Interfacial tension controlled W/O and O/W 2-phase flows in microchannel†
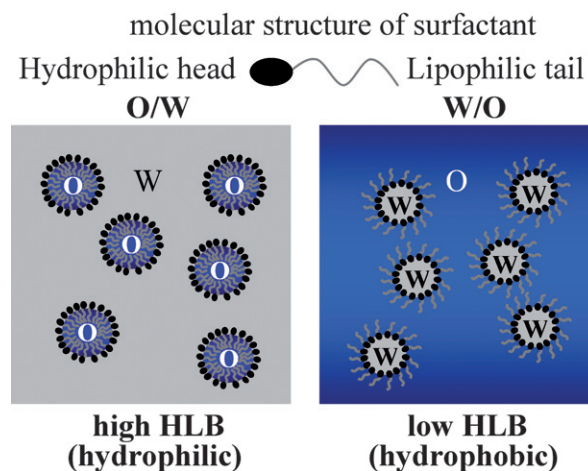
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In microfluidic systems, interfacial tension plays a predominant role in determining the two-phase flow behavior due to the high surface area to volume ratio. We investigated the influence of both solid–liquid (σ_{SL}) and liquid–liquid (σ_{LL}) interfacial tensions on water–oil two-phase flows in microfluidic devices. Experimental results show that, unlike macroscopic systems, σ_{SL} plays a dominant role, determining the emulsion type created in microchannels: oil-in-water (O/W) flow in hydrophilic microchannels and water-in-oil (W/O) flow in the corresponding hydrophobically treated microchannels. Modification of σ_{LL} by surfactants only plays a secondary role. By tuning σ_{LL}, oil–water two-phase flow patterns could be changed from droplet-based to stratified flows under constant flow conditions in the same device. In addition, also droplet deformation, coalescence and emulsion inversion could be achieved by tailoring σ_{SL} and σ_{LL} in microfluidic devices. Microfluidic technology therefore provides a valuable additional tool for quantitatively manipulating and evaluating these phenomena which are difficult to realize in the macroscale devices.

1 Introduction

An emulsion is a mixed system (water and oil) in which one phase (referred to as the dispersed phase) is suspended in the other one (referred to as the continuous phase) as small droplets. The basic simple emulsion types are water-in-oil (W/O) and oil-in-water (O/W). In terms of (technological) applications, emulsions are vital in our daily life. Food, cosmetic, pharmaceutical and oil industries need to control emulsion properties, such as emulsion type, viability and stability, to obtain the desired products.[1–3] However, an emulsion produced by simply mixing oil and water without adding any surfactant is not stable and will quickly revert to the two individual phases. Emulsifiers such as surfactants are used to create stable emulsions; where their function is to decrease interfacial tension in order to reduce the mixing energy and to generate stable interfaces between the two phases. Emulsification is typically not a spontaneous process, but extra energy needs to be supplied for instance by stirring, shaking, spraying or sonication. Recently, microfluidic technology has become an alternative reliable method to create controlled and monodisperse emulsions.[4–6] When device dimensions shrink to the micrometer scale, surface-to-volume ratio greatly increases, and consequently the interfacial tensions are found to have a dramatic effect on the multiphase flow phenomena. The manipulation of the interfacial tension (solid–liquid, liquid–liquid) is currently becoming a very important aspect in the trend toward miniaturization.

The liquid–liquid interfacial properties are usually tuned by applying surfactants. A typical surfactant (or surface active agent) molecule consists of a hydrophilic head and a hydrophobic tail (Fig. 1). At the macroscale, without the solid surface effect, the nature of an emulsion is mainly determined by the respective affinity of the surfactant molecules for the water and the oil phases. The affinity of a surfactant molecule to water and oil can be empirically evaluated by the balance of the size and strength of the hydrophilic and hydrophobic parts in a surfactant molecule which is called Hydrophilic–Lipophilic Balance (HLB) value.[7,8] In macroscale emulsion fabrication, this affinity scale is a way of predicting the emulsion type from the surfactant molecular composition. Surfactants with high HLB values (more hydrophilic) preferentially encapsulate oil as

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† Electronic supplementary information (ESI) available: Movie showing a two-phase emulsion inversion process: from water-in-oil to oil-in-water. See DOI: 10.1039/b813724b

Fig. 1 Surfactant structure and emulsion types in macroscale emulsion preparation corresponding to HLB values. O and W indicate oil and water phases, respectively.

droplets in water, and *vice versa*, surfactants with low HLB values (more hydrophobic) give W/O emulsions easily (Fig. 1). A requisite HLB value for different purposes can be obtained by blending two surfactants.[9–11] Selection of surfactants is therefore crucial in creation of emulsions at the macroscale.

When the size of the emulsion container decreases down to the micrometric scale (<capillary length), it will become equal to the typical size of the emulsion droplets. Furthermore the effect of gravity and inertial forces on microfluidics can be neglected due to the small Weber and Bond numbers,[4] and the surface-to-volume ratio increases dramatically. As a result the solid–liquid interfacial tension plays a dominant role for emulsions created in a microsystem.[12–14] Fig. 2 illustrates how the formation of an emulsion where the non-wetting phase is the continuous phase (lower) involves the creation of one extra interface when compared to an emulsion where the wetting phase is the continuous phase (upper). The extra surface necessitates the introduction of extra surface energy, so that the resulting emulsion is thermodynamically unstable. This argument can also be made in a more formal way. It is well-known that, when two immiscible liquids L_1 and L_2 (oil and water, for instance) contact a solid surface (S), one preferentially wets the surface. The contact line shapes itself due to the differences among interfacial tensions.[12,13] If we confine circular droplets (diameter $2r$) of L_1 and L_2 together in an L_1-philic cylindrical microchannel of equal diameter and of length $2r$ (Fig. 2), the minimum amount of energy required to form an L_2-in-L_1 emulsion is

$$\Delta E_{L_2/L_1} = 4\pi r^2 \sigma_{SL_1} + 4\pi r^2 \sigma_{L_1 L_2} \tag{1}$$

However, formation of L_1-in-L_2 emulsion requires

$$\Delta E_{L_1/L_2} = 4\pi r^2 \sigma_{SL_1} + 4\pi r^2 \sigma_{L_1 L_2} + 4\pi r^2 \sigma_{L_2 L_1} \tag{2}$$

In the latter case, since the channel is preferentially wetted by L_1, there must exist a thin layer of L_1 on the surface and an extra interface is introduced.[15] Since $\Delta E_{L_2/L_1} < \Delta E_{L_1/L_2}$, an L_2-in-L_1 emulsion is energetically preferred in an L_1 wetting microchannel, and *vice versa*. In general, if $r_{\text{droplet}} \approx r_{\text{container}}$, the creation of the wetting phase as the continuous phase is always
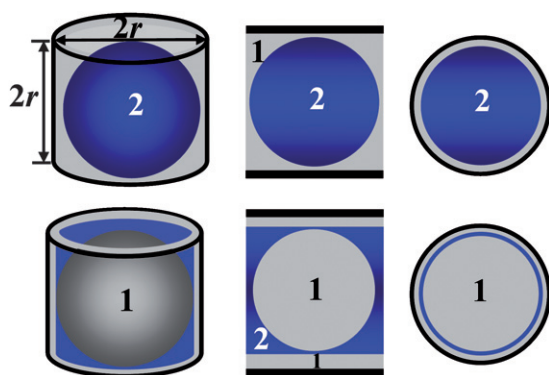
favorable in a channel of any diameter when gravity and inertial forces can be neglected. However, the energy difference between L_1-in-L_2 and L_2-in-L_1 emulsifications, $(\Delta E_{L_1/L_2} - \Delta E_{L_2/L_1})$, can be small if $\sigma_{L_1 L_2}$ is low.
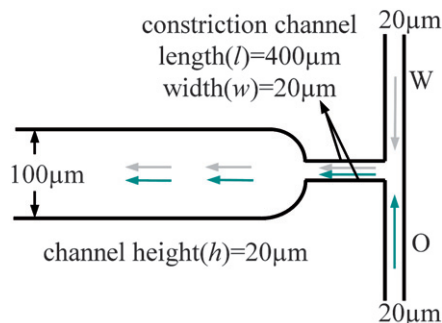
The manipulation of surface wettability is therefore critical for droplet manipulation in microfluidic devices.[16–19] The materials which are commonly used to make microfluidic devices are oxide-covered silica and glass which are natively hydrophilic, or PDMS which is normally hydrophobic.[20–24] Simulations[25–31] have demonstrated that surface wettability of fluids is crucial to describe the flow of two immiscible fluids flow in microfluidic devices. However, only a few works[17,18] have been reported on the effect of surfactants on oil–water two-phase microfluidics.

In this article, we investigate the influence of both solid–liquid and liquid–liquid interfacial tensions on water–oil two-phase flow in microfluidic devices. Head-on microfluidic devices (Fig. 3) are designed and used to ensure the same entry conditions for the water and oil phases. Solid–liquid interfacial tension is modified by either using natively hydrophilic microchannels or the same microchannels chemically hydrophobized by silane molecules. Fluid–fluid interfacial tension is controlled by using different surfactants (SDS, Tween80 and Span80), looking at the influence of the wettability in the range of HLB values of 4–40 and the interfacial tension in the range of 10^{-2}–10^{-4} N m^{-1}. The combination or competition of solid–liquid and liquid–liquid interfacial properties in the microchannel will be seen to engender complex flow behaviors. A precise theoretical study of these is postponed for subsequent studies. By applying the same flow conditions using our devices, we can investigate how interfacial tensions influence oil–water two-phase flow behaviors at the micrometric scale.

2 Experimental procedures

2.1 Chip fabrication

The design of the microfluidic device is shown in Fig. 3. Microchannels were fabricated (reactive ion etched) in a silicon (100) wafer using the standard photolithography process. Interconnection holes were opened from the backside of the wafer using powder-blasting techniques. The silicon wafer was then bonded to an empty Pyrex (transparent borosilicate glass) wafer using anodic bonding techniques. The resulting bonded wafers were then diced into 10 mm × 20 mm chips. Chips were fixed in a home-made chip holder and connected to syringes *via* capillary

Fig. 2 Schematic of L_2-in-L_1 (upper) and L_1-in-L_2 (lower) emulsions formed in a L_1-philic cylindrical microchannel (cylinder diameter $2r$, length $2r$). 1 and 2 represent L_1 and L_2. The left, middle and right pictures are a 3D, side-view and top-view sketch, respectively.
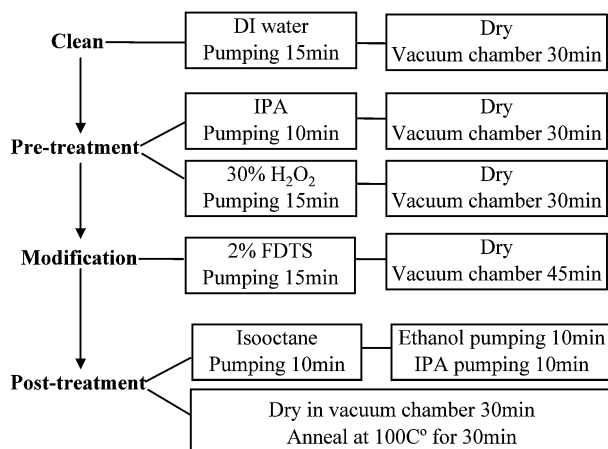

Fig. 3 Schematic of the microfluidic device.

tubing (OD 1/16 inch, ID 50 μm) and Nanoport connectors including a filter (INACOM INSTRUMENTS BV, Upchurch Scientific, Holland). Flow was controlled using a dual syringe pump (Harvard PHD 22/2000, HUGO SACHS ELECTRO-NIK-HAVARD APPARATUS Gmbh) to ensure constant flow ratios for the two phases introduced into the two inlets. The water and oil phases met at the entrance of the constriction channel, and then flowed through constriction and wide outlet channel (Fig. 3). The flow was visualized using an inverted microscope (Leica DMIRM) and recorded by a CCD camera (Orca ER).

In order to avoid the dependence of phase volume ratio and shear conditions,[10,32] we performed all experiments under the same volume ratio (1:1), flow rate (shear) and flow rate ratios in the microfluidic devices. The flow rates of water (Q_w) and oil (Q_o) phases were both 0.10 μL min^{-1} (Re ≈ 0.1). In order to preserve the channel wettability, note that the hydrophilic and hydrophobic microfluidic devices were stored in water and hexadecane in glassware and a plastic container, respectively, before using.

2.2 Surface modification of microchannels

Our microfluidic devices were made of hydrophilic native oxide covered silica and Pyrex (borosilicate glass). The same microfluidic devices from the same wafer were also modified to become hydrophobic using a silanization treatment with a solution of isooctane containing 2 v/v% 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS, $C_{10}H_4Cl_3F_{17}Si$, 97%, ABCR GmbH & Co. K G, Karlsruhe). The coating process is sketched in Fig. 4.

The organosilane molecules adsorb onto the surface and a Si–Cl group of each organosilane reacts with a surface OH group to form Si–O–Si bonds. The remaining Si–Cl bonds on each molecule react with neighboring organosilane molecules in the presence of trace pre-adsorbed water molecules to form a network of Si–O–Si bonds over the surface. The presence of the resulting long fluorinated hydrocarbon chain on the treated surface consequently causes water repulsion from the surface, which therefore exhibits a preferential affinity for organic solvents. A water droplet exhibits a contact angle of 110 °C on the FDTS covered surface. The FDTS treated surface is strong and stable, withstanding long time, high temperature and different chemical treatments.[19]

2.3 Preparation of fluids

The water phase was made fluorescent by dissolving fluorescein sodium salt (Sigma-Aldrich Chemie GmbH, Germany) in DI water at a final concentration of 0.01 M. The organic phase consists of hexadecane without any added fluorescent markers. Two-phase flows were visualized in fluorescent mode.

Solutions were prepared by solving hydrophilic surfactants in water and hydrophobic surfactant in hexadecane. Surfactant concentrations were all above the critical micelle concentration (cmc). Hydrophilic surfactants used were sodium dodecyl sulfate (SDS 99+ %, $CH_3(CH_2)_{11}OSO_3Na$, HLB = 40, cmc = 0.2 wt%, Sigma-Aldrich Chemie GmbH, Germany) and Tween80 (HLB = 15, cmc = 0.1 wt%, Sigma-Aldrich Chemie GmbH, Germany), while the hydrophobic surfactant was Span80 (HLB = 4.3, cmc = 0.02 wt%, Sigma-Aldrich Chemie GmbH, Germany). Solutions were degassed under vacuum. The components of solutions and water–hexadecane interfacial tensions are listed in Table 1.[18,33–42] The resulting water–hexadecane interfacial tensions are ~10^{-2} N m^{-1} except for (SDS + Span80) which is <10^{-4} N m^{-1}

3 Results and discussion

3.1 Emulsion types at the macroscale.

The macroscale emulsion types were determined by mixing different solutions (Table 1) at a volume ratio of 1 : 1. Every mixture was sonicated for 5 min in a glass cuvette. A drop of mixture was then deposited onto a glass slide and imaged. Emulsion types can be easily determined since the fluorescein dye in the water phase shows bright white in the images while the oil phase is in black.

The emulsion types are listed in Table 2. It is seen that the type of emulsion obtained in the macroscale device depends primarily on the surfactant used. The single hydrophilic surfactants Tween80 (HLB = 15) and SDS (HLB = 40) create O/W emulsions, while the single hydrophobic surfactant Span80 (HLB = 4.3) creates W/O emulsion. The HLB value of Tween80 and Span80 blended at 1 : 1 volume ratio is 9.65 which falls between hydrophilic and hydrophobic regions,[7,11] therefore both W/O and O/W emulsions are obtained in the same system. The (water + SDS)/(hexadecane + Span80) interfacial tension is less than 10^{-4} N m^{-1}, multi-emulsion (W/O/W or O/W/O) can be created.[43–46] Double emulsions, mainly W/O/W, are obtained by using SDS and Span80 together in our experiments.

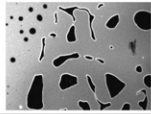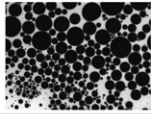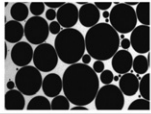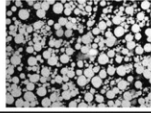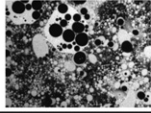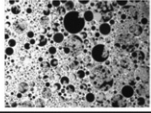### 3.2 Emulsions in microchannels

3.2.1 Emulsion types—solid–liquid interfacial tension (surface wettability). When water and oil phases meet at the entrance of the constriction channel without the use of surfactants, O/W flows are generated in native hydrophilic microchannels (Table 3a), while W/O flows are formed in the same channels modified by FDTS (Table 3b).

In the same channel (hydrophobic or hydrophilic), under identical flow conditions, the emulsion types subsequently do not change from the ones obtained without surfactants when using

Fig. 4 Schematic process of microchannel hydrophobic surface modification.

The flow diagram contains the following boxes:

- Clean: DI water Pumping 15min → Dry Vacuum chamber 30min
- Pre-treatment: IPA Pumping 10min → Dry Vacuum chamber 30min; 30% H$_2$O$_2$ Pumping 15min → Dry Vacuum chamber 30min
- Modification: 2% FDTS Pumping 15min → Dry Vacuum chamber 45min
- Post-treatment: Isooctane Pumping 10min → Ethanol pumping 10min IPA pumping 10min; Dry in vacuum chamber 30min Anneal at 100C° for 30min

Table 1 Oil–water interfacial tensions (N m^{-1}) of different solution compositions

O \ W	DI water+0.01M Fluorescein (W1)	W1+2wt% Tween80 (W2)	W1+0.3wt% SDS (W3)
Hexadecane (O1)	5×10^{-2}	1×10^{-2}	1×10^{-2}
O1+2wt% Span80 (O2)	1×10^{-2}	1×10^{-2}	$<10^{-4}$

Table 2 Emulsion types at the macroscale

O \ W	W1	W2	W3
O1	unstable	O/W	O/W
O2	W/O	W/O&O/W	W/O/W

— 50μm

different surfactants, indicating the predominance of σ_{SL} in determining emulsion type. Such behavior can indeed be explained from eqn (1) and (2) as discussed above. In a silicon or glass microchannel the water phase is energetically inclined to flow along the hydrophilic channel walls as the continuous phase, creating an O/W flow; while a W/O flow can be obtained in a FDTS-coated hydrophobic microchannel. Increase of the concentration of Span80 and Tween80 concentration from 1 wt% to 10 wt% in hexadecane and water does not change the emulsion type. Although surfactants, such as Tween80, can temporarily coat the channel surface, the coating layer will be removed when the water flows through the microchannel at 0.1 μL min^{-1}. Surfactants therefore do not remain to modify the channel surfaces and the original surface properties determine the solid–liquid interfacial tension. Although surfactants with different HLB values were used in water or hexadecane, the emulsion types did not change. Both stable droplet deformation (Tables 3(a) and 3(b): W2 + O2) was observed as well as coalescence (Table 3(b): W2 + O1 and W3 + O1) when the HLB value and the contact angle tended to create opposite interfacial curvatures.

Emulsion types in these microfluidic devices thus depend only on the original microchannel surface wettability, independent of what surfactant is used. We can therefore easily control emulsion types (O/W or W/O) in microfluidic devices by simple surface modification methods. This behavior is different from the normal macroscale emulsification techniques which are strongly surfactant-dependent (liquid–liquid interface).

3.2.2 Flow patterns—liquid–liquid interfacial tension (surfactants). When inspecting the experimental results listed in Table 3, it is seen that, in these microfluidic devices, at the flow rate and flow rate ratios used, droplet-based flows are obtained for all surfactants except for the combination of SDS and Span80 where stratified flows are generated. This can be explained in the following way.

At the microscale, two forces—interfacial force and viscous force—dominate with respect to inertial and gravity forces. The capillary number is the ratio of these two competitive forces, and can be expressed as:

$$Ca = \frac{\eta v}{\sigma} \qquad (3)$$

where η (Pa s) and v (m s^{-1}) are the continuous phase viscosity and flow velocity, and σ (N m^{-1}) is the oil–liquid interfacial tension. Addition of surfactants decreases the interfacial tension. Water–hexadecane interfacial tensions are about 10^{-2} N m^{-1} when using Tween80, SDS, Span80 or (Tween80 + Span80), and Ca falls in the range of 10^{-3}–10^{-2} ($\eta = 10^{-3}$ Pa s, $Q = 0.1$ μL min^{-1}) for these surfactants. The viscous force is much smaller than the interfacial force; therefore, droplet-based flows are

Table 3 Emulsions in microfluidic devices. (a) O/W emulsions created in hydrophilic microchannels, $Q_o = Q_w = 0.10$ μL min^{-1}. (b) W/O emulsions created in hydrophobic microchannels, $Q_o = Q_w = 0.10$ μL min^{-1a}

(a)

— 50μm

(b)

— 50μm
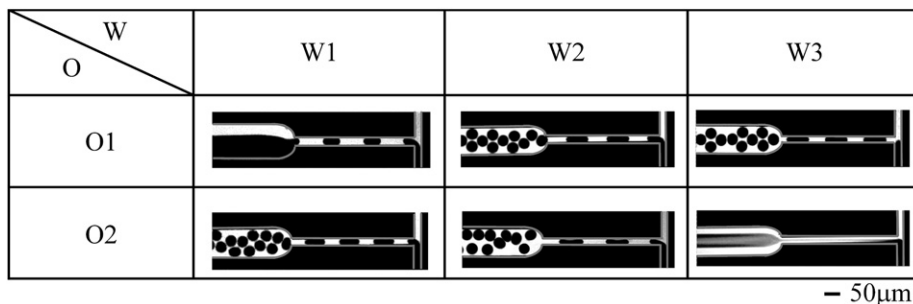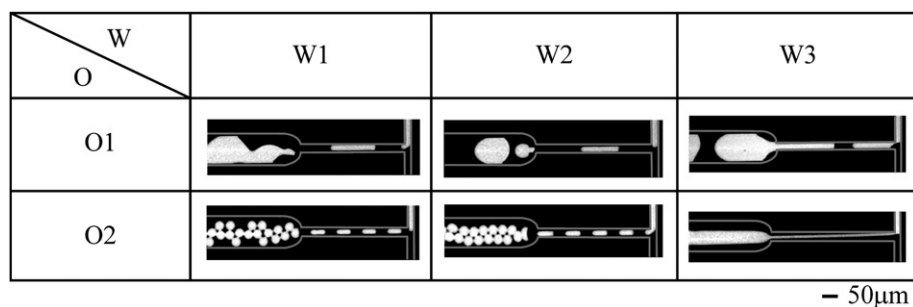
^{a} The gray lines in the pictures are used as a guide to the eye to indicate the channel walls.

generated in these systems. However, the interfacial tension of water–hexadecane is less than 10^{-4} N m^{-1} when using (SDS + Span80). Ca then is in the range 0.1–1 under the same flow conditions. In this case, the viscous force dominates interfacial force, and a stratified flow pattern is obtained.

Furthermore, as shown in Table 3, the combination or competition between solid–liquid and liquid–liquid interfacial properties can create complex two-phase flow phenomena, such as deformation and coalescence, when the flow conditions slightly change. We only showed important phenomena but omitted some detailed fluidic dynamics which is out of the scope of this manuscript. In microfluidic systems, the use of surface and surfactant combinations can be a useful tool for quantitatively manipulating and evaluating droplet generation, deformation and coalescence phenomena which are difficult to realize in macroscale devices.

3.3 Emulsion inversion in microchannels

As discussed in previous sections, in microchannels the solid–liquid interfacial tension is the determinant factor for emulsion type. It has been shown that change of microchannel surface wettability can therefore induce coalescence. Here we will demonstrate that it can even cause emulsion inversion. We prepared a microchannel patterned with adjacent hydrophobic and hydrophilic patches. Fig. 5 shows a water-in-oil two phase emulsion moving through this channel from top to bottom (see also the online movie†). A water droplet in oil flow (top of the picture) arriving at the interface between both patches turns,
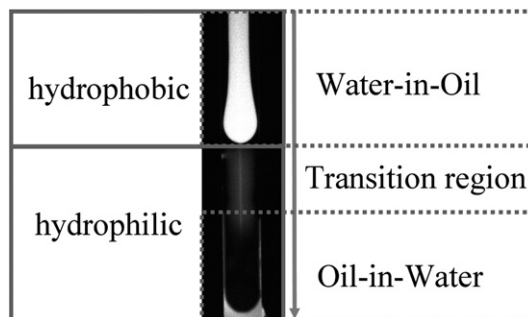
Fig. 5 The emulsion inversion in a hydrophobic–hydrophilic microchannel: $h = 20$ μm and $w = 100$ μm. The two-phase emulsion moves from top (hydrophobic walls) to bottom (hydrophilic walls). The emulsion type is seen to change from W/O (a white droplet in a black background) to O/W (a black droplet in a white background) after a brief transition region between. The two phases were oil (hexadecane, shown in black) and water (aqueous solution with 0.01 M fluorescein and 0.3 wt% SDS, shown in white).

after a brief rearrangement phase in which no clear emulsion type is visible, into an oil droplet in water flow (bottom of the picture).

For the first time, we could hereby realize an emulsion inversion in the same microchannel. The capability of inversing emulsions might be very useful in real life, for instance to obtain desired food products.[3,47] Furthermore, this result proves our previous conclusion that it is the solid–liquid interfacial tension which determines the emulsion type in microfluidic devices.

4 Conclusions and outlook

The surface-to-volume ratio increases on downscaling. The predominance of interfacial tension in microfluidic systems can be harnessed to tailor the two-phase flow behavior within the system. We experimentally investigated the influence of solid–liquid and liquid–liquid interfacial tensions on oil–water two-phase flow behavior in microchannels. The emulsion types, at the macroscale, were predominantly determined by surfactant wettability (HLB value). However, at the microscale, the channel wall wettability (the solid/oil with respect to the solid/water interfacial tension) determines the emulsion types generated in microchannels under the same flow conditions. Emulsion inversion could be realized by reversing microchannel surface wettability. The surfactants play a secondary role, determining the flow type. Both droplet-based flows and stratified flows have been obtained under the same flow condition by varying liquid–liquid interfacial forces in the range 10^{-2}–10^{-4} N m^{-1}. Microdroplet deformation and coalescence have also been observed by combining solid–liquid and liquid–liquid interfacial properties.

Microfluidic technology can thus be useful to manipulate generation, deformation and coalescence of microdroplets. Furthermore, by observation and analysis of these flow behaviors under precisely controlled flow conditions using a microfluidic device, we might be able to estimate interfacial properties. The phenomenon of surface-wettability-determined emulsion types may be useful to invert emulsion types, such as food emulsions, to change food product types. The channel surface properties will be even more important if the dimension decreases further. Surface-determined flow phenomena may then be able to explain fluid transfer in some biological processes, such as water permeation in leaves.

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