hours.

Under oscillatory flow, the lamellar  $L_\alpha$  to MLV transformation is readily observed, and Fig. 5.14 illustrates our findings for a specific flow condition (5 mL h<sup>-1</sup> volumetric flow rate with 50  $\mu$ L displaced volume, or ‘amplitude’). Optical microscopy shows progressively finer textures and an oriented morphology upon cycling, corroborated by the FFT; this contrasts with the *decrease* in orientation observed by SANS. Within a few cycles ( $\sim$ 5 in this case) MLVs form, as shown by SANS, and upon further cycling, these arrange over 10s of micron lengthscales into progressively ordered arrays. Under the conditions studied long range order was not observed [33].

The onset of MLV formation is found to be dependent on the total shear applied, with higher flow rates form the MLVs faster, requiring an approximately similar number of cycles. As expected, MLV size decreases with flow, and thus shear rate, but with following a  $\alpha \simeq 1/4$  power law (although the shear rate estimate may not be sufficiently precise). Once MLVs form, they remain stable for several hours to days as indicated by SANS 2D and <sup>2</sup>H NMR data, in line with the reported metastability of various systems.

The findings and reported methodology are relevant for the industrial processing of complex fluid formulations, often carried out in tubular formulators and continuous flows, and employing a combination of extensional and shear flows.

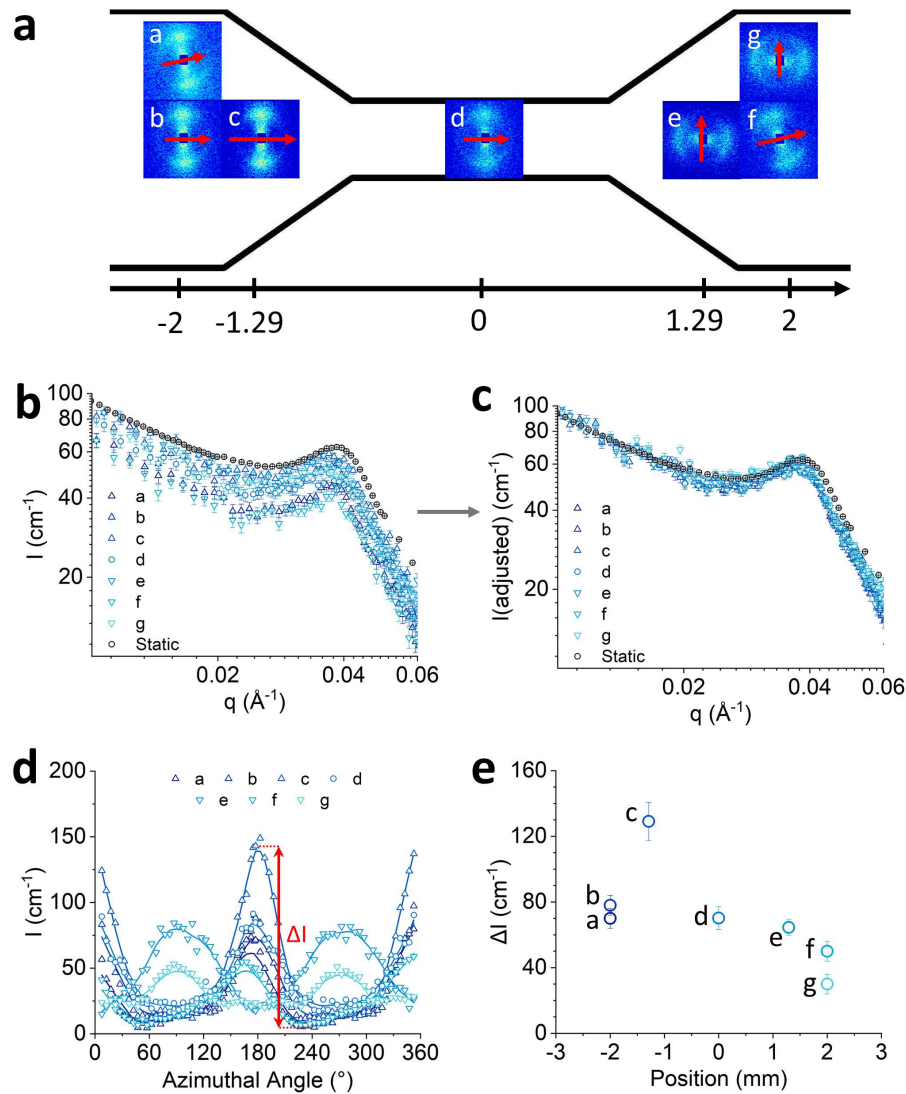


Figure 5.15: Lamellar phase alignment along the contraction-expansion microfluidic chip subjected to  $5 \text{ mL h}^{-1}$  flow rate. a) 2D scattering patterns along the chip; b) Radially-averaged SANS intensity acquired at the positions a, b, c, d, e, f and g of the contraction-expansion geometry, at flow rates of  $5 \text{ mL h}^{-1}$ ; c) Radially-averaged SANS intensity data collapsed on one curve to demonstrate that  $S(q)$  remains unchanged; d) Azimuthal average within  $0.035 \leq q \leq 0.045 \text{ Å}^{-1}$  computed from the 2D data shown in panel a), from where an orientation parameter  $\Delta I$  is estimated from the difference between the maximum and minimum intensities as a function of azimuthal angle; e)  $\Delta I$  in different positions along the channel. The x axis coordinate refers to the distance from the center of the channel.

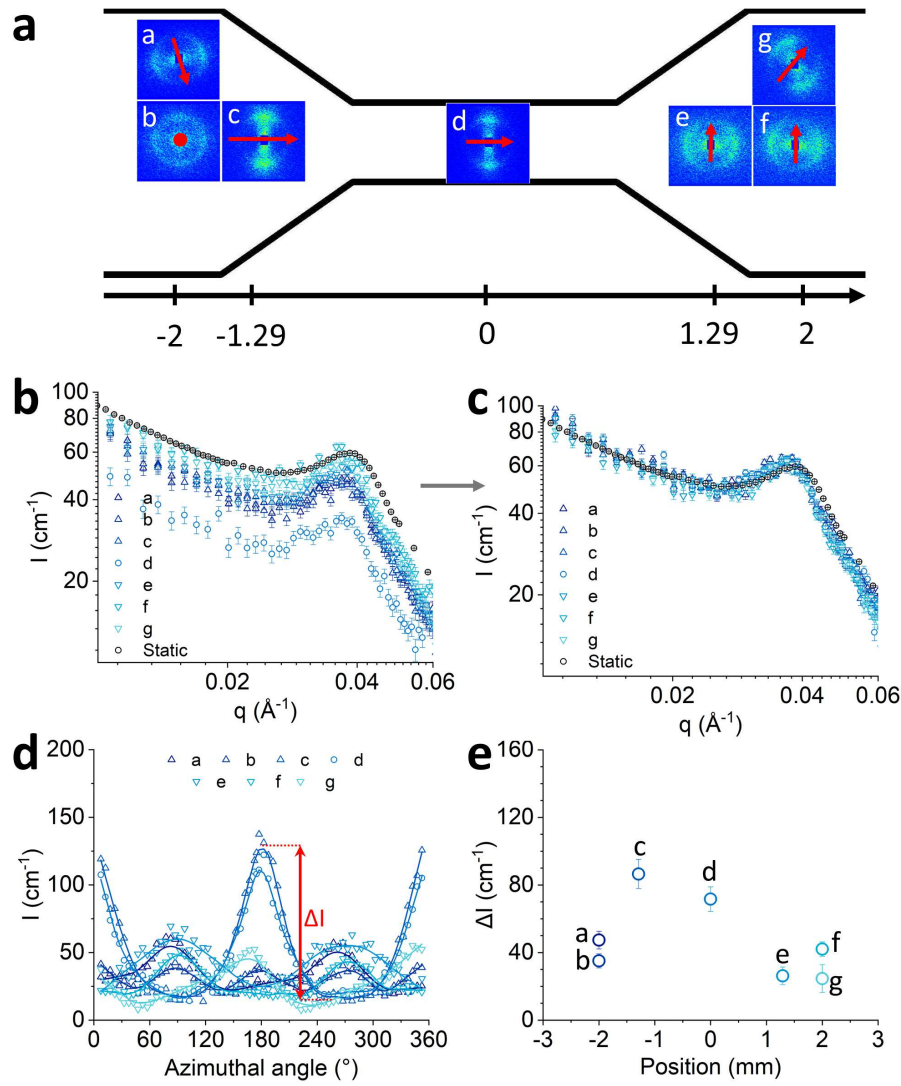


Figure 5.16: Lamellar phase alignment along the contraction-expansion microfluidic chip subjected to  $0.5 \text{ mL h}^{-1}$  flow rate; a) 2D scattering patterns along the chip ; b) Radially-averaged 2D SANS intensity acquired at positions a, b, c, d, e, f and g of the contraction-expansion geometry, at flow rates of  $0.5 \text{ mL h}^{-1}$ ; c) Radially-averaged SANS intensity data collapsed on one curve to demonstrate that  $S(q)$  remains unchanged; d) Azimuthal average within  $0.035 \leq q \leq 0.045 \text{ Å}^{-1}$  computed from the 2D data shown in panel a), from where an orientation parameter  $\Delta I$  is estimated from the difference between the maximum and minimum intensities as a function of azimuthal angle; e)  $\Delta I$  in different positions along the channel. The  $x$  axis coordinate corresponds to the distance from the center of the channel.

## Chapter 6

# Science outreach: Paper marbling as a teaching tool for surface tension, surfactants and the Marangoni effect

### 6.1 Introduction

In this chapter, I explore how the wider public can be engaged with the field of surfactant science and fluid dynamics, at the intersection with art. I describe an interactive workshop centered around the interfacial science of paper marbling, a historical printing technique often found in 18<sup>th</sup> century book art. The experiments and activities were designed and coordinated by me, and first conducted as part of the Great Exhibition Road Festival (GERF) in June 2022, as highlighted in <https://blogs.imperial.ac.uk/molecular-science-engineering/2022/07/11/2022-great-exhibition-road-festival/>. The activity was designed for children (6 years old, or older) and adults, generally in mixed groups and/or in child-adult pairs. Over 200 attendees took part in hands-on ‘paper marbling’ sessions, and 50-60 actively participated in ‘soap racing’ activities (and many more as observers), over the 2 day festival. Student applicants from widening participation backgrounds were given priority in the activities, as part of an invitation to visit Imperial

ahead of ‘A-level results day’. The workshop content and delivery have since evolved and resulted in a successful RSC ‘large grant’ application (2022-2023).

Paper marbling, a UNESCO Heritage Craft [215], is a centuries-old printmaking technique that involves floating ink on water to create prints. Marbling has a rich history dating back to the 10<sup>th</sup> century in Japan, where it was called ‘suminagashi’ (Fig. 6.1a) and used for calligraphy paper decoration [216], [217]. This form of art emerged later in the Middle East, across present Iran, and Turkey, in the 15<sup>th</sup> century, known as ‘ebru’ or ‘floating clouds’ [217] (Fig. 6.1b), before eventually reaching the British Empire in the 18<sup>th</sup> century, where it was widely used in the bookbinding industry [218].

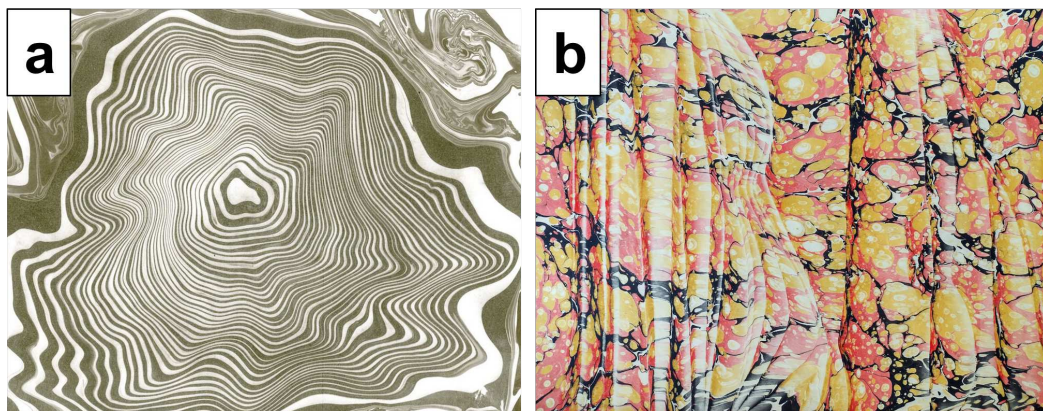


Figure 6.1: Examples of paper marbling. a) Suminagashi; b) Ebru (own work).

Paper marbling relies on the interaction of three basic components: ink, water or thickened water, and paper [217]. The ‘marbling water’, traditionally prepared by boiling different plants such as gum tragacanth, flaxseed, linseed, salep, gum hog, or carrageenan (Irish moss), is used to ‘thicken’ the liquid. The ink, which is a mixture of pigment and binding agent (gum arabic), floats on top of the marbling water, with its buoyancy depending on the density of the water and the dispersibility of the ink, which is regulated by the surface tension [217]. Traditionally, ox gall extracted from the gall bladder of oxen was added to the ink to enhance its spreading. Bile salts, derived from cholic and chenodeoxycholic acids, which act as surfactants to emulsify fats in the mammalian small intestine, are the primary components of ox gall [217]. Nowadays, synthetic ‘gall solutions’ and commercial detergent products like Fairy liquid or Kodak Photoflow are frequently used as substitutes

[219].

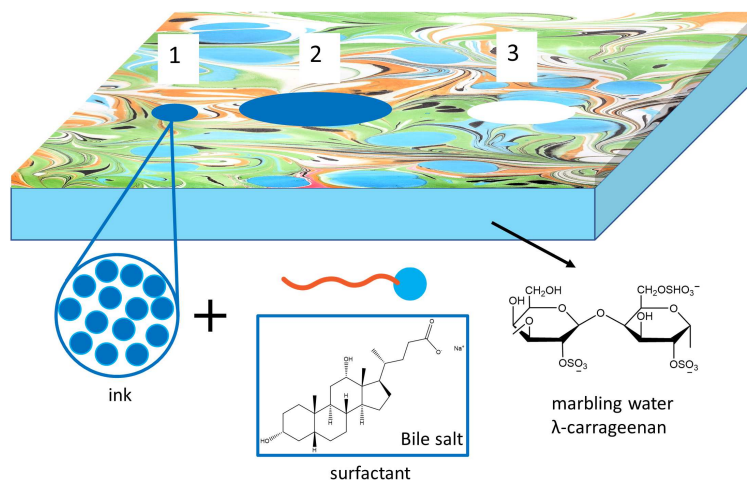


Figure 6.2: Components of ebru marbling. Paper marbling consists of three components: marbling bath made out of carrageenan containing mucilaginous liquid and ink (1) that has been mixed with surfactant solution in micellar phase, historically bile salts (2). Negative space can be created by the addition of pure surfactant solution to the surface.

The interplay between the surface forces of marbling liquid and inks is crucial when marbling. Surface tension describes the cohesive forces between molecules at the air/liquid interface. Water has relatively high surface tension due to hydrogen bonding between the molecules, 72 mN/m. Addition of surfactants, amphiphilic molecules with a hydrophobic tail and hydrophilic head, can greatly reduce surface tension. When surfactant molecules are added to the water surface, a surface tension gradient will be created. This difference in surface tension will lead to transport across the interface, as surface tension is equalised. This mass transfer along the interface is called Marangoni flow and is the driving force behind phenomena such as tears of wine, a water beetle propelling itself across the interface and motion of living organisms [220], [221] and cells [222]. This is also the basis behind the spreading of marbling inks across the interface. By adjusting the levels of surfactant added to the inks, one can achieve various degrees of ink spreadability. In the marbling world, this is called balancing the inks which aims to accomplish similar levels of spreadability for all inks used to create a print.

Surface tension is reflected on the extent of the Marangoni flow, as the greater the surface tension gradient, the greater the Marangoni flow. This concept has been quantified by

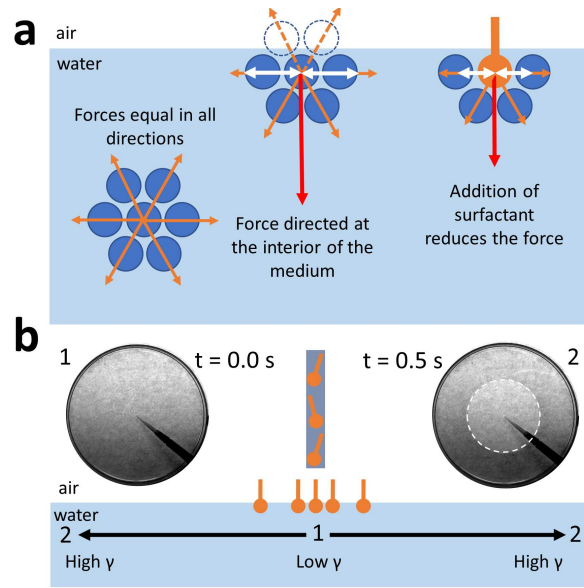


Figure 6.3: Surface tension and gradient induced flow. a) Surface tension; b) Flow caused by gradient in surface tension

Roché et al. [223], where the authors related the velocity  $u$  and radius  $r$  describing the persistence length of Marangoni flow,

$$u = A \left( \frac{(\gamma_w - \gamma_s)^2}{\eta \rho r} \right)^{\frac{1}{3}} \quad (6.1)$$

where  $\gamma_w$  is the surface tension of the substrate,  $\gamma_s$  surface tension of the surfactant solution,  $\eta$  is the dynamic viscosity and  $\rho$  is the density of the substrate.  $A$  is a dimensionless pre-factor approaching unity [223].

The workshop at GERF was organised across two different activity zones: paper marbling zone and the soap racing zone, where festival attendees could experience being an artist or a scientist, respectively. Based on the concepts of surface tension and Marangoni flows, I designed an interactive activity/experiment which aimed to explore the Marangoni flows generated by a range of surfactants. To replicate conditions used for marbling, 5% w/w carrageenan in DI water was used as the substrate, and Liquitex acrylic ink was used as the contrast agent. Festival attendees were invited to participate in a simple experiment, where they pipetted a drop of surfactant solution onto the marbling ink in a Petri dish and measured how quickly the surfactant spread. This activity was called the "soap racing".

The details and findings of the experiment are outlined below, demonstrating the level of community engagement.

## 6.2 Soap racing: Methods

Described below is the preparation process and activity structure for the "soap racing" zone in GERF 2022.

### 6.2.1 Surfactant solution preparation and surface tension measurements

100 mM surfactant solutions of common industrial surfactants, dioctyl sulfosuccinate sodium salt, AOT (Sigma-Aldrich,  $\geq 97\%$ ), polyoxyethylenesorbitan monopalmitate, Tween 40 (Sigma-Aldrich,  $\sim 90\%$ ), sodium dodecyl sulfate, SDS (Sigma-Aldrich BioXtra,  $\geq 99.0\%$ ), N,N-dimethyldodecylamine N-oxide, DDAO (Sigma-Aldrich,  $\sim 30\%$ ), polyoxyethylene (9) isooctylphenyl ether, Triton-X100 (Sigma-Aldrich, laboratory grade), sodium dodecylbenzenesulfonate, SDBS (Sigma-Aldrich, technical grade) were prepared by dissolving 0.01 mol of surfactant to 100 mL with DI water. Additionally, 5.8% w/v commercial detergent Fairy (corresponding to about 100 mM concentration calculated based on sodium lauryl sulfate molecular weight) was dissolved in DI water to serve as a reference for real-life applications for attendees.

Pure surfactant solution surface tension values were obtained using pendant drop tensiometry with Krüss EasyDrop standard drop shape analysis system (DSA1) and ADVANCE software. The image analysis relates the drop curvature to the surface tension  $\gamma$  via Young-Laplace equation  $\Delta P = \gamma_s \left( \frac{1}{R_1} - \frac{1}{R_2} \right)$ , where  $\Delta P$  is the pressure difference between the inside and outside of the droplet and  $R_1, R_2$  the radii of curvature of the droplet surface [141]. Overview of surfactants used alongside their measured  $\gamma_s$  values and molecular descriptors are given in Table 6.1. Surfactant area per molecule  $A_{cmc}$  describes the surface coverage of the surfactant at the air-water interface and was calculated as  $A_{cmc} = \frac{1}{\Gamma_{cmc} N_A}$

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Table 6.1: Surfactants used for soap racing activity.  $A_{cmc}$  calculated from maximum surface excess values  $\Gamma_{max}$  taken from literature [224]–[228];  $\rho_{layer}$  calculated from  $M_{w(tail)}/V_{layer}$

| Surfactant  | $M_w$<br>(g/mol) | $A_{cmc}$<br>( $\text{\AA}^2$ ) | $\rho_{layer}$<br>(g/cm <sup>3</sup> ) | $\gamma_s$<br>(mM/m) | Structure |
|-------------|------------------|---------------------------------|----------------------------------------|----------------------|-----------|
| AOT         | 444.6            | 75 [224]                        | 0.30                                   | 30.8                 |           |
| Tween 40    | 1283.6           | 117 [225]                       | 0.09                                   | 45.0                 |           |
| SDS         | 288.4            | 47 [226]                        | 0.24                                   | 32.5                 |           |
| DDAO        | 201.4            | 31 [227]                        | 0.33                                   | 31.7                 |           |
| Triton-X100 | 625              | 87 [228]                        | 0.19                                   | 34.0                 |           |
| SDBS        | 348.5            | 50 [228]                        | 0.26                                   | 33.5                 |           |

where  $N_A$  is the Avogadro number and  $\Gamma_{cmc}$  the concentration at which no more surfactant can be adsorbed at the water/air interface [228], [229]. From  $A_{cmc}$ , the adsorbed surfactant layer density was estimated as  $\rho_{layer} = \frac{M_{tail}}{A_{cmc}l_{tail}}$  [229], where  $M_{tail}$  is the molecular weight of the tail group and  $l_{tail}$  was given by Tanford relation [230]. The density of surfactant tail layer  $\rho_{layer}$  correlates approximately with surface tension, with more densely packed surfactants leading to lower surface tension values [229], as can also be observed for the surfactants used in the soap racing experiments (Fig. 6.4)

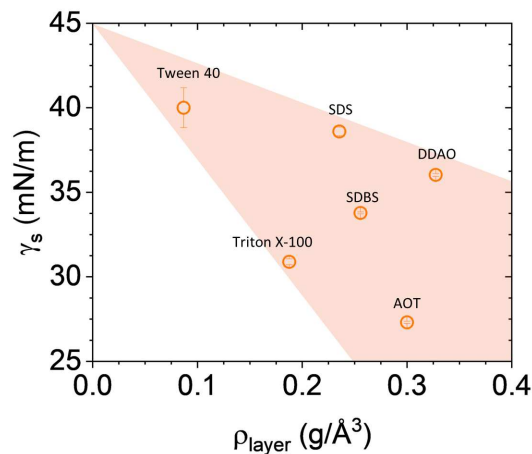


Figure 6.4: Surface tension  $\gamma_c$  as a function surfactant tail density  $\rho_{layer}$  at the air/water interface.

This analogy was used as the basis for explaining the differences observed between surfactants in the soap racing experiment with surfactants with bulkier head and tail groups demonstrating lower  $\rho_{layer}$  values and consequently higher surface tensions [229]. Each surfactant was shown as a cartoon illustration demonstrated in Fig. 6.6, and some 3D molecular models were made available to visitors.

## 6.2.2 Soap racing: activity structure

The objective of this activity was to introduce festival attendees to surface tension, surfactants and Marangoni effect by using a participatory element, that is then compiled as a citizen science activity. The data were collected during the exhibition, and velocities and radii measured with a ruler and stopwatch (and recorded with a laboratory grade camera, with image calibration). Participants initially ‘guessed’ what surfactant structures would be fastest, based on simple concepts of headgroup size and charge, number and length of tails, in order to introduce the potential of molecular design. Concepts of critical micelle concentration, surface coverage, diffusion, etc would be discussed with more mature participants. One or two volunteers would monitor the activity and ensure safe handling of materials, and provide basic concepts of surfactant activity. The list of equipment used is given in Table 6.2.

During the activity the following questions were tackled:

- What is surface tension and how surfactants weaken it?
- What are Marangoni flows?
- What does the surface tension have to do with the speed of Marangoni flow and how that relates to surfactant structure?

Individual attendees (or small <3 groups) attempted the ‘paper clip experiment’ where a paper clip is floated on water (Fig. 6.5a). The surface tension was then broken by application of small amount of Fairy liquid in the centre of the paper clip. Following that,

Table 6.2: List of equipment used for soap racing activity

| Item                                             | Amount |
|--------------------------------------------------|--------|
| High speed camera (Basler acA640-750uc)          | 1      |
| Edmund Optics C-mount Objective                  | 1      |
| A4 cutting board                                 | 1      |
| Whiteboard with markers                          | 1      |
| Petri dishes (15 cm in diameter)                 | 6      |
| 100 $\mu$ L pipette                              | 1      |
| Pipette tips                                     | 100    |
| Camera stand                                     | 1      |
| Beaker for pipette disposal                      | 1      |
| Calculator                                       | 1      |
| Laptop with Pylon Viewer                         | 1      |
| Marbling water (5% w/w carrageenan in DI water)  | 5 L    |
| 100 mM surfactant solutions in dropper bottles   | 7      |
| Liquitex Acrylic ink (Phthalocyanine Blue 30 mL) | 1      |
| 100 mL measuring cylinder                        | 1      |
| Paper clips                                      | 10     |
| Beaker containing DI water                       | 1      |
| Surfactant molecule example (SDS)                | 1      |

the attendees were offered to partake in the soap racing which is inspired by the soap boat experiment [221] but re-contextualised for marbling (Fig. 6.5b). They selected one of 7 surfactant solutions of their choice at random. In our case, 100 mL marbling liquid (5% w/w carrageenan gel with measured surface tension  $\gamma = 74$  mN/m and dynamic viscosity  $\eta = 0.5$  Pa s) and 30  $\mu$ L Liquitex acrylic ink to emulate the marbling workshop setup and allow the attendees to more easily link the two activities. The higher viscosity of carrageenan solution also allowed to slow down the Marangoni flow as  $u \propto \frac{1}{\eta^{1/3}}$ . Attendees were then instructed to pipette a single drop of the surfactant from the dropper (volume of each drop  $\sim 36$   $\mu$ L) and timing how long it takes for the moving front to cross the 5 cm finish line. Upon addition of a drop of surfactant they observed the ink being pushed to the side of the Petri dish at various degrees. The attendees then calculated the speed at which the front moved as 5 cm/ $t$ , where  $t$  is the time needed for the front to cross the finish line. Each experiment was simultaneously recorded with Pylon Viewer software controlled Basler acA640-750uc camera (50 fps frame rate) for later analysis. The data collected by the attendees at the festival were compared to velocities captured by the

camera and plotted against  $\gamma_c$  values obtained by the pendant drop experiment.

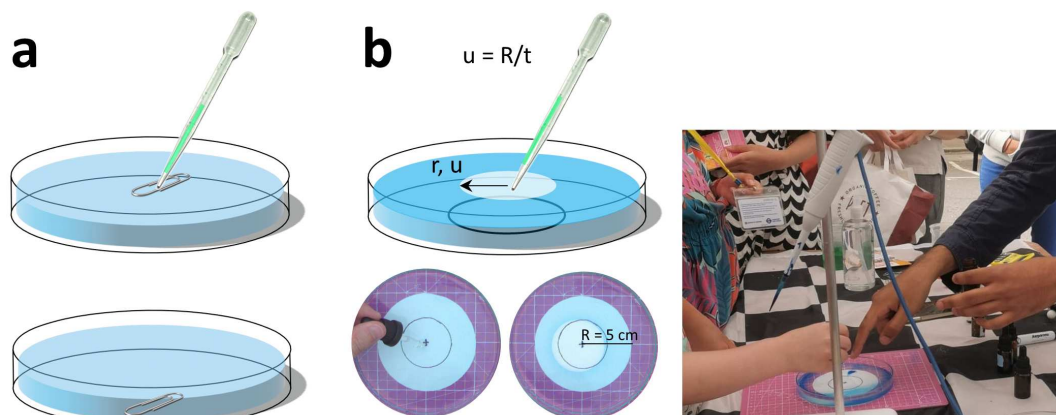


Figure 6.5: Soap racing zone. a) Paper clip experiment demonstrating how surfactant (Fairy liquid) breaks the surface tension; b) Soap racing setup.

Following the soap racing experiment the attendees were invited to speculate as to why their selected surfactant was fast or slow, referring back to the cartoon illustrations of the surfactants. Generally, the greater the density of the surfactant tail layer, the better the surface coverage and the more efficient surfactant is at reducing surface tension (greater surface reduction means faster speeds in soap racing). Then the attendees were reminded about the surface tension and Marangoni flow which was previously demonstrated in the paper marbling zone.

### 6.2.3 Soap racing: Results

The main objective of collecting the surfactant soap racing data was to assess the feasibility of reproducibly measuring the Marangoni flow and comparing the digital image analysis to those obtained by the attendees measuring the time required to cross the 5 cm finish mark. The findings are summarised in Fig. 6.6.

The image analysis of the soap racing revealed that the Marangoni flows generated by the surfactants were reproducible for a range of different surfactants and compared well with the repeats performed in a laboratory-controlled setting (Fig. 6.6 a-h). Values for  $u_{max}$  were estimated by linear fit to the initial  $R$  values and  $r_{max}$  estimated by fitting exponential

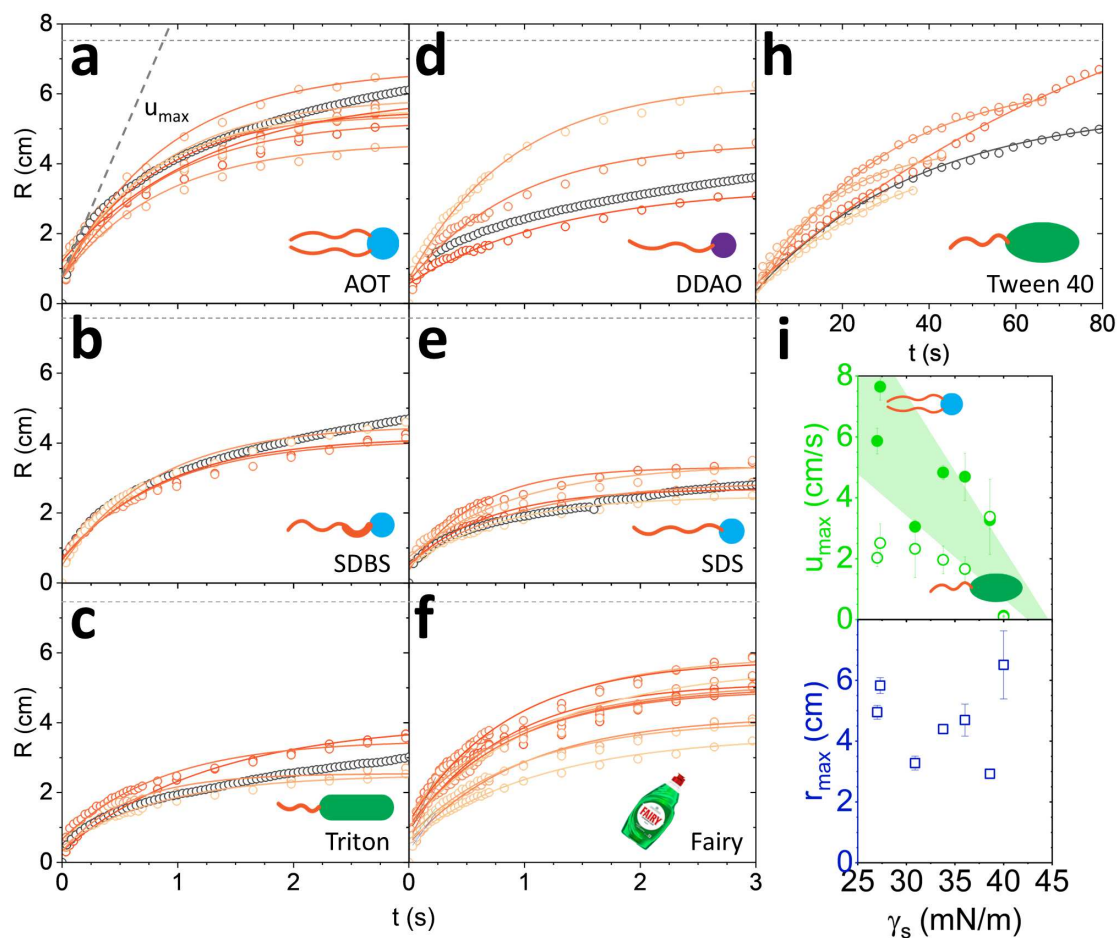


Figure 6.6: Marangoni flows of different surfactants. a-h) Growth of surfactant spreading zone  $r$  as a function of time elapsed. Orange coloured circles display experiments carried out by the festival attendees while black circles indicate the repeats in the laboratory.  $u_{max}$  was calculated from the gradient of fitted linear function. Dotted line when  $r = 7.5$  cm indicates the radius of the Petri dish. i) (top)  $u_{max}$  as a function on surface tension  $\gamma_s$  estimated by Basler image analysis (closed circles) and stopwatch at the time of the festival (open circles). (bottom) Maximum radius  $r_{max}$  as a function of  $\gamma_s$  indicating the extent of which the surfactant will spread.

decay function. When plotted against surface tension  $\gamma_s$ ,  $u_{max}$  displayed a general trend of decreasing with increasing surface tension  $\gamma_s$  (shaded circles in Fig. 6.6i (top)) as expected from equation  $u = A \left( \frac{(\gamma_w - \gamma_s)^2}{\eta \rho r} \right)^{\frac{1}{3}}$  [223]. In simpler terms, when the difference between  $\gamma_s$  and  $\gamma_w$  (in this case carrageenan solution) is smaller, the Marangoni flows will be weaker, leading to slower speeds. The velocities measured by the attendees (open circles in Fig. 6.6i (top)) mapped well with this prediction too, however the velocities observed were smaller. This was to be expected as the attendees are not measuring the initial velocity

$u_{max}$  but rather an average velocity  $\bar{u}$  over 5 cm travel distance. The  $r_{max}$  showed a less clear dependence on  $\gamma_s$ , which is also expected as the soap racing experimental set-up was different from the one reported in [223], which relied on continuous release of the surfactant solution to the interface.

## 6.3 Paper marbling

A series of 'paper marbling workshops' were carried out at GERF 2022 over two days, in groups of 12-14 attendees, with two demonstrators. A summary of materials is provided in 6.3 followed by the workshop structure and example prints.

### 6.3.1 Materials

Table 6.3: Paper marbling equipment and materials

| Item                                            | Quantity |
|-------------------------------------------------|----------|
| Golden acrylic inks                             | 6        |
| A4 paper, e.g. sugar paper or calligraphy paper | 10       |
| Metal trays (e.g. these)                        | 1        |
| Methyl cellulose or lambda carrageenan          | 1        |
| Fan brushes                                     | 1        |
| Small brushes                                   | 1        |
| Wooden skewers                                  | 1        |
| Cups for rinsing brushes                        | 1        |
| Kitchen Roll                                    | 1        |
| Scrap newspaper strips                          | 10       |
| Alum                                            | 100 g    |
| Immersion blender                               | 1        |
| 1 % Fairy liquid                                | 100 mL   |

**Marbling water.** First, 7 g in 1 L of methyl cellulose or carrageenan were dissolved in water. In the case of methyl cellulose, it was first dispersed in small amounts of boiling water followed by the addition of room temperature water to reach the desired volume (1 L is enough for one person marbling in A4 sized tray). If the mixture was not smooth, the solution was blended with immersion blender and transferred to a shallow tray for the

bubbles to settle. However, in this activity series, carrageenan solution was used which was prepared by simply blending 6 g of carrageenan powder in 1 L of water (scaled to requirements).

**Paints.** Golden acrylic inks were diluted in 2:1 ratio of water:ink and tested on the prepared marbling solution for their spreadability. If the inks were not spreading sufficiently, a few drops of the Fairy liquid were added to the ink solution (concentration of Fairy liquid solution was 1 g in 100 mL).

**Paper mordanting with alum.** To ensure that the ink does not bleed/wash away, the paper needs to be treated with a mordant (alum). To prepare the solution, 45 g of alum were dissolved in 300 mL of boiling water and transferred to a shallow dish (to fit A4 size paper sheet). The paper was treated by dipping one side of it (marked by 'X') in the alum bath and dried by sticking two paper sheets alumned sides together.

### 6.3.2 Activity structure

Each 30 minute workshop began with a 5 min overview of the history of paper marbling, its components and the underlying principles of surface tension and surfactants. In each session, participants made two prints.

Marbling was started by cleaning the surface of marbling water with a scrap piece of newspaper. This ensured removal of any residual paints, dust and air bubbles.

When marbling "less is more", hence the attendees were encouraged to apply the marbling ink by gently tapping a fanned brush on their index finger. This ensured an even coverage of the surface. Applying too much ink too quickly results in it sinking and contaminating the marbling bath.

Generally, the number of colours should be limited to about 4 per print, but a good rule of thumb is to stop applying inks once they slow down in spreading/start sinking to the bottom of the tray. Once the desired inks had been applied, the pattern was manipulated with various tools (e.g. wooden skewers or combs). Instructions for two commonly used

patterns, feathers and flowers, are given in Fig. 6.7. Once the desired print had been arranged, it was transferred onto the pre-treated paper (X-marked side facing the water). Marbling water can be re-used several times by cleaning the surface with scrap newspaper and can be stored at room temperature for up to two weeks.



Figure 6.7: Instructions on how to create feathers and flowers in ebru marbling

Finally, the attendees were instructed to hang the artwork to dry, and to tidy up, ahead of a group changeover.

### 6.3.3 Summary

In this chapter, I demonstrate the feasibility of gathering meaningful and reproducible data in an outreach festival setting. Overall, the measurements obtained during GERF 2022 showed that it is feasible to achieve reproducible assessment of Marangoni flows of different surfactants. This has offered insight on how to design experiments for future outreach events. For example, one well known demonstration of Marangoni effect is the "soap boat" [231]. One could envision a "soap boat race" where different commercially available detergents and personal care products are used to compare their ability to reduce the surface tension and relate it to their cleaning power.

In a broader context, facilitating science outreach activities provides opportunities to involve individuals in STEM fields which is reported to be crucial for the economic development of a nation, promoting social mobility, and fostering a more equitable society



Figure 6.8: Marbling examples of prints created by outreach event participants.

[232]. Exposure to science during early education plays a pivotal role in shaping the career aspirations of primary school children and young adults [232]. In a longitudinal study conducted by Archer et al., termed 'ASPIRES', the authors define the concept of "science capital" as a determinant of young adults' (aged 10-17) career aspirations [232]. The term, derived from the sociologist Pierre Bourdieu's concept of social capital, refers to an individual's attitudes, knowledge, environment, and social connections in relation to science. Notably, students from disadvantaged socioeconomic backgrounds are often underrepresented in science-related fields, with a staggering 80% of students possessing 'low' science capital never envisioning a future in the sciences [232]. This often goes hand-in-hand with individual views of what constitutes as science/scientific

and broadening this definition in classroom context can be helpful for more students to recognise science in their daily lives. Hence, designing workshops and activities that can be easily reproduced in a classroom/ home setting and broaden the context of science might aid the participation of currently underrepresented groups in STEM careers.

On a more academic level, discussions about the role of creativity in science, have become more prevalent in recent years [233]. I believe that there are many opportunities to explore the role of science in art, at both research and public engagement levels. The latter include primary and secondary school students considering their career choices, and who might have strong views on the boundaries of science and art, and have compartmentalised their perceived abilities and strengths. In the context of fluid dynamics and surface phenomena, there have been a few studies that have quantified the artistic effects achieved by painters. For example, a study that looked at why Jackson Pollock’s kinetic paintings featured uncoiled strokes and identified that the specific viscosity of the paint and the speed/height at which the paint was applied meant that the artist avoided hydrodynamic instabilities [234]. Similarly, researchers looking at David Alfaro Siqueiros “accidental painting” technique revealed that it arises from density differences in the paints layered leading to Rayleigh-Taylor instability [235]. A collaboration between physicists and contemporary artist Holton Rower, investigated how the artist’s ‘pour’ paintings produce a range of effects when the paint is poured from varying heights [236]. Paper marbling is currently an endangered craft in the UK with less than 20 professional practitioners [237]. Since the technique relies on materials that belong to the field of soft matter area, it appears beneficial to consider and examine the scientific aspects of the craft, quantifying what leads to successful printing to aid the preservation and possible evolution of the craft.

# Chapter 7

## Conclusions

This work explored the equilibrium and flow behaviour of a model pseudo-quaternary system comprising the ubiquitous sodium dodecyl sulfate (SDS) surfactant, mixed with co-surfactant octanol and 2% NaCl brine. The lamellar phase  $L_\alpha$  of this system is known to exhibit a rich flow phase behaviour, including a lamellar-to-MLV transformation, and the formation of highly ordered ‘onion’ phases. The reproducibility and long metastable nature of these transitions led to the introduction of the (paradoxical) term ‘flow phase diagrams’. Previous work had focused on specific shear geometries and a narrow composition and temperature ranges for this system. This project set out to explore the effect of complex (and practically relevant) flow fields, accessible in microfluidics, including tubular and contraction-expansion flows, both continuous and oscillatory, in conjunction with in-line SANS and microscopy, to examine such flow ‘phase behaviour’.

To ensure a robust foundation in quiescent, equilibrium properties, Chapter 3 describes the microstructure of SDS/octanol/brine equilibrium phases along the  $L_3$ ,  $L_\alpha$ , mixed  $L_\alpha/L_1$  and  $L_1$  dilution lines. While the phase behaviour had been previously reported [17], I provide the first comprehensive examination of the molecular and mesoscale structures that form within those phases, employing primarily SANS (and ancillary techniques). A transition from  $L_\alpha$  to sponge phase ( $L_3$ ) above 35 °C was found along the octanol:SDS = 1.21 isopleth (nearest to the  $L_3/L_\alpha$  phase boundary) with phase coexistence above  $\phi_v \approx 0.14$  weight

fraction of surfactant and co-surfactant. The lamellar bilayers were found to swell upon dilution, with an approximately linear increase of d-spacing, accompanied by a decrease of the Caillé parameter, indicative of greater membrane rigidity. At a lower octanol:SDS ratio of 0.62, coexistence of oblate micelles and vesicles was observed with preferential formation of vesicles at low concentrations. Dilution of the  $L_1$  phase, along octanol:SDS = 0.08, resulted in elongated micelles, as the NaCl:SDS ratio increases, while higher temperatures favour the formation of less elongated micelles. The results provided a detailed map of equilibrium structures found in the  $L_\alpha$  vicinity of this extensively investigated flow-responsive surfactant system, specifically revealing that  $L_\alpha$  composition corresponding to 6.5% SDS/7.9% octanol/ 85.6% brine readily undergoes phase transformation to sponge phase  $L_3$ .

SDS/octanol/brine microstructure was then tuned by changing the charges present in the system, as discussed in Chapter 4. The influence of salt (NaCl) in a fixed model system of SDS/octanol/brine sample 6.5% SDS/7.9% octanol/85.6% brine (extensively studied under shear flow) was examined with varying NaCl concentrations ranging from 0 to 2.5% NaCl. The microfluidic processing of these solutions revealed that  $\sim 1.8\%$  w/w NaCl addition results in MLV formation within the shortest time (or equivalent lengthscale) and yields near-centrosymmetric scattering profiles characteristic of MLVs (at a reference  $1 \text{ mL h}^{-1}$  flow rate and  $\simeq 90 \text{ s}^{-1}$  shear rate). Further salt addition yields biphasic systems that remain strongly aligned under flow, while lower salt content also increases scattering anisotropy, accompanied by higher membrane rigidity and solution viscosity. Increasing flow rate causes greater initial  $L_\alpha$  alignment, and thus flow anisotropy, but also faster evolution towards isotropy and MLV formation. A future opportunity here could be to look more closely at membrane bending rigidity through neutron spin echo (SE) scattering studies, to enable the decoupling of membrane properties, uniquely accessible by combining SE and SANS.

In Chapter 5, the lamellar-to-MLV transition requirements at varying flow velocity, oscillation amplitude, frequency, and number of oscillatory cycles were established for 6.5% SDS/7.9% octanol/ 85.6% brine (2 % NaCl in  $\text{H}_2\text{O}$ ) composition which has been

often investigated in shear induced MLVs studies. The spatio-temporal evolution of the hierarchical fluid structure was elucidated: lamellar sheets initially aligned with flow direction upon entering a constriction and then perpendicularly upon exiting; the formation of MLVs at the nanoscale was first observed by SANS within a few ( $<5$ ) oscillatory cycles, followed by the gradual appearance of a regular MLV arrangement, at the micronscale, by optical microscopy after tens of cycles, under the conditions investigated. Once MLVs were formed under flow, they remained metastable for several days. Tubular and contraction-expansion (or constriction) flow geometries were employed, as these are most relevant for processing of these systems in continuous flow reactors and nozzles. These flow fields impose, primarily, wall shear and extensional flows. However, microfluidic systems allow the study of flow fields with a judicious combination of extension and rotational flows, including pure shear (not attainable in macroscale devices), thus providing ample opportunities for the rigorous study of complex fluids subjected to complex flows.

Finally, the last Chapter departs from fundamental research in interfacial science to consider how surfactant science can be popularised in an outreach setting. An activity incorporating surface tension and Marangoni flows with the ancient craft of paper marbling, was designed to enthuse the general public and school-age (6-14) children in particular. These activities were initially devised for the Great Exhibition Road Festival 2022, including a ‘surfactant soap race’ where the attendees considered the extent of surfactant-induced Marangoni flows and the relation to the molecular properties of surfactants. Then, attendees had the opportunity to learn about paper marbling and to create mesmerising prints to take and reproduce at home with common materials and ingredients. The results collected during the festival demonstrate the feasibility of collecting meaningful insights via ‘community science’ with a range of attendee skills, and introduce a platform to inspire the public to reflect upon the many and fascinating intersections between art and science. This seems important in particular for underprivileged school children, or those with low ‘science-capital’, and who might have not consider further study of STEM disciplines.

# Chapter 8

## Appendix

Described below are the fitting results described in Chapter 3.

### Dilution fitting results at 25°C, 35°C and 45°C

Table 8.1:  $L_\alpha$  Caillé model fitting results for dilution along the 1.21 oct:SDS ratio. Constant parameters,  $\delta_{head} = 3 \text{ \AA}$ ,  $SLD_{brine} = 6.23 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{tail} = -0.416 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{head} = 1.7 \cdot 10^{-6} \text{ \AA}^{-2}$

| T, °C | $\phi_v$ | $I_{incoh}, \text{cm}^{-1}$ | scale | $\delta_{tail}, \text{\AA}$ | $\delta_m, \text{\AA}$ | $N_{layers}$ | d, \AA          | $\eta$          | $p_D$ | $\chi^2$ |
|-------|----------|-----------------------------|-------|-----------------------------|------------------------|--------------|-----------------|-----------------|-------|----------|
| 25    | 0.189    | 0.121                       | 0.91  | $8.5 \pm 0.1$               | 23.0                   | 1000         | $128.1 \pm 0.3$ | $0.91 \pm 0.01$ | 0.08  | 2044     |
|       | 0.158    | 0.109                       | 0.91  | $9.2 \pm 0.1$               | 24.4                   | 2000         | $150.7 \pm 0.3$ | $1.00 \pm 0.01$ | 0.10  | 1870     |
|       | 0.127    | 0.099                       | 1.00  | $9.5 \pm 0.1$               | 25.0                   | 1000         | $199.0 \pm 0.3$ | $1.00 \pm 0.01$ | 0.19  | 1850     |
|       | 0.096    | 0.064                       | 0.3   | $9.5 \pm 0.1$               | 25.0                   | 1000         | $273.7 \pm 0.3$ | $1.00 \pm 0.01$ | 0.22  | 96       |
|       | 0.064    | 0.055                       | 0.45  | $9.5 \pm 0.1$               | 25.0                   | 1000         | $395.0 \pm 0.3$ | $1.00 \pm 0.01$ | 0.25  | 161      |
| 35    | 0.189    | 0.113                       | 0.90  | $9.0 \pm 0.1$               | 24.0                   | 1000         | $118.1 \pm 0.3$ | $0.75 \pm 0.07$ | 0.06  | 9150     |
|       | 0.158    | 0.109                       | 0.35  | $9.0 \pm 0.1$               | 24.0                   | 1000         | $126.8 \pm 0.3$ | $0.82 \pm 0.01$ | 0.12  | 654      |

Table 8.2:  $L_3$  model fitting results for dilution along the 1.21 oct:SDS ratio. Constant parameters,  $\delta_{head} = 3.0 \text{ \AA}$ ,  $A = 0.001$ ,  $\xi_{io} = 1000 \text{ \AA}$ ,  $SLD_{contrast} = 5.9 \cdot 10^{-6} \text{ \AA}^{-2}$

| T, °C | $\phi_v$ | $I_{incoh}, \text{cm}^{-1}$ | scale | B        | $\xi_3, \text{\AA}$ | $\delta_m, \text{\AA}$ | $\xi, \text{\AA}$ | $\sigma, \text{\AA}$ | $\chi^2$ |
|-------|----------|-----------------------------|-------|----------|---------------------|------------------------|-------------------|----------------------|----------|
| 35    | 0.189    | 0.121                       | 0.03  | 3.1E-04  | 150.0±1.5           | 23.5±0.2               | 236.1±0.2         | 30.0±0.2             | 9150     |
|       | 0.158    | 0.109                       | 0.65  | 1.82E-04 | 117.8±0.4           | 24.3±0.1               | 253.2±0.1         | 34.9±0.1             | 854      |
|       | 0.127    | 0.099                       | 0.89  | 0.63E-04 | 150.3±0.3           | 24.1±0.1               | 276.1±0.2         | 51.8±0.1             | 94       |
|       | 0.096    | 0.064                       | 0.97  | 0.7E-04  | 174.2±0.3           | 24.5±0.1               | 387.7±0.2         | 61.7±0.1             | 88       |
|       | 0.064    | 0.055                       | 1.00  | 1.5E-04  | 175.6±0.3           | 23.9±0.1               | 658.9±0.2         | 62.6±0.1             | 112      |
| 45    | 0.189    | 0.121                       | 0.91  | 2.6E-04  | 96.4±0.5            | 24.5±0.1               | 174.9±0.2         | 25.0±0.1             | 54       |
|       | 0.158    | 0.109                       | 0.98  | 1.3E-04  | 110.1±0.3           | 24.5±0.1               | 223.4±0.2         | 37.9±0.1             | 195      |
|       | 0.127    | 0.099                       | 0.85  | 1.6E-04  | 114.5±0.3           | 24.0±0.1               | 281.7±0.1         | 41.8±0.1             | 5        |
|       | 0.096    | 0.064                       | 0.75  | 1.5E-04  | 151.9±0.3           | 24.5±0.1               | 393.9±0.1         | 46.2±0.1             | 145      |
|       | 0.064    | 0.055                       | 0.70  | 1.8E-03  | 138.9±0.7           | 24.5±0.3               | 688.2±0.1         | 31.4±0.1             | 136      |

Table 8.3:  $L_\alpha$  Caillé model with power law results for dilution along the 1.15 oct:SDS ratio. Constant parameters,  $\delta_{head} = 3 \text{ \AA}$ ,  $SLD_{brine} = 6.23 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{tail} = -0.415 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{head} = 1.74 \cdot 10^{-6} \text{ \AA}^{-2}$

| T, °C | $\phi_v$ | $I_{incoh}, \text{cm}^{-1}$ | scale | $\delta_{tail}, \text{\AA}$ | $\delta_m, \text{\AA}$ | $N_{layers}$ | d, \AA     | $\eta$    | $p_D$ | $\chi^2$ |
|-------|----------|-----------------------------|-------|-----------------------------|------------------------|--------------|------------|-----------|-------|----------|
| 25    | 0.184    | 0.151                       | 0.67  | 8.8±0.1                     | 23.6                   | 2000         | 120.3±0.6  | 0.88±0.01 | 0.11  | 422      |
|       | 0.154    | 0.121                       | 0.64  | 9.0±0.1                     | 24.0                   | 1000         | 137.0±0.9  | 0.99±0.02 | 0.12  | 436      |
|       | 0.123    | 0.101                       | 1.00  | 10.2±0.2                    | 26.5                   | 1000         | 171.0±1.7  | 1.00±0.02 | 0.21  | 452      |
| 35    | 0.184    | 0.151                       | 0.72  | 8.3±0.1                     | 22.5                   | 5000         | 119.5±0.5  | 0.88±0.02 | 0.08  | 732      |
|       | 0.154    | 0.121                       | 0.51  | 10.5±0.1                    | 27.0                   | 1000         | 137.0±0.9  | 1.00±0.02 | 0.13  | 754      |
|       | 0.123    | 0.101                       | 1.0   | 10.2±0.2                    | 26.4                   | 1000         | 182.9±1.9  | 1.00±0.02 | 0.22  | 273      |
| 45    | 0.184    | 0.151                       | 0.72  | 8.3±0.1                     | 22.5                   | 5000         | 119.0±0.5  | 0.85±0.04 | 0.08  | 452      |
|       | 0.154    | 0.121                       | 0.57  | 9.3±0.1                     | 24.6                   | 300          | 144.0±0.9  | 0.98±0.04 | 0.13  | 713      |
|       | 0.123    | 0.101                       | 1.005 | 10.4±0.1                    | 26.7                   | 1000         | 187.72±1.9 | 1.00±0.02 | 0.21  | 614      |
|       | 0.093    | 0.065                       | 1.00  | 10.0±0.6                    | 25.9                   | 1000         | 247.9±2.8  | 1.00±0.05 | 0.23  | 395      |

Table 8.4:  $L_\alpha$  Caillé model fitting results for 1.08 oct:SDS ratio temperature scan. Constant parameters,  $\delta_{head} = 3 \text{ \AA}$ ,  $SLD_{brine} = 6.23 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{tail} = -0.414 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{head} = 1.81 \cdot 10^{-6} \text{ \AA}^{-2}$

| T, °C | $\phi_v$ | $I_{incoh}, \text{cm}^{-1}$ | scale | $\delta_{tail}, \text{\AA}$ | $\delta_m, \text{\AA}$ | $N_{layers}$ | d, \AA    | $\eta$    | $p_D$ | $\chi^2$ |
|-------|----------|-----------------------------|-------|-----------------------------|------------------------|--------------|-----------|-----------|-------|----------|
| 25    | 0.177    | 0.114                       | 0.55  | 9.7±0.1                     | 25.4                   | 250          | 128.0±0.9 | 1.00±0.01 | 0.15  | 944      |
|       | 0.148    | 0.107                       | 0.44  | 11.5±0.1                    | 28.9                   | 500          | 151.0±1.9 | 1.00±0.01 | 0.26  | 1393     |
| 35    | 0.177    | 0.114                       | 0.54  | 9.8±0.1                     | 25.5                   | 1000         | 128.4±0.9 | 1.00±0.01 | 0.15  | 563      |
|       | 0.148    | 0.107                       | 0.47  | 10.8±0.1                    | 27.6                   | 500          | 151.5±1.7 | 1.00±0.01 | 0.22  | 1219     |
| 45    | 0.177    | 0.114                       | 0.54  | 9.7±0.1                     | 25.4                   | 3000         | 129.3±0.7 | 0.95±0.01 | 0.11  | 439      |
|       | 0.148    | 0.107                       | 0.52  | 10.0±0.1                    | 26.0                   | 500          | 152.5±1.2 | 0.99±0.01 | 0.16  | 1150     |

Table 8.5:  $L_4/L_1$  lamellar + flexible cylinder fitting results for 0.62 oct:SDS ratio dilutions. Constant parameters,  $SLD_{brine} = 6.23 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{head} = 2.2 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{tail} = -0.45 \cdot 10^{-6} \text{ \AA}^{-2}$ , scale = 0.25-0.4,  $l_{tail} = 9.5 \text{ \AA}$ ,  $l_{head} = 3.0 \text{ \AA}$ ,  $N_{layers} = 5$ ,  $\eta = 1$ ,  $b = 14 \pm 1 \text{ \AA}$ ,  $R = 14 \pm 0.5 \text{ \AA}$

| T, °C | $\phi_v$ | $I_{incoh}, \text{ cm}^{-1}$ | d, \AA    | L, \AA | $L_4/L_1$ | $\chi^2$ |
|-------|----------|------------------------------|-----------|--------|-----------|----------|
| 25    | 0.135    | 0.102                        | 89.0±0.3  | 490±30 | 0.63      | 133      |
|       | 0.113    | 0.095                        | 105.2±0.3 | 309±35 | 2.22      | 245      |
|       | 0.09     | 0.085                        | 108.2±0.3 | 284±29 | 3.15      | 185      |
|       | 0.068    | 0.067                        | 111.1±0.3 | 291±40 | 4.28      | 134      |
|       | 0.045    | 0.073                        | 112.7±0.3 | 304±53 | 4.34      | 90       |
| 35    | 0.135    | 0.104                        | 91.3±0.1  | 480±30 | 0.60      | 143      |
|       | 0.113    | 0.092                        | 106.9±0.4 | 330±28 | 2.31      | 231      |
|       | 0.09     | 0.084                        | 108.7±0.4 | 287±30 | 3.17      | 204      |
|       | 0.068    | 0.067                        | 112.9±0.4 | 303±42 | 4.48      | 140      |
|       | 0.045    | 0.073                        | 114.4±0.4 | 311±55 | 4.49      | 93       |
| 45    | 0.135    | 0.103                        | 97.1±0.4  | 493±37 | 0.62      | 120      |
|       | 0.113    | 0.091                        | 112.4±0.4 | 402±37 | 2.23      | 267      |
|       | 0.09     | 0.082                        | 118.4±0.1 | 354±30 | 3.64      | 174      |
|       | 0.068    | 0.065                        | 120.5±0.1 | 391±72 | 5.16      | 95       |
|       | 0.045    | 0.071                        | 120.7±0.1 | 386±48 | 4.35      | 65       |

Table 8.6:  $L_1$  fitting results for 0.08 oct:SDS ratio dilution. Constant parameters,  $\delta_{shell} = 3 \text{ \AA}$ ,  $SLD_{brine} = 5.7 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{shell} = 3.0 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{core} = -0.45 \cdot 10^{-6} \text{ \AA}^{-2}$

| T, °C | $\phi_v$ | scale | $I_{incoh}, \text{ cm}^{-1}$ | R, \AA    | L, \AA | $\chi^2$ |
|-------|----------|-------|------------------------------|-----------|--------|----------|
| 25    | 0.085    | 0.09  | 0.07                         | 15.6±0.2  | 54±10  | 40       |
|       | 0.071    | 0.07  | 0.07                         | 15.3 ±0.3 | 68±15  | 20       |
|       | 0.057    | 0.05  | 0.06                         | 14.8 ±0.3 | 150±20 | 34       |
|       | 0.043    | 0.04  | 0.05                         | 14.8 ±0.7 | 210±40 | 26       |
| 35    | 0.085    | 0.09  | 0.07                         | 15.3±0.2  | 50±10  | 56       |
|       | 0.071    | 0.07  | 0.07                         | 15.0±0.3  | 62±15  | 108      |
|       | 0.057    | 0.05  | 0.06                         | 14.5±0.2  | 130±20 | 39       |
|       | 0.043    | 0.04  | 0.05                         | 14.5±0.4  | 170±20 | 24       |
| 45    | 0.085    | 0.09  | 0.07                         | 14.8±0.1  | 45±10  | 113      |
|       | 0.071    | 0.07  | 0.07                         | 15.4±0.3  | 53±15  | 113      |
|       | 0.057    | 0.05  | 0.06                         | 14.2±0.2  | 115±40 | 113      |
|       | 0.043    | 0.04  | 0.05                         | 14.1±0.4  | 140±30 | 113      |

**Temperature scan fitting results**Table 8.7:  $L_\alpha$  Caillé model fitting results for 1.21 oct:SDS ratio temperature scan. Constant parameters,  $I_{incoh} = 0.109$ ,  $\delta_{head} = 3 \text{ \AA}$ ,  $N_{layers} = 50$ 

| T, °C | scale | $\delta_{tail}$ , Å | $\delta_m$ , Å | d, Å      | $\eta$    | $p_D$ | $\chi^2$ |
|-------|-------|---------------------|----------------|-----------|-----------|-------|----------|
| 25    | 0.65  | 9.2±0.1             | 24.4           | 137.0±0.3 | 1.00±0.01 | 0.12  | 654      |
| 30    | 0.64  | 8.9±0.1             | 23.9           | 137.0±0.3 | 1.00±0.07 | 0.11  | 718      |
| 35    | 0.32  | 9.2±0.1             | 24.5           | 137.0±0.2 | 1.00±0.06 | 0.06  | 475      |

Table 8.8:  $L_3$  model fitting results for 1.21 oct:SDS ratio temperature scan. Constant parameters,  $I_{incoh} = 0.12$ ,  $\delta_{head} = 3 \text{ \AA}$ ,  $N_{layers} = 50$ 

| T, °C | scale | B       | $\xi_3$ , Å | $\delta_m$ , Å | $\xi$ , Å | $\sigma$ , Å | $\chi^2$ |
|-------|-------|---------|-------------|----------------|-----------|--------------|----------|
| 35    | 0.68  | 4.6E-05 | 194.0±1.5   | 26.0±0.2       | 243.4±0.2 | 42.7±0.2     | 604      |
| 40    | 1.45  | 1.0E-04 | 114.9±0.4   | 27.0±0.1       | 219.2±0.1 | 39.8±0.1     | 234      |
| 45    | 1.47  | 1.4E-04 | 100.9±0.3   | 25.5±0.1       | 219.0±0.2 | 40.1±0.1     | 281      |
| 50    | 1.48  | 1.4E-04 | 97.0±0.3    | 25.3±0.1       | 215.3±0.2 | 40.7±0.1     | 252      |
| 55    | 1.52  | 1.4E-04 | 94.0±0.3    | 25.1±0.1       | 208.7±0.2 | 40.4±0.1     | 386      |
| 60    | 1.56  | 1.4E-04 | 91.0±0.3    | 25.9±0.1       | 202.0±0.1 | 40.0±0.1     | 570      |
| 65    | 1.56  | 1.5E-04 | 87.2±0.3    | 25.9±0.1       | 195.3±0.1 | 39.2±0.1     | 729      |
| 25    | 1.26  | 4.6E-5  | 151.1±0.7   | 25.5±0.0       | 237.3±0.1 | 49.6±0.1     | 552      |

Table 8.9:  $L_\alpha$  Caillé model fitting results for 1.15 oct:SDS ratio temperature scan. Parameters have been kept constant  $I_{incoh} = 0.12$ ,  $\delta_{head} = 3 \text{ \AA}$ ,  $N_{layers} = 50$ 

| T, °C | scale | $\delta_{tail}$ , Å | $\delta_m$ , Å | d, Å      | $\eta$    | $p_D$ | $\chi^2$ |
|-------|-------|---------------------|----------------|-----------|-----------|-------|----------|
| 25    | 0.86  | 10.2±0.3            | 26.3           | 137.0±3.0 | 1.00±0.02 | 0.14  | 263      |
| 30    | 0.86  | 10.2±0.3            | 26.3           | 137.0±3.0 | 1.00±0.02 | 0.14  | 306      |
| 35    | 0.87  | 10.2±0.3            | 26.4           | 137.0±3.0 | 1.00±0.02 | 0.13  | 604      |
| 40    | 1.00  | 9.4±0.3             | 24.9           | 142.1±3.0 | 1.00±0.02 | 0.13  | 234      |
| 45    | 0.98  | 9.2±0.3             | 24.4           | 144.2±3.0 | 0.99±0.01 | 0.12  | 281      |
| 50    | 0.99  | 9.0±0.3             | 24.1           | 145.6±3.0 | 0.97±0.02 | 0.12  | 252      |
| 55    | 0.90  | 8.9±0.3             | 23.7           | 146.2±2.0 | 0.98±0.02 | 0.11  | 386      |
| 60    | 0.99  | 8.7±0.3             | 23.4           | 146.7±2.0 | 0.98±0.02 | 0.11  | 570      |
| 65    | 0.90  | 8.5±0.3             | 23.0           | 148.4±2.0 | 0.90±0.01 | 0.12  | 729      |
| 25    | 0.99  | 9.3±0.3             | 24.5           | 150.0±1.0 | 0.98±0.01 | 0.12  | 552      |

Table 8.10:  $L_\alpha$  Caillé model fitting results for 1.08 oct:SDS ratio temperature scan. Constant parameters,  $I_{incoh} = 0.11$ ,  $\delta_{head} = 3 \text{ \AA}$ ,  $N_{layers} = 20$ ,

| T, °C | scale | $\delta_{tail}$ , Å | $\delta_m$ , Å | d, Å      | $\eta$    | $p_D$ | $\chi^2$ |
|-------|-------|---------------------|----------------|-----------|-----------|-------|----------|
| 25    | 0.47  | 10.5±0.2            | 27.0           | 152.9±0.6 | 1.00±0.02 | 0.24  | 184      |
| 30    | 0.50  | 10.1±0.2            | 26.2           | 153.6±0.5 | 1.00±0.02 | 0.22  | 169      |
| 35    | 0.53  | 9.7±0.1             | 25.3           | 154.2±0.4 | 1.00±0.01 | 0.18  | 224      |
| 40    | 0.55  | 9.3±0.1             | 24.6           | 154.5±0.4 | 1.00±0.01 | 0.15  | 201      |
| 45    | 0.56  | 9.1±0.1             | 24.2           | 155.0±0.3 | 1.00±0.01 | 0.13  | 252      |
| 50    | 0.56  | 8.9±0.1             | 23.8           | 155.4±0.4 | 1.00±0.02 | 0.12  | 284      |
| 55    | 0.56  | 8.7±0.1             | 23.3           | 156.5±0.3 | 0.99±0.02 | 0.11  | 429      |
| 60    | 0.56  | 8.5±0.1             | 23.0           | 157.0±0.4 | 0.98±0.02 | 0.11  | 585      |
| 65    | 0.55  | 8.4±0.1             | 22.9           | 157.1±0.4 | 0.97±0.01 | 0.11  | 641      |
| 25    | 0.50  | 9.4±0.1             | 24.7           | 160.0±0.4 | 1.00±0.01 | 0.13  | 625      |

Table 8.11:  $L_4$ - $L_1$  fitting results for 0.62 oct:SDS ratio temperature scan. Constant parameters,  $I_{incoh} = 0.86$ - $0.89 \text{ cm}^{-1}$ ,  $SLD_{brine} = 6.23 \cdot 10^{-6} \text{ \AA}^{-2}$

| T, °C | d, Å      | L, Å     | $L_4/L_1$ | $\chi^2$ |
|-------|-----------|----------|-----------|----------|
| 25    | 13.6±0.1  | 309±25   | 2.22      | 245      |
| 30    | 105.2±0.2 | 329±28   | 2.37      | 333      |
| 35    | 107.1±0.2 | 330±28   | 2.31      | 231      |
| 40    | 106.9±0.2 | 331±27   | 2.05      | 235      |
| 45    | 106.6±0.3 | 402±35   | 2.23      | 267      |
| 50    | 112.4±0.3 | 493±43   | 2.12      | 242      |
| 55    | 118.3±0.3 | 654±18   | 1.55      | 258      |
| 60    | 119.4±0.4 | 846±71   | 1.29      | 224      |
| 65    | 142.7±0.6 | 1008±86  | 1.02      | 227      |
| 25    | 157.2±0.7 | 1213±108 | 1.29      | 194      |

Table 8.12:  $L_1$  fitting results for 0.08 oct:SDS ratio temperature scan. Constant parameters, scale = 0.068-0.070  $I_{incoh} = 0.067$ - $0.069 \text{ cm}^{-1}$ ,  $\delta_{shell} = 3 \text{ \AA}$ ,  $SLD_{brine} = 5.7 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{shell} = 3.0 \cdot 10^{-6} \text{ \AA}^{-2}$ ,  $SLD_{core} = -0.45 \cdot 10^{-6} \text{ \AA}^{-2}$

| T, °C | R, Å     | L, Å    | $\chi^2$ |
|-------|----------|---------|----------|
| 25    | 15.2±0.3 | 67.9±20 | 19       |
| 30    | 15.7±0.3 | 61.6±20 | 20       |
| 35    | 15.0±0.3 | 61.8±18 | 19       |
| 40    | 14.9±0.3 | 58.8±15 | 19       |
| 45    | 15.4±0.3 | 53.4±14 | 111      |
| 50    | 15.3±0.3 | 51.2±12 | 109      |
| 55    | 15.2±0.3 | 48.9±10 | 108      |
| 60    | 15.0±0.3 | 46.7±8  | 110      |
| 65    | 14.9±0.3 | 44.6±6  | 113      |
| 25    | 15.8±0.3 | 65.8±20 | 135      |

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