Influence of surface modifications and channel structure for microflows of supercritical carbon dioxide and water

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ABSTRACT

Miniaturization offers a possibility to increase the performance and decrease the time scales of systems. Existing microsystems using supercritical CO2 mainly utilizes multiphase segmented flows. To allow for a broader toolbox for future systems, also parallel flows are useful which eases the separation of the different phases. Here, the effect of different surface coatings are studied for multiphase flows of scCO2 and H2O in flat microchannels, with and without a 4 µm high ridge guide, which allows for pinning of the fluid interface inside the 190 µm wide and 35 µm high channel. Three different surfaces with different wettings toward scCO2 and H2O are studied, where a surface terminated with a hydrocarbon-based silane was observed to be neutral in the H2O/scCO2 system, a surface terminated with a fluorocarbon-based silane was hydrophobic, and an uncoated glass surface was hydrophilic.

Using two flow rates of 5:5 µl/min (CO2:H2O) and 6:3.5 µl/min (CO2:H2O), a parallel flow between scCO2 and H2O was observed for uncoated and flat channels where the H2O flow pushed the CO2 to the side, before the flows eventually breaks up into segments. With a ridge guide in the middle of the channel, the interface was pinned at half the channel width, although still breaking up into segments. The neutral hydrocarbon-based surface coating with approximately 90° contact angles resulted in evenly created segments without a ridge guide. Including a guide in the middle of the channel, a parallel flow was observed throughout the channel, although occasionally small CO2 segments entered the H2O outlet. Using the fluorocarbon-based silane resulted in an unstable segmented system with pressure fluctuations.

Using surface modifications, an increased control can be achieved for either segmentation or parallel flow where a neutral surface is favored for a stable flow behavior. Together with a ridge guide, the fluid interface was pinned at the center.

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1. Introduction

In chemistry, and especially green chemistry and bioprocesses, synthesis and analyses often excel at high densities and high temperatures. Higher pressure enables the use of supercritical CO2 (scCO2) as a green solvent with properties that can be fine-tuned by changing temperature and pressure. To reach the supercritical state for CO2, the temperature and pressure needs to be increased above 31.1 °C and 7.38 MPa, respectively, both having a large influence on the density [1] and the viscosity [2] of CO2. Miniaturization offers a possibility to increase the performance and decrease the time scales of systems. Also, it allows for processing at high pressures without loss in safety. With an increasing utilization of scCO2 in green chemistry [3], the new field of “supercritical microfluidics” is emerging, where the advantages of supercritical fluids are combined with the effects of miniaturization, e.g. lower reagent consumption, and fast mass and heat transfer [4].

Existing microsystems using supercritical fluids mainly utilize segmented flows of scCO2 and H2O. Using a glass–silicon chip, Tiggelaar et al. studied the formation of carbamic acid from N-benzylmethylamine and scCO2 [5]. Also, scCO2 has been used as a solvent to extract vanillin from an aqueous solution in a segmented flow [6], and aromatic monomers from lignin oxidation products [7], using a glass/silicon microfluidic device. Recently, Marre et al. have demonstrated how a simple glass/silicon chip can be used for many applications, e.g. a pressure–volume–temperature cell for scCO2 [8], quantum dot synthesis using supercritical hexane [9], and supercritical water oxidation [10].

High-pressure microfluidics using segmented flows offers reliable systems and stable conditions for processes. For both analysis and separation, fully separated phases ease the handling.
However, separating the different phases from a segmented flow at high pressures is a challenge that requires additional components and existing systems have not been able to split up scCO₂ and H₂O efficiently [6,7,11].

Apart from the physical properties of the two fluids, their surface interactions have been shown to have a strong influence in a parallel flow chip [12,13]. Modifying the surface inside a channel is also a well-known strategy in microfluidics to control the wetting, and thus the surface tension. Combining a surface treatment with pinning of multiphase interfaces to a guide, stable parallel flows have been created for situations where instabilities otherwise are expected to break up the flow [13]. Hibara et al. demonstrated how combining structuring together with a modified surface allowed for a counter-current flow between nitrobenzene and H₂O inside a glass microchip using an octadecylsilane coating [14]. Depositing self-assembled monolayers of silanes with low surface energy tail groups is a common method to avoid stiction effects in MEMS devices [15,16], and glass surfaces are readily made hydrophobic with silanes to reduce sticking of valuable reagents in biological applications [17].

Guillaumet et al. modeled the effect of changing the wetting toward the surrounding surface in coaxial co-flows of H₂O and scCO₂, which was varied from hydrophobic to hydrophilic [18]. The surface tension was found to be an important parameter for the flow behavior in micro-channels and an increased jetting length of scCO₂ for lower surface tensions were predicted and experimentally verified in glass capillaries.

A parallel flow between scCO₂ and H₂O has been demonstrated by Ohashi et al., where extraction of tris(acetylatedonato)-cobalt(III) from scCO₂ into H₂O was studied [11]. To achieve this, two guided ridges separated three sections of the channel, where the middle section was coated using dimethylchlorosilane to prevent the H₂O from breaking up the scCO₂-flow in the middle channel. However, as H₂O also entered the CO₂ outlet, concentrations at the CO₂ outlet could not be analyzed.

Other previously mentioned studies have used different geometries and coatings to improve the applicability of two-phase systems of scCO₂ and H₂O [6,11,14]. To better understand the fluid mechanics of such modifications, this study investigates how the co-flow of scCO₂ and H₂O is affected by introducing a guide in-between the two fluids in a double Y-channel, and how three very different surfaces interact with the fluids. Apart from the uncoated glass surface, two surface modifications are studied for a fully coated channel; one hydrocarbon-based that is similar to what has previously been used for scCO₂ [11], and one fluorocarbon-based, not previously studied for scCO₂-based microflows, with an expected strong interaction with scCO₂.

2. Theory

In microfluidics, dimensionless numbers are often used to describe the flow mechanic regime of the system [19]. The Reynolds number (Re) describes the relation between the inertial forces (\( \rho U \)) and the viscous forces (\( \eta \)) depending on the fluid density \( \rho \), the flow velocity \( U \), a characteristic length \( R \), and the viscosity of the fluid \( \eta \). For \( Re < 2000 \), the viscous forces dominate and hence, no turbulence is present. The capillary number (Ca) and Weber number (We) describes the relation of the viscous forces (\( \eta U \)) and fluid inertia (\( \rho U^2 \)), respectively, in relation to the interfacial tension (\( \gamma \)).

For compressible systems where the density of the fluids varies, the volumetric flow rate will vary, while the mass flow rate will remain constant. Thus, by using the conservation of mass, the varying volumetric flow rate, \( Q \), will be described by

\[
\rho_1 Q_1 = \rho_2 Q_2.
\]

where \( \rho \) is the density and the subscripts denotes different locations in the system.

The wetting conditions between the two fluids of H₂O and scCO₂ inside the channel will depend on both the variable fluid density, together with surface interactions in the system, where Young’s relation describes the wetting as

\[
\gamma_{wc} - \gamma_{wh} = \gamma_{ch} \cos(\theta).
\]

Here, \( \gamma_{wc} \) is the tension between channel wall and CO₂ and \( \gamma_{wh} \) is the surface tension between the wall and H₂O, Fig. 1. \( \gamma_{ch} \) is the surface tension between the two fluids of CO₂ and H₂O, and \( \theta \) is the wetting angle of H₂O. Further, the capillary pressure in a rectangular channel can be described by the Young–Laplace equation,

\[
\Delta P = 2\gamma_{ch} \left( \frac{1}{w} + \frac{1}{h} \right) \cos(\theta),
\]

where \( w \) and \( h \) are the width and the height of the channel respectively [20]. Low capillary pressures are reached for situations where the surface tension \( \gamma_{ch} \) is low or where the wetting angle \( \theta \) approaches 90°. The surface tensions between the glass wall and each of the two fluids, \( \gamma_{wc} \) and \( \gamma_{wh} \), is determined by intermolecular forces, and for contact angles of 90°, both fluids will have a similar interaction with the wall, i.e. \( \gamma_{wc} = \gamma_{wh} \).

The surface tension between CO₂ and H₂O is dependent on the densities of the two fluids, with an empirical dependence on the two fluids densities according to

\[
\gamma_{ch} = C (\rho_h - \rho_r)^4,
\]

where \( \rho_h \) and \( \rho_r \) are the densities of CO₂ and H₂O, respectively, and \( C \) is an empirical constant [21]. At 50 °C, as the densities increase, the surface tension decreases, varying from 45 mN/m at 5 MPa to 35 mN/m at 15 MPa for saturated solutions [22]. Saraji et al. have studied the wetting angle between CO₂ and H₂O on a quartz surface, where the H₂O-droplet advancing and receding contact angles were reported to vary from 12° to 30° and 8° to 15° respectively, when the pressure and temperature was increased from 3.4 MPa at 35 °C to 11.7 MPa at 60 °C [23].

To provide hydrophobic surfaces, both hydrocarbon and fluorocarbon based tail groups have been used for silane coatings on silicon dioxide structures, with reported wetting angles above 110° of H₂O in air, respectively [16].

Influencing the surface interactions will change the fluid–wall surface tension, \( \gamma_{wc} \) and \( \gamma_{wh} \). These surface tensions will be connected to intermolecular forces. Fluorocarbons have weak cohesive forces and this leads to immiscibility with more high-energy interacting compounds such as H₂O. This immiscibility is also seen with hydrocarbons [24]. CO₂ on the other hand is any high degree of miscibility with fluorocarbon compounds and this miscibility is higher compared to hydrocarbons [25]. Therefore, for a wetting system composed of H₂O in CO₂ with a wall coated by either
fluorocarbon based or a hydrocarbon based silane, different wetting angles can be expected.

3. Material and methods

3.1. Design and manufacturing

The glass chip used in this study consists of two Y-intersections connected by a 10 mm long channel, approximately 190 μm in width, Fig. 2. The channel was 35 μm deep and was either etched planar, or with a ridge guide, initially approximately 10 μm high before bonding, in the middle at the bottom of the channel, Fig. 3.

The glass chips were manufactured from two 4” borofloat-33 glass wafers (Schott) using isotropic hydrofluoric acid wet chemical etching and standard UV lithography. To pattern the wafers, a positive photoresist was deposited and developed on top of 12 nm Cr layer followed by a 100 nm Au layer. Initially, 90 μm deep trenches were etched on both wafers to allow for connections. The channel and guide were etched only on one of the wafers using isotropic etching of hydrofluoric acid, where a 30 μm small strip was kept masked at the center of the channel before etching, and by under-etching of the mask, an approximately 10 μm high guide remained in the middle, as measured using a surface profilometer, Dektak 150 (Vecco). The wafers were manually aligned before being fusion bonded at 625 °C for 6 h, with a ramp of 2 °C/min. Due to the high temperature bonding at long times the surfaces smoothen and the guide shrunk to 4 μm, but with a sharper edge, Fig. 3. Glass capillaries (i.d. 75 μm, o.d. 150 μm) were glued to the outlets of the glass chip using Araldite Rapid (Huntman Advanced Materials).

The surface inside the channel was hydroxylated by first flushing with alcoholic potassium hydroxide solution followed by a deionized H2O rinse, after which the glass chip was dried for 20 min in a N2 flow. The alcoholic potassium hydroxide solution was prepared by dissolving 56 g potassium hydroxide in 70 ml H2O, after which the solution was diluted to 1000 ml with denatured ethanol.

To modify the channel walls, two different silanes were used, dimethylchlorosilane (DMDCS) and trichloro(1H,1H,2H,2H-perfluorooctyl)silane (FOTS). The reactive head group of chlorosilanes can bond to silanol groups present on hydroxylated glass surfaces [26]. The solutions were prepared of 68 mM DMDCS (Sigma Aldrich, >99.5%) in toluene as well as 1 mM FOTS (Sigma Aldrich, 97%) in isooctane. After flushing the whole channels with the silane solution for the intended coating, the channel was rinsed with the corresponding solvent, followed by a 20 min drying in a N2 flow.

To compare the contact angles of the surface coatings for water droplets in air, soda lime glass slides were cleaned, first in a piranha solution (1:1, H2SO4:H2O2) for 10 min, followed by RCA1 (5:1:1, DI:NH4OH:H2O2) and RCA2 (5:1:1, DI:HCl:H2O2) at 60 °C for 10 min, respectively. The glass slides were then coated in the same way as the glass chips with DMDCS and FOTS.

3.2. Measurement procedure

The glass chips for each of the coatings were supplied with a total flow rate of 10 μl/min at the pumps, and two flow rate ratios of 5:5 (μl/min CO2:H2O) and 6.5:3.5 (μl/min CO2:H2O) were used, hereafter denoted as flow ratios 1:1 and 2:1, respectively. A constant temperature of 40 °C for the fixed length backpressure capillary resulted in pressures of 11.4 MPa ± 0.5 MPa (95% confidence interval). The pressure varied because of the lower flow resistance with increasing CO2:H2O ratio at the outlet capillary. The temperature of the glass chip was kept at 49.6 ± 1.2 °C (95% confidence interval). Re, We, and Ca were calculated using linearly interpolated values from tabulated data of CO2 for density [1], viscosity [2] and the interfacial tension between H2O and CO2 [27]. For all measurements the Re were in the range of 10–20, Ca varied between 2.8 × 10−5 and 4.0 × 10−5, and We varied between 3.1 × 10−4 and 7.5 × 10−4, all calculated at the inlet channel of the CO2 flow for the corresponding temperature and pressure. To ensure an even CO2 flow rate when measuring, before each measurement, the standard deviation of the pressure variations were observed to be below 20 kPa for at least 10 min.

The glass chips were positioned on a heating stage next to a glued Pt-100 element to measure the chip temperature. The glass chips were fixated by Wacker P12 silicon paste, also covering the inlet and outlet glass capillaries, Fig. 4. Two ISCO Teledyne DM-100 syringe pumps were used to supply the two flows of CO2 and H2O. The outlets of the glass chip were connected to a T-junction, from where the system pressure was regulated using a 1.5 m long 25 μm i.d. glass capillary that was submerged in a temperature regulated H2O bath, kept at 40 °C. To achieve a stable CO2 flow, the pump was cooled down to 8 °C using a Lauda RK20 compressor, connected in parallel with a Lauda E100 heater using a parallel plate heat exchanger, giving temperature stability below 0.01 °C. The channel was imaged at 2500 fps using a high-speed camera, Phantom Miro M310, mounted to a microscope.
To ease interpretation, the two fluids were colorized during the post-processing using Gimp 2.8 image editing software.

To measure the contact angle between H₂O and air on the different surfaces, a H₂O droplet was dispensed on the glass slide surfaces using a 0.8 mm o.d. needle connected to one of the syringe pumps. Using the dead volume inside the outlet valve (HIP 15-11AF2) at the pump, the droplet volume was increased and decreased to measure the advancing and receding contact angles using the sessile drop technique [23]. For each surface coating, six measurements were collected, from which a mean value was extracted for the contact angles using Image J v1.47 software with drop shape plug-in.

4. Results

Fig. 5 shows a comparison for uncoated glass chips with and without a guide. For flat channels at equal flow ratio of 5:5 μL/min of scCO₂ and H₂O, the flow breaks up into segments approximately 1 mm after the channel entrance. Increasing the scCO₂ flow ratio, top right, the flow becomes parallel and breaks up further down the channel, after approximately 5 mm. Here, the scCO₂ is seen to be pushed to the channel side, resulting in a width only one quarter of the H₂O width. With a ridge guide in the middle for equal flow ratio, bottom left, the flow still breaks up into segments after 3 mm, but the scCO₂ flow width remained about half the channel width. When the flow ratio was increased, the parallel length increased to 6 mm before breaking up into segments.

Fig. 6 shows a comparison for the DMDCS coating, with and without a guide. Without a guide, the flow became segmented with evenly formed 0.5 mm long scCO₂ segments and 0.3 mm long H₂O segments for equal flow ratio at the two pumps. When increasing the flow ratio to 2:1 scCO₂:H₂O, the scCO₂ segments increased to 0.9 mm, although the H₂O segments remained 0.3 mm long.

Combining the DMDCS coatings with a guide, a parallel flow was achieved, where the parallel flow was sustained throughout the channel for equal flow rates of scCO₂ and H₂O with equal flow widths. Increasing the flow ratio, the scCO₂ flow occasionally pushed over to the H₂O side in small segments, which caused the parallel flow to temporarily break up, however never occupying the H₂O side with more than one segment at the time over the whole length.

For the FOTS coating at the flow ratio of 1:1, the flow behavior became cyclic with a period of approximately 30 s and pressure fluctuations were observed at the pumps of ±10 kPa resulting in an alternating segmented flow, Fig. 7. During pressure buildup, the H₂O segments were 1.4 mm long with 0.6 mm long scCO₂ segments, and for decreasing pressure, the scCO₂ segments became 1.4 mm long, with 0.6 mm long H₂O segments. Increasing the flow ratio to 2:1 scCO₂:H₂O, the flow stabilized with a continuous segmented flow with segment lengths of 0.5 mm for H₂O and 0.9 mm for scCO₂.

Combining the FOTS coating with a guide, the behavior was observed to be the same as without a guide for the 1:1 flow ratio, and the flow varied periodically between a partly parallel flow for 2.8 mm during a decreasing pressure, and a segmented flow with equal segment sizes of 0.9 mm during the increasing pressure. Again, the period was 30 s with pressure fluctuations of ±10 kPa. When increasing the flow ratio to 2:1, the flow behavior stabilized and was parallel for 1.0 mm before breaking up into segments with 0.5 mm long H₂O segments and 2.1 mm long scCO₂ segments.

The fluid behavior at the outlet is summarized in Fig. 8. For uncoated channels, one of the outlets was completely filled with H₂O, and a segmented flow was present at the outlet. Using the DMDCS coating without a guide, a segmented flow was present at both outlets. Together with a guide, the DMDCS coating resulted in an almost complete separation of the two fluids, although a thin scCO₂ flow was observed at the H₂O outlet, slowly moving in parallel with the H₂O flow. With the FOTS, one outlet was scCO₂ filled, and a segmented flow was present in the other.

The advancing and receding contact angles of the three surfaces; uncoated, DMDCS and FOTS, used for the three phase interface of air/H₂O/glass, together with the advancing and receding contact angles inside the channels are summarized in Table 1.

With regard to the contact angle experiments with H₂O droplets on a glass surface, they wetted very well on the uncoated surface, Fig. 9. With the two coatings, there was a clear hysteresis with much higher advancing contact angles, indicating an uneven surface coating with pinning effects. The DMDCS and FOTS coatings were weakly hydrophilic, with an advancing contact angle of 61° and 77°, respectively.

Fig. 10 shows the triple contact point inside the channel for each of the different surface coatings. With a hydrophilic contact angle, the H₂O was seen to have a much better wetting toward the uncoated glass surface compared to scCO₂. For the DMDCS coating, the contact angle was around 90°, which indicates a more equal wetting for the two fluids. The FOTS coating resulted in a hydrophobic contact angle much above 90°, with scCO₂ clearly wetting better toward the surface. Once again, the surface coatings had a clear hysteresis.

5. Discussion

For different surface modifications, the flow behaviors are different and flat, uncoated channels result in an initial parallel flow, which eventually breaks up into segments. For the parallel flow,
H₂O covers the majority of the cross section area. Hence, the flow velocity of scCO₂ is much higher than that of H₂O. The addition of a small ridge guide made the important change to keep the scCO₂ flow width pinned at approximately half the channel width and thus gave a lower velocity of the CO₂ flow. This should in general be favorable for applications were a longer residence time of scCO₂ in the channel is preferred.

With a DMDCS coating on flat channels, where the contact angles were close to 90° for both H₂O and scCO₂ inside the channel which indicates a balance between the three surface tensions: wall–CO₂, wall–H₂O, and CO₂–H₂O, the flow became segmented without an initial parallel flow at the inlet. Higher flow rates of scCO₂ resulted in larger scCO₂ segments. No tendency of a parallel flow was observed, as otherwise would have been expected with increasing the scCO₂-ratio [28]. For the combination of a guide and DMDCS coating, the flow was parallel with an equal width of the two flows. When the volumetric flow rate of scCO₂ was higher inside the channel compared to the volumetric flow rate of H₂O, the scCO₂ occasionally push itself into the H₂O side with small segments. With an increasing scCO₂ ratio, this phenomenon was more pronounced. The inclusion of a guide or not in a DMDCS coated channel may offer interesting design opportunities. Without the guide, instead of a stable parallel flow, a stable segmented flow was achieved for the two fluids. This enables micro devices to be created combining parallel flows and segmented flows in different sections of the chip, only governed by the presence of a guide or not. However, if this behavior will remain in more complex designs remains to be investigated since the pressure drop in a segmented flow channel is different to that of a channel with parallel flow.

Earlier studies using a DMDCS coating have reported parallel flow using a guide together with a half coated channel on one side of the ridge guide, although some parts of the H₂O flow entered the scCO₂ outlet [11]. With a good control over the system stability, a similar result was here demonstrated by coating the whole channel. However, instead of H₂O in the scCO₂ outlet, some scCO₂ entered the H₂O outlet. This offers a new functionality for microfluidic extraction as a pure CO₂ flow can be separated.

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**Fig. 5.** For flat uncoated channels at equal flow ratio of scCO₂ (lower entrance, green) and H₂O (upper entrance, blue), top left, the flow breaks up into segments approximately 1 mm after the channel entrance. Increasing the CO₂ flow ratio, top right, the flow becomes parallel and breaks up after approximately 5 mm. Here, the CO₂ is seen to be pushed to the channel side to a quarter of the H₂O width. With a guide in the middle for equal flow ratio, bottom left, the flow still broke up into segments, now after 3 mm, but the CO₂ flow width is remaining about half the channel width. Increasing the flow rate ratio, the parallel length increased to 6 mm before breaking up into segments. The two fluids were colorized during post-processing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 6.** For flat channels coated with DMDCS at equal flow ratio of CO₂ (lower entrance, green) and H₂O (upper entrance, blue), top left, the flow breaks up into segments, 0.3 mm and 0.5 mm long for H₂O and scCO₂ respectively, at the channel entrance. Increasing the scCO₂ flow ratio, top right, the scCO₂ segments increases to 0.9 mm with the H₂O segments still being 0.3 mm long. With a guide in the middle for equal flow ratio, bottom left, the flow became parallel, with an equal width for the two fluids, which remained throughout the whole channel. Increasing the flow rate ratio to 2:1 scCO₂:H₂O, the flow remains mostly parallel, although occasional segments appeared as the scCO₂ pushed over to the H₂O channel side, hence splitting up the flow. The two fluids were colorized during post-processing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Coating with FOTS resulted in an unstable system when the flow ratio at the pumps was kept equal. As the pressure was observed to vary in 30 s cycles, the compressibility of CO₂ resulted in two different regimes, one for increasing pressure and one for decreasing pressure. During the increasing pressure, the H₂O segments dominate. For decreasing pressure the opposite was observed with large scCO₂ segments. Using the hydrophobic FOTS coating, H₂O was observed to have an initial resistance of entering the channels, where H₂O always reached the wall on the CO₂ side before moving forward. This could in part be linked to the need of overcoming a capillary pressure induced by the low H₂O wetting created by the FOTS coating. For a mean contact angle of 125°, the capillary pressure is approximately 3 kPa at the channel inlet. This pressure is one order of magnitude lower compared to the observed system fluctuations and cannot alone explain the dynamics. However, given the complex situation of a multiphase flow with one compressible fluid and a single backpressure capillary regulator, the smaller fluctuations could be amplified by the system due to the varying segment sizes at the outlet capillary. In the FOTS coated microchip for the 1:1 flow ratio, no stable pressure was expected because of the changing flow resistance resulting from a completely H₂O-filled outlet capillary for short periods of time during the observed 30 s long pressure fluctuations, which periodically results in a much higher flow resistance compared to the multiphase flow, and therefore increasing the back-pressure. However, reaching the backpressures of a completely H₂O-filled capillary, the large expansion of CO₂ during the periods of decreasing pressure results in a CO₂-filled capillary with a much lower flow resistance, and therefore much lower backpressures, and the system would fluctuate between these two extremes. For higher flow ratios, the lower ratio of H₂O is believed to suppress this behavior, which consequently resulted in a more stable system.

The contact angles in the air/H₂O system were measured for each surface coating as a reference value. However, a surface resulting in low contact angles in air does not imply that the contact angle will remain low in scCO₂. For the uncoated glass surface, with hydrophobic contact angles around 6° in air, a similar behavior was observed inside the glass channels for the scCO₂ and H₂O segments where hydrophilic contact angles were observed. Here, γ_{air} is smaller as compared to γ_{wet} and the H₂O flow will have a favorable wetting. For H₂O in air on the DMDCS coating, higher contact angles were observed although still being hydrophilic. Interestingly, for the H₂O/scCO₂ system, the surface was more neutral inside the channels with contact angles between fluid segments close to 90°, i.e. γ_{wet} and γ_{wet} are similar. Hence, both fluids have a similar interaction with the wall and no capillary pressure gradient is present. Also worth noticing is that the magnitude of the surface tension between the two fluids for 90° angles is orthogonal toward the flow direction and the contact situation is therefore independent on the magnitude of the surface tension.

The FOTS coating resulted in a slightly larger contact angle for H₂O in air compared to the DMDCS. For the H₂O/scCO₂ system, this coating resulted in a hydrophobic contact situation where γ_{wet} was larger compared to γ_{wet}, resulting in a favorable wetting for scCO₂.

CO₂ is soluble in H₂O and when the amount of CO₂ in H₂O varies, the density will change until a full saturation of each of the two phases are reached [29]. As the density vary, the surface tension will also vary in accordance with Eq. (4). The phases entering the channel are initially non-saturated, and the density variations over the channel length are unknown, resulting from diffusion toward the full saturation of each of the two phases. However, here no visible variations in contact angles were observed along the channel, which indicates that this effect was small at the timescale studied.
When the temperature changes, the density of the fluid will change. For H₂O, with a critical point at 374 °C and 22 MPa, the variations in density at lower temperatures are very small within the temperature and pressure range used in this study. However, close to and beyond the critical point, the density variation is significant for both H₂O and CO₂. With varying density, the volumetric flow rate will vary. Thus, controlling and knowing the CO₂ flow rate inside the microchip is a challenge. Within the scope of this study, the volumetric flow rate of scCO₂ is estimated to be approximately 60%–120% higher at the entrance to the main channel compared to the flow rate at the CO₂ syringe pump. This will shift the volumetric flow ratio inside the channel and also affect the segment sizes, which can be seen for the flat DMDCS coated channel with an 1:1 ratio at the pumps, where the estimated flow rate, considering the large variation in density of CO₂, is 5 μl/min H₂O and 10 μl/min scCO₂ at the chip. This correlates well to the measured segment sizes of 0.3 mm for H₂O and 0.5 mm for scCO₂.
6. Conclusions

For the uncoated and flat glass channels, a parallel flow between \( \text{H}_2\text{O} \) and scCO\(_2\) was observed, where scCO\(_2\) only was occupying approximately a fifth of the channel width before eventually breaking up into segments. By including a ridge guide in the middle of the channel, the interface was pinned at half the channel width, although still breaking up into segments. When coating the surface with a DMDCS-coating, the contact angles between \( \text{H}_2\text{O} \) and scCO\(_2\) was measured to be approximately 90°, indicating a neutral surface. This resulted in evenly created segments for flat channels, and when including a guide in the middle of the channel, a parallel flow was observed throughout the channel. Using a FOTS coating, a hydrophobic coating in the scCO\(_2)/\text{H}_2\text{O}/\text{glass} \) system was created. This resulted in an unstable segmented system with large pressure fluctuations.

The result presents clear effects from surface modifications on the fluid behavior. Correct surface modifications offer increased control over segmentation and parallel flow behavior. Furthermore, by including a ridge guide, the fluid interface can be pinned at the center of the channel, providing well-defined cross sectional areas and lowering the scCO\(_2\) flow velocity.

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