Complex fluids under microflow probed by SAXS: rapid microfabrication and analysis

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Abstract. We report a combined microfluidic and online synchrotron small-angle X-ray scattering (SAXS) study of complex surfactant mixtures under flow. We investigate the influence of a series of flow constrictions, generating well-defined, periodic extensional flow fields, on the microstructure of two model surfactant mixtures containing SDS and CTAC. Specifically, the lamella spacing, orientation and structural order are reported and correlated with the imposed flow field: geometry, flow velocity and residence time. The design, fabrication and operation of a microfluidic system using rapid prototyping is described in detail. We show that polydimethyl siloxane (PDMS), ubiquitous in microfabrication, provides a suitable matrix for SAXS microdevices provided that: (i) PDMS thickness are kept to a minimum while retaining structural integrity ($\sim$1000$\mu$m) and (ii) scattering from the structure of interest is sufficiently decoupled from the amorphous background scattering. The combination SAXS-microfluidics provides unprecedented opportunities to elucidate the non-equilibrium structure formation and relaxation of complex fluids, demonstrated here for concentrated surfactant mixtures.

1. Introduction

Microfluidic technologies have evolved rapidly in the last two decades and find a multitude of applications, particularly in the fields of chemistry and biology. Microdevices \cite{1–3} miniaturize and expedite discovery, synthesis of new chemicals and drugs, \cite{4–6} facilitate process automation and provide novel opportunities for analytical tools such as separation techniques and large mapping and screening for protein crystallisation. \cite{7,8} Although far less exploited, microfluidics provides unprecedented opportunities in physical sciences. \cite{9,10} High degree of flow field control and uniformity are achieved through exploiting the change of fundamental physics upon reducing processes to the microscale. \cite{11} Particularly, viscous dissipation dominates mass transport whilst inertial effects may be generally neglected. With very little or no inertia, flow control is increased with disappearance of numerous flow instabilities making prominent other phenomena and their effects. \cite{12,13} Further, non-Newtonian rheology of complex fluids in confinement opens so far unexplored fluid mechanics, for example when fluid characteristic timescales and flow dynamics

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become comparable. [14] In this study, we take advantage of this particular advantage offered by microfluidics to impose highly defined and controlled flow fields to investigate flow contributions to ordering surfactant systems under processing. Such mixtures are ubiquitous in personal care and food industries and their non-equilibrium behaviour under shear have been extensively investigated. [15] For surfactant mixtures containing surfactant, co-surfactant and water, an interesting reversible phase transition from lamellar phase to multilamellar phase with shear is observed. [16, 17] Typical shear flows imposed on these systems are generally pure shear or extensional shear. The range of applied shear may be extended with microfluidics and allow the decoupling of different components [9] and the understanding of their impacts on the flow. Microfluidics brings an innovative approach to applying a designed and controlled flow while simultaneously analysing its effects on the microstructures of a system of interest.

In this article, we present a novel approach combining Small-Angle X-ray Scattering (SAXS) measurements online in a microfluidic chip which is illustrated by the results obtained for a complex fluid microflow containing a surfactant, co-surfactant and water. A few other microfluidic SAXS experiments have already been explored with different materials such as polycarbonates, polyimides, [18], which scatter very little X-rays. The importance of the chosen material for fabricating microdevices, which will be used with X-rays is reviewed by Greaves and Manz. [19] The micro-fabrication technique presented in this paper offers many advantages: a rapid prototyping fabrication technique, the use of materials chosen according to the studied flow and their scattering behaviour with X-rays, and the flexibility of measuring at any desired location on the entire chip with minimal beam damage.

2. Experimental

2.1. Microfluidic device fabrication

The microfluidic chips were custom made for SAXS measurements using a modified soft lithography method with polydimethylsiloxane (PDMS) and glass. Both materials were chosen for their compliance with soft lithography, replication fidelity, low cost, chemical compatibility with the studied systems, and relatively low X-ray scattering properties. The soft lithography methodology employed is schematised in Figure 1.

The microchannels are designed using a CAD program and the negative is printed on acetate sheets at high resolution of 20000 dpi (CAD-Art, California) to create a photomask. Photoresist SU-8 2025 (Microchem) is spin coated with desired thickness for the microchannel height on a silicon wafer ([100] single side polish, Compart Technology). The photomask is then used to polymerise the photoresist and form the microchannels on the silicon wafer using a dose of 380 mJcm$^{-2}$ UV light. The unpolymerised photoresist is washed away. A thin film of approximately 1 to 2 mm of PDMS monomer mixed with curing agent is cast on the silicon wafer. Separately, a block of 1cm thick PDMS is made in the shape of the window that will cover the majority of microchannels. The block is placed in a 40kHz oxygen plasma chamber (Diener) at a power of 60W for 5 minutes twice with turning the slab in between to glassify all its surface. Once the surface of the PDMS block transformed into glass, the block is positioned on the silicon wafer on top of the PDMS layer where the microchannels are located. A second thicker layer of PDMS and curing agent is poured around the glassified PDMS block to provide mechanical strength. Once the PDMS cured, the central block is lifted to reveal a window on top of the microchannels where the SAXS measurements will be performed. The microfluidic chip is cut out and separated from the silicon wafer. Holes are punched where the silicon tubings will be fixed within the thicker PDMS walls and the PDMS stamp is irreversibly sealed to a glass coverslip. A schematic of ready to use microfluidic chip is shown in Figure 2.
Figure 1. Soft lithography methodology employed for SAXS microfluidic chip fabrication: Photomask design and print; SU8 master fabrication; microdevice replication in PDMS thin film; PDMS structural reinforcement; coring for inlet/outlet ports and irreversible oxygen plasma sealing.

Figure 2. Wireframe design of an illustrative tubular micro-SAXS chip.

The channel sizes were approximately 70 microns in height, 16 cm in length and with widths varying from 100 to 2000 µm. Figure 3 depicts a profilometry of the microchannels used for the SAXS measurements. Three-dimensional surface maps were obtained using vertical scanning interferometry on a Wyko NT9100 Optical Profiling System (cf. Figure 3).

2.2. Surfactant systems: CTAC and SDS

Two model surfactant systems were investigated. One system consists of a mixture of 17.4 wt% of hexadecyl trimethyl ammonium chloride (CTAC: C_{16}H_{33}N(CH_{3})_{3}Cl\textsuperscript{−}), 20 wt% of 1-pentanol (C_{5}H_{11}OH) and 62.6 wt% of water. The CTAC/Pentanol/Water system is compared to another surfactant system made up of 6.5 wt% sodium dodecyl sulfate (C_{12}H_{25}NaO_{4}S), 7.9 wt% 1-octanol (C_{8}H_{17}OH) in brine (20g/L NaCl in water). The phase behaviour of SDS/Octanol/Brine was reported earlier by Roux and co-workers. [17,20,21] The thermodynamics of the CTAC system is reported elsewhere. [22] Both systems were chosen for their lamellar equilibrium phase forming multi-lamellar vesicles under shear. In both cases, the surfactant is dissolved into the aqueous phase and then the co-surfactant is added to the solution and vigorously mixed by shaking the sample for approximately one minute.
2.3. SAXS measurements and microdevice setup

Synchrotron SAXS measurements were carried out at the I22 beamline at Diamond Light Source, Oxfordshire, U.K with an X-ray beam of $\lambda=1.4\text{Å}$, energy of approximately 8.9keV and beam cross-section of $150\times100\ \mu\text{m}^2$. The microdevice comprises PDMS and glass, chemically compatible with the systems under flow. To minimise background scattering, the glass and PDMS thicknesses were kept to a minimum: a glass microscope coverslip (1x3 inch$^2$) of thickness 150 $\mu\text{m}$ was used as the base material, imparting mechanical strength to the microdevice. X-ray scattering of the PDMS as a function of thickness is depicted in Figure 4 and defined an acceptable range of elastomer thickness, namely that it should be kept below 1.5mm; a cm-thick layer of PDMS reinforces the microdevice outside the scattering region (cf. Figures 1 and 2).

![Figure 3. Profilometer scan of a representative contraction/expansion microchip.](image)

![Figure 4. Radially averaged SAXS profile of PDMS microchips with varying PDMS thicknesses ranging from approximately 0.9 mm (top) to 1.8 mm (bottom) and constant glass coverslip thickness of 150 $\mu\text{m}$; indicating strong attenuation with increasing PDMS thickness. Device thickness is kept around 1 mm near the microchannels and background subtraction is carried out by measuring spectra adjacent, but outside, the channel to minimise uncertainty.](image)

The scattering range of interest is important in the choice of appropriate background
materials, as illustrated in Figure 5c where two different systems, CTAC and SDS surfactants systems, were analysed with SAXS in the PDMS/glass microchips. The characteristic scattering halo of PDMS is located at a q-range between 0.01 and 0.1Å⁻¹. In the case of our chosen flow with the CTAC surfactant system, its scattering peak is located at the end of the scattering q-range of the PDMS with q = 0.1065Å⁻¹ and is therefore easier to pick up the Bragg peak for the system under flow. Whereas with the SDS surfactant system, its characteristic scattering peak is located at a rather low scattering angle at approx. 0.04Å⁻¹ and overlaps with the scattering region of PDMS. Although a careful background subtraction reveals the scattering pattern of the SDS system under flow, results presented in this paper will concentrate on the CTAC system with stronger and more distinguishable SAXS measurements.

The microchip was firmly clamped on a upright stand mounted on a programmable XYZ stage and connected to a Harvard PHD 2200 syringe pump controlled by LabVIEW. The microchip holder was leveled on the XYZ stage and the sample-detector distance (defined as the z-coordinate) remained unchanged throughout the measurements. Locating the exact position of the X-ray beam can be technically challenging when performing SAXS measurements on a microdevice positioned on a XYZ stage. By placing small markers of lead tape beside various reference locations around the network of microchannels and by scanning the chip in both the x and y directions to detect the lead tape markers, the exact coordinates of the microchannels were determined.

3. Results and discussion

3.1. Microdevice background scattering and optimisation

Figure 5a depicts the 1D-SAXS of the two surfactant systems at equilibrium. The scattering peak for the SDS system is located at lower q (q = 0.0409Å⁻¹) than the CTAC scattering peak (q = 0.1065Å⁻¹). Both systems form lamellae at these concentrations and the scattering peaks thus correspond to the interlamellar distances, respectively 153.7Å for the SDS/Octanol/brine and 59Å for the CTAC/Pentanol/Water. Upon shear (Figure 5b), the interlamellar distances decrease by typically 0 to 5Å. The scattering patterns of both systems in the microfluidic chip is shown in Figure 5c. The background scattering contribution of the microfluidic chip is also graphically represented. As observed, the scattering peak of CTAC/Pentanol/Water is clearly visible despite the background contribution since its location is at higher q than the PDMS hallow. In contrast, the scattering peak of the SDS/Octanol/Brine mixture under flow is masked due to the microfluidic chip scattering. Therefore, a thin PDMS/glass microfluidic chip appears to be of good choice for SAXS measurements of a CTAC/Pentanol/Water flow, while a more optimal choice of materials, or careful background subtraction, would be necessary to perform online SAXS measurements on SDS/Octanol/Brine system.

3.2. Beam damage and reference locations

Another important aspect to consider for SAXS measurements is the impact and X-ray beam damage on microchips. The X-ray beam cross-section employed was 150x100 µm and measurement acquisition times ranged from 10s to several minutes cumulatively. Since the measured system is under flow, the actual exposure time of the specimen is determined by the flow velocity and is typically 0.01s. Figure 6 shows how at the same beam location on the microfluidic chip, the scattering intensity is not affected by multiple acquisitions of 10s and Figure 7 is an optical micrograph of a microfluidic chip post-SAXS measurements highlighting how the PDMS is minimally marked by the X-ray beam, which turns out to be an advantage in terms of precisely locating on the chip measurements made by the X-rays.
Figure 5. (a): 1D-SAXS graph of quiescent SDS/Octanol/aq. NaCl (○) and quiescent CTAC/Pentanol/Water (△); (b): 1D-SAXS graph of quiescent (●) and sheared (○) SDS/Octanol/aq. NaCl, and quiescent (▲) and sheared (△) CTAC/Pentanol/Water; (c): 1D-SAXS of microflows of SDS/Octanol/aq. NaCl (○) and CTAC/Pentanol/Water (△) and microfluidic chip background only (□). (d) 2D-SAXS pattern for a CTAC microflow specimen before (top) and after (bottom) background subtraction.

Figure 6. Radially averaged SAXS profile of three sequential measurements (black, red and green consecutively and each of 10s acquisition time) acquired for PDMS microchip at the same location showing minimal SAXS beam damage.

3.3. Surfactant mixtures under periodic microfluidic flow
We present two examples of online microfluidic SAXS measurements. First, the flow profile of the CTAC/Pentanol/Water system across the width of a simple microfluidic channel is illustrated
in Figure 8 at different locations down the microfluidic chip. The flow rate in this example is of 1 ml/h corresponding to an average flow velocity of approximately 7 mm/s. These three flow profiles at sequential locations down a microchannel characterise the microstructural alignment under flow. For the first flow profile at $x_a$, the lamellar structures in the CTAC system are orientated with the flow near the channel walls and reach an orientation orthogonal to the flow in the middle of the channel. For the following two flow profiles at $x_b$ and $x_c$, the microstructures relax in time through an unpatterned wide microchannel and become generally aligned with the flow. This orientation flip can be rationalised as follows: the first flow profile was acquired immediately after a microchannel width expansion from $1000 \, \mu m$ to $2000 \, \mu m$ causing a flow deceleration which in turn forces the lamellae to rotate perpendicular to the flow at the centreline. The microstructures then relax back to flow alignment as shown in the following two flow profiles.

Next, we report on the influence of a series of periodic contraction/expansion flows on the CTAC surfactant mixture, shown in Figure 9. The surfactant system was first flowed through a series of four constrictions from widths of $1000$ to $100 \, \mu m$ and length of $700 \, \mu m$ with a flow rate of $5 \, mL/h$ (Figure 9a). The effects of the extensional flow field are seen in both orientation and size of the structures present. The lamellae sheets change orientation after the constriction to align themselves perpendicularly to the flow at the centreline. The 2D-SAXS patterns clearly show this orientation flip in Figure 9b in accord with the observation of Figure 8. The change in orientation is analysed by plotting the integrated scattering intensity at different azimuthal angles (Figure 9c). For structures aligned with the flow, the integrated scattering intensity is maximum at azimuthal angles of $90$ and $270^\circ$, while for those aligned perpendicularly to the flow, peaks are expected at $0$ and $180^\circ$. Along the channel width, shifts in the azimuthal angles of the intensity peaks are clearly observed: close to the walls lamellae are aligned with the flow and the maximum intensity is thus found at $90$ and $270^\circ$ associated with wall shear; in the flow centreline, the intensity maxima sharpen at azimuthal angles of $0$ and $180^\circ$ corresponding to highly oriented lamellae structures perpendicularly aligned to the flow. As for the effects on the interlamellar spacing, Figures 9d and 9e show that the extensional flow field had no immediate effect as the scattering peak location remains constant within measurement uncertainty in $q$ across the width of the channel. Figure 9f plots the relative intensity of the scattering peak across the channel width. The structural order therefore depends on channel position and is evidently associated to the parabolic velocity profile that occurs in pipe flow. Upon a series of constrictions followed by relaxation (not shown here), the rheological properties of the CTAC system and the lamellar spacing are significantly altered, depending on the microchannel geometry. The combination of synchrotron SAXS and microflow processing thus permits continuous monitoring of structural changes and the impact of a well-defined flow fields on non-equilibrium phase behaviour of complex mixtures.
Figure 8. 2D-SAXS profiles of CTAC/Pentanol/Water across a microchannel of width 2000 \( \mu \text{m} \) at different locations indicated a, b, and c along the microfluidic channel at a flow rate of 1 ml/h corresponding to residence times of 9, 26 and 73s. Coordinates on the left axis indicate position orthogonal to flow. Top left schematic in each 2D-SAXS profiles relate to the orientation and intensity of the scattering pattern.
Figure 9. (a) microchannel design for a series of four 100 µm wide constrictions; (b) 2D-SAXS flow profiles of CTAC/Pentanol/Water across microchannel width (1000 µm) located after the first constriction, subject to a flow rate of 5 ml/h. \( y_0 \) indicates the centre of the channel and on either sides \( y_1, y_2, y_{-1}, \) and \( y_{-2} \) annotate the locations where the SAXS measurement was acquired across the width of the channel on, each spaced out by 250 µm. White arrows indicate the orientation of the lamella sheets and are proportional to the scattering intensity; (c) azimuthal scattering intensity at the structural peak; (d) 1D-SAXS patterns corresponding to the locations indicated in panel (b); (e) lamellar spacing as a function of the position across the channel; (f) intensity of the structural peak as a function of the position across the channel.
4. Concluding remarks

Online microfluidic SAXS measurements on model surfactant mixtures were successfully carried out in custom made microchips. These measurements were possible after a careful choice of materials and methodology for microchip fabrication for the systems of interest. A modified rapid prototyping approach enabled fast, effective and inexpensive fabrication of chips. The SAXS results illustrate the insight obtainable for surfactant microstructures under continuous flow: size, orientation and order of lamellar sheets were monitored under straight and contraction/expansion flows. Online microfluidic SAXS measurements elucidate the impact of specific flow fields on surfactant systems, providing guidance for industrial processes and further understanding of fundamental behaviour of such complex systems under external fields.

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