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Coalescence of oil droplets in microchannels under brine flow

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ABSTRACT. We use the microfluidics technique to study the coalescence of model oil droplets in microchannels. Different stages of the coalescence: convergence of the droplets and liquid film drainage, collision, interfacial film rupture, and merging are captured by high-speed imaging. The coalescence time is studied, defined as the merging time for the droplets after physical contact. Adding salts into the water phase may slow down the coalescence process. Cations Na\textsuperscript{+}, Ca\textsuperscript{2+} and Mg\textsuperscript{2+} do not significantly affect the coalescence time, while the presence of the anion SO\textsubscript{4}2- produces much higher times than of Cl\textsuperscript{-}. The presence of a surface-active component, stearic acid, increases the coalescence time, in a clear correlation with the interfacial tension. At higher pH stearic acid is deprotonated into stearate; correspondingly, the interfacial tension decreases further and the electrostatic repulsion of the head groups of fatty acids increases. The interface between droplets and water is thereby stabilized and the coalescence time increases. A pH value higher than the pKa of stearic acid induces highly stable plastic-like oil-water interfaces. We discuss the implications of our results on the applications in the petroleum industry concerning e.g. enhanced oil recovery under smart waterflooding.

Keywords: Coalescence, oil droplet, microfluidics, fatty acid, smart water

1. Introduction

Coalescence of drops and bubbles has attracted tremendous interest of researchers for decades and keeps undergoing intense studies in both fundamental science and engineering fields [1][2][3]. The droplet coalescence plays a central role for the behavior of raindrops [4], spray coatings [5], emulsions in food and cosmetic industry [6][7], biomedical engineering [8], as well as in wastewater treatment and in the oil and gas industry, where water and oil are often co-produced [9].

Microfluidics exhibits great potential for the study of droplet behavior in liquid or gas streams. It has been applied widely in different fields due to its advantages, like small scale, low sample consumption, high throughput, and, last but not least, the approximation of the natural or industrial processes of interest [10].

The generation of monodispersed droplets requires them to be stable against fusion. The stability can either be achieved thermodynamically or kinetically. Thermodynamic stability is achieved by lowering the free energy through decrease of the interfacial tension. Achievement of the kinetic stability is by introducing an activation barrier for the fusion process [11][12]. Surfactants can stabilize droplets by both mechanisms. Large surfactant molecules can also create steric repulsion counteracting coalescence [13]. The presence of the surfactants may induce hydrodynamic flow, i.e. Marangoni effect, around droplets, which stabilizes them kinetically [13]. The surfactants dissolved in one of the phases can adsorb onto the interfaces, approaching them by diffusion and convection [14][15][16]. Adsorption affects changes in surface tension and colloid stability. It is greatly influenced by mass transport. The adsorption at the interface for low molecular weight surfactants is expected to be fast, while the Marangoni effect can be neglected because of the fast continuous phase velocity [17]. The rate of transport may also be influenced by partitioning [18] and interfacial properties [19].

The process of droplet coalescence has a particular interest in the petroleum industry. After waterflooding of a petroleum reservoir, residual oil exists mainly in the form of separate droplets trapped in the pores of reservoir rocks [20]. Mobilization of such droplets is the key step for further enhanced or improved oil recovery. One of the ways to mobilize the residual oil is to cause merging the droplets since larger droplets are easier to move out of the pores [21]. In this process, the oil droplets are located in a confined space and surrounded by saline
water. Coalescence also occurs in other petroleum-related processes, e.g. demulsification of crude oil emulsions [22], oil desalting [9], cleaning of the produced water containing dispersed oil drops [23] and cleaning of the seawater from oil spills [24]. Common processes for the treatment of produced oil field water are gravity settling, centrifugation, flotation, and filtration. In the last case, oil droplets are forced into the pores of the filters, where their coalescence plays an important role in the cleaning process [25]. The pore sizes in natural rocks and filters are of a micrometer scale. Microfluidics can be a powerful tool to study the behavior of droplets in such environments and for such pore sizes.

It is generally assumed that, when coalescence occurs, the liquid between two approaching droplets is drained out. Subsequently, a liquid bridge is formed [26]. A large number of studies investigated the drainage times and the dynamics of the liquid bridge formation, deriving various ‘scaling laws’ [2][27][28]. The film rupture and the droplet merging are considered to take a much shorter time compared to drainage and thus are usually neglected. This leaves a lack of understanding of these processes. The droplet studies are mostly related to relatively large volumes, and only a few works analyze the coalescence in the confined space with surrounding fluid flow [29][30][31][32][33][34][35][36]. These studies focus either on the design of channel geometry and active control methods to induce coalescence; or on capturing the process of coalescence and exploring the conditions under which coalescence may happen. A limited number of works report the time needed for the droplets to merge after their physical contact in a confined space under external fluid flow. Applications of microfluidics to the coalescence concern mainly water droplets in oleophilic/lipophilic environments, due to the simplicity of the fabrication of hydrophobic microfluidic chips and their biomedical applications. To the best of our knowledge, the only studies of coalescence of oil droplets surrounded by flowing brines in micro-confined channels include those by Dudek et al. [37][38][39] and Kovalchuk et al. [40]. Dudek et al. characterized the coalescence frequency in a microchannel for the coalescence between oil droplets and between droplets and gas bubbles, while Kovalchuk et al. monitored the evolution of liquid bridge formation. Kreb et al. studied the coalescence time of mineral oil droplets in microchannels, although they did not systematically examine the effect of the surrounding solution and surfactants [41].

Crude oil has a complex composition and may contain a variety of species influencing interfacial properties, such as resins, asphaltenes, and naphthenic acids. To extract the physical mechanisms of the coalescence, we study simple model systems consisting of toluene as the main “oil” component of the droplets, and synthetic brines with well-defined composition and salinity. Compared to the previous works, we carry out a systematic study of the coalescence of the oil droplets surrounded by flowing brines in the microchannels. The effects of stearic acid (surfactant), salinity, pH, cations, and anions in the solution are studied. The effects of flow hydrodynamics and the droplet positions in the flow are also observed and described. We concentrate on the times required for the droplets to merge after the first contact. The flow is manipulated by the adjustment of the injection pressure, which makes the flow conditions similar to the flow in the porous rocks or membrane filters.

2. Materials and Methods

2.1. Materials

Sodium chloride (≥99%), sodium sulfate (≥99%), calcium chloride dihydrate (≥99%), and magnesium chloride hexahydrate (99.0 - 102.0%) were purchased from Sigma-Aldrich. Water used in all experiments was ultrapure water with a resistance of 18 MΩ·cm from a Milli-Q water purification system. All the aqueous solutions that went into the microfluidic system were filtered with Pall Acrodisc syringe filters containing Supor membranes with a pore size of 0.2 μm.

Toluene (99.5%, VWR Chemicals) was used as the model oil for droplet generation and coalescence studies in our experiments, as it is a common component in crude oil. The interfacial tension of toluene/water is about 36 mN·m⁻¹ at room temperature, which facilitates
the generation of the droplets in our microchannels. Stearic acid (98.5 %, Sigma-Aldrich), was added into toluene in various concentrations, as a lipophilic surface-active component. It was chosen for the following reasons. First, stearic acid is a common “naphthenic acid” that may be found in crude oil. Second, it has a high partition coefficient (of the order of \( \sim 10^3 \) in heptane/aqueous phosphate buffer [42][43]) and sufficient solubility in toluene, which facilitates stabilization of the interface between water and toluene. Besides, it has a relatively simple structure, as shown in Figure 1. When the acid reaches the interface, the hydrophilic carboxyl group faces the water phase, while the hydrophobic alkyl group faces the toluene phase. The interfacial properties with fatty acids are well studied in the literature, providing a point of reference. Some relevant properties of stearic acid are summarized in table 1.

All the chemicals mentioned above were used without further purification. The oil phase was filtered with a Whatman PTFE syringe filter with a pore size of 0.2 μm.

2.2. Droplet generation

A glass microfluidic chip with flow-focusing geometry (2 Reagent Droplet Chip, Dolomite, UK) was used to generate oil droplets. The geometry of the chip is schematically shown in Figure 2. The oil droplets are generated at the flow-focusing junction, with a channel width of 50 μm. Afterward, they are directed immediately into the expanding channel, up to the width of 360 μm. The channel slows down the movement of the droplets and induces coalescence. The height of the microchannel is 50 μm so that the droplets are constrained in the transverse direction. This keeps them aligned and ensures the persistence of the plane of symmetry.

Liquids (aqueous and oleic phases) are held in reservoir containers, which are tightly sealed and connected to the OB1 pressure controller produced by Elveflow, France. The outlet is connected to the microfluidic chip by FEP tubing (internal diameter 360 μm). The fluid flows are driven by the desired pressures set by the pressure controller. The flow control system is schematically shown in Figure 2. The toluene flow is driven into the middle channels, while the aqueous phase flows into the channels on the sides, as illustrated in Figure 2 (inset). When the flows of the two phases meet at the flow-focusing point, toluene flow may be cut into separate droplets. This happens due to shear forces at certain ratios of the pressures driving the flows of the phases. The sizes of toluene droplets and the generation frequency can be manipulated by adjusting this pressure ratio. This corresponds to the adjustment of the ratio of the flow rates between the two-phase fluids in the syringe pump controlling microfluidic experiments. The pressure range in both channels is 0 – 2000 mbar, corresponding to a flow rate range of 0 to 800 μL/min. In a typical set of experiments, the pressure change was within 100 mbar, so that a small amount of the nitrogen dissolved in liquids had a limited impact on coalescence behavior of the droplets.

In order to generate oil droplets in the aqueous phase, the chip was treated overnight with 0.1 M NaOH solution to ensure that the surface became hydrophilic. A large amount of water sufficient for cleaning the residual NaOH was flushed through the chip before the experiments. In a typical experiment, aqueous solutions were injected initially into all the channels of the chip. Then the flow was stopped. The liquid flowing into the two middle channels was switched to toluene. Pressures for the flows were adjusted until the oil flow was stable and droplets were generated. Then the pressure for the water phase flow was kept constant, and the generation frequency was similar for each data set. For the droplets of pure toluene, the events that happened at a distance of less than 500 μm from the beginning of the channel, were counted. When the droplets contained stearic acid, the coalescence events usually happened later, and the events at the distances 500 to 1000 μm from the entrance were counted. All the data on coalescence times are presented as averages with standard deviations for at least 20 coalescence events.

2.3. Imaging system

The glass chip was placed on a Motic AE2000 inverted microscope. Droplet generation and
coalescence were imaged with a high-speed video camera FASTCAM Mini UX100 (Photron, Japan) equipped with a 1.6 × adapter attached to the microscopic port. Pictures were recorded at 4,000 to 20,000 frames per second. The time of coalescence was analyzed based on the taken images.

2.4. Interfacial tension measurement

The interfacial tension between water and toluene with different amounts of stearic acid was measured by the dynamic pendant drop method. Toluene (with different amounts of stearic acid) was loaded into a syringe, which is connected to a U-shape needle immersed in a water reservoir from the bottom in a cuvette. A droplet was then formed at the tip of the needle. The volume of the droplets was controlled to be about 50 μL. The measurements were recorded with the ADVANCE software that fits the digital droplet profile by a surface of constant curvature. Each measurement was stopped when the interfacial tension reached a stable value, which typically took more than half an hour. Three measurements for each model oil composition were performed. Average tensions and standard deviations are reported here.

3. Results

3.1. Droplet generation

The formation of the droplets results from an interaction between the shear forces and the interfacial tension. The shear forces act to separate a droplet from the emerging thread of the dispersed phase, while the interfacial tension stabilizes the droplet.

The droplets generated in our experiments were highly monodispersed. The polydispersity index \( \sigma \) is defined as

\[
\sigma = \frac{\delta}{d_{av}} \times 100\% 
\]

where \( \delta \) is the standard deviation of the droplet diameter, and \( d_{av} \) is the average droplet diameter \([44]\). This value was calculated to be approx. 1%, by measuring 50 droplets from the recorded images.

For the toluene-water experiments under moderate pressures, different flow regimes were observed. At a higher pressure ratio (toluene: water ~ 1.12:1), toluene wetted the downstream channel. As the water pressure gradually increased, the stratified flow was formed, with the water phase wetting the channel wall and the toluene stream in the middle of the channel. The width of the toluene flow decreased with the water pressure until it reached a critical point where the toluene flow began to break up into separate droplets. The generation frequency was high at this moment, and small droplets coalesced instantaneously after formation in the flow-focusing junction (Figure 3 (a)). Several droplets merged into larger slugs before breaking up into separate slugs and flowed into the downstream channel (Figure 3 (b)). Upon further increase of the water pressure, the slugs turned into round droplets and broke up from the original flow, while eventual small droplets still merged at a high rate when they left the junction and came into contact with the previously generated droplets (Figure 3 (c)). Further increase of the water pressure resulted in that a larger amount of small droplets could appear in the flow before readily coalescing with a neighboring droplet. Even further increase of the pressure for water flow resulted in falling generation frequency, and the droplets could move separately downstream without colliding with each other (Figure 3 (d)). A stable interface was formed close to the junction when the pressure in the water channel reached a certain value (usually, approximately equal to the toluene pressure, Figure 3 (e)). If the pressure continued growing, water could penetrate the toluene channel. We concentrate on cases similar to the conditions of Figure 3 (c) to characterize the coalescence times.
3.2. Coalescence

Four main stages for the coalescence of toluene (0.05 wt % stearic acid) droplets can be resolved in our experiments, as shown in Figure 4. Consider the flow-focusing point, after which the channel expands. Initially, the first generated droplet flows out of this point. The water flow rate slows down as the channel expands, and so does the droplet velocity. The next generated droplet has initially a larger velocity than the previous one. Driven by hydrodynamic forces, it may catch the previous droplet in the downstream channel. When the two droplets get close to each other, the interfaces between them become flattened and the water film between the two droplets drains out (Figure 4 (a)). When it becomes thin enough, the van der Waals forces and other intermolecular forces start working. The two droplets come into contact with each other (Figure 4 (b) (c)), followed by the rupture of the interfacial films (Figure 4 (d)), which results in fusion (Figure 4 (e)). Eventually, the two droplets merge into a larger droplet (Figure 4 (f)). Due to the flow in the horizontal direction, the new droplet is initially elliptical with an elongated vertical axis (Figure 4 (g)). After some shape adjustment (Figure 4 (h) (i) (j) (k)), under oscillations and damping of surface waves [26], the droplet becomes round in the focal plane (Figure 4 (l)).

The coalescence times of the droplets were measured and used to characterize the coalescence process. In the following, the coalescence time is defined as the time needed for two droplets to form a new round droplet after they have had physical contact. In the example of Figure 4, the coalescence time is defined as the time from $t = 0.45$ ms (Figure 4 (b)) to $t = 1.25$ ms (Figure 4 (l)). The coalescence time is directly related to:

1) Sizes of the droplets, as it takes a longer time to finalize the confluence of liquid between larger droplets. Here we only compare the average coalescence times for the droplets in the diameters in the range between 70 $\mu$m and 140 $\mu$m (the volumes between $1.4 \times 10^5$ $\mu$m$^3$ to $6.6 \times 10^5$ $\mu$m$^3$); and

2) The initial hydrodynamic forces pushing the two droplets to each other, which depend on their velocity difference.

3.3. Head-on collision vs. glancing collision

When the pressure for both toluene and water flows increased to a certain value, the generation frequency became so large that the droplets stopped flowing in line and started moving more chaotically. This was mainly caused by overcrowding at the entrance of the downstream channel. The droplets could still coalesce into larger droplets that were found in the whole space of the downstream channel. However, collisions of droplets became in this case rather glancing than head-on, as schematically shown in Figure 5. The coalescence times for head-on collisions and glancing collisions of toluene droplets in water and in 0.1 M NaCl solution were analyzed as shown in Figure 6. The coalescence time for a glancing collision is slightly longer than that for a head-on collision. This effect is more pronounced when the salts are present in the system. In the presence of salts and surface-active components, two droplets may be attached and travel side by side without merging for the whole time of observation. Sometimes, they may also slide relative to each other. This may be an indication of the formation of a condensed elastic or repulsive interface.

The two droplets come into contact due to the hydrodynamic force originating from the velocity difference between the droplets. This force is the largest when the two droplets collide along the flow direction; otherwise, only a fraction of the force (projection onto the line connecting centers of the droplets) is working. In some cases, the droplets can even travel close to each other for some time without coalescing, and subsequently, be separated by the water flow. In the following discussion about toluene droplets, we compare the coalescence times for the head-on collisions. For toluene droplets stabilized by stearic acid, the coalescence times for glancing collisions were studied.
The film thinning and the coalescence time depend on the fluid properties and the chemical environment in which the droplets flow, e.g. salt composition, presence of surface-active components and pH [1]. This will be discussed below.

### 3.4. Salt effect

NaCl, Na₂SO₄, CaCl₂, and MgCl₂ were separately dissolved in water to study the effect of salinity and salt composition on the coalescence times. The salt concentrations were 0.1 M, 0.2 M, 0.4 M and 0.6 M. Figure 7 shows the coalescence time as a function of the concentration of the different salts. For all the species examined, the coalescence time increases with the salt concentration. The different cations affect similarly on the coalescence time. Meanwhile, when the anion changes from chloride into sulfate, a pronounced increase in the coalescence time is observed. The difference is about three-fold at the high salt concentration (0.6 M).

### 3.5. Effect of the surface-active component

The dependence of the coalescence time on the concentration of stearic acid in toluene is shown in Figure 8 (a). The coalescence time increases with the concentration of stearic acid. As described in the previous section, we measured the interfacial tension of toluene/stearic acid in water by the method of pendant drop. The surface pressure was calculated, as the difference of the interfacial tension with the value for the system of toluene (without stearic acid) and water, and plotted against the concentration of stearic acid. Figure 8 (a) shows that the dependencies of the coalescence time and the surface pressure on the concentration of the stearic acid have a similar shape. The coalescence time was further plotted as a function of the surface pressure. Figure 8 (b) shows a clear linear relationship between them. It suggests that a strong correlation exists between the interfacial tension and the coalescence time.

### 3.6. pH effect

The pH values of water without dissolved salts were adjusted with the NaOH solution to a desired value, ranging from 6.3 to 12. The obtained solutions were used to study the pH effect on the coalescence time of toluene droplets with and without stearic acid. When there were no surface-active components in the system, pH did not influence significantly the coalescence time. However, in the presence of 0.1 wt% stearic acid, the coalescence times increased with the increase of pH. Moreover, no coalescence event was observed at pH higher than 8.5, at least, within our microchannels. This suggests that toluene droplets are largely stabilized by stearic acid at higher pH. When the pH value of the water phase became larger than ~10, stable plastic-like interfaces were formed between the water and toluene/stearic acid phases (Figure 9 (a)). The droplet generation was stopped due to the high resistance of the interfaces, and the flow-focusing point of the channel was blocked after some time. The behavior of toluene droplets at different pH values is illustrated in Figure 9 (b).

### 4. Discussion

The coalescence of droplets is driven by the viscous and interfacial forces. The viscous forces create hydrodynamic drag that results in the droplet collision. The interfacial forces create a thermodynamic drive to minimize the total interfacial area of the fluids. The capillary number $Ca$, which represents the relative strength of the viscous and interfacial forces, is calculated as

$$Ca = \frac{\mu v}{\gamma} \quad (2)$$

Here $\mu$ is the dynamic viscosity of water, $v$ is the velocity of the droplet movement in the channel before coalescence, and $\gamma$ is the interfacial tension between toluene and water. For the systems investigated herein, the calculated value of $Ca$ is of the order of $10^{-3}$. 

7
Additionally, the Weber number $We$, which characterizes the relative importance of the fluid inertia compared to the interfacial forces, was calculated:

$$ We = \frac{\rho v^2 l}{\gamma} $$  

Here $\rho$ is the density of water, and $l$ is the droplet diameter. The calculated value is around $2 \times 10^{-3}$.

These numbers suggest that the interfacial force is dominant for our microfluidic system. This explains the relation between the coalescence time and the concentration of stearic acid. On the other hand, viscous forces cannot be completely neglected, which is indicated by a comparison of the head-on and glancing collisions. The interfacial forces start working when the two droplets approach each other and start merging. To initiate merging, a certain energetic barrier should be overcome, and this is done by the viscous forces.

For the surfactant-free droplets, the event of coalescence depends on the distance $h$ between the droplet surfaces. This distance has to fall, at some point, below a critical value along the rim [26]. When the droplets approach each other the fluid between them is drained gradually. Below a critical value (typically $< 100 \, \text{Å}$), the van der Waals forces start acting. The surfaces spontaneously confluence at one or several points, and conjunction is built [45][46]. A thin liquid bridge has been reported to form upon contact of the two droplets due to attraction between the surface molecules [47]. A high-curvature meniscus around the bridge creates an imbalance of the surface tension. The interfacial films become unstable and rupture, which results in quick merging of the two droplets [48]. It has been hypothesized that the breakup is a stochastic process dominated by capillary waves [49]. Before and after the breakup, hydrodynamics is the main driving factor. The flow inside the droplets is reported to be a synergic action between the thermal motion of constituent molecules that acts to distort the interface between two phases, and surface tension suppressing increases in the interfacial area [50].

After coalescence, larger droplets are formed. They move faster than the smaller droplets ahead of them and may catch and absorb these smaller droplets, as shown in Figure 10 (a). A “train” of toluene droplets exists at $t = 0$. The leftmost droplet has a relatively larger size than the others due to coalescence that has happened previously. After 0.8 ms, the larger droplet catches the small droplet ahead of it and they merge upon collision. The process continues until the last small droplet is caught and merged with the large droplet. The phenomenon of larger droplets moving faster than the smaller ones may be understood by an analysis of the mass conservation for the fluid flow. Consider the two droplets of different sizes. Since liquids are incompressible, the total water flow rate is the same around the droplets, as illustrated in Figure 10 (b): $v_1 S_1 = v_2 S_2$, where $v_1$ and $v_2$ are average velocities of the water bypassing the droplets 1 and 2, and $S_1, S_2$ are cross-sections of the capillary that are left for water to bypass the droplets. Larger droplets leave less space for water flow in the same cross-section: if $S_1 > S_2$ (droplet 2 is larger), then $v_1 < v_2$ (water will flow faster around the second droplet). A higher velocity of the surrounding water accelerates the large droplet compared to the small one. This is how the large droplet catches up with smaller droplets ahead of it. The two separate droplets have a greater surface area than that of a single droplet formed after their coalescence. As a consequence, energy is released during the process of coalescence. A part of the released energy may turn into kinetic energy of the formed droplet, thereby increasing its velocity. Rearrangement of the fluid interface due to the geometry of the chip channel may also contribute to the increase of the droplet velocity after the coalescence. The microfluidic chip is a typical rectangular glass chip with corner gutters on the two sides. It has been shown that the velocities in the corner gutter regions are up to 10 times faster than predicted for bubbles in polygonal channels [51][52]. For larger droplets formed by coalescence, there may be lateral drainage of fluid from the thin films into the gutters, which minimizes the resistance to flow.
The addition of surfactants reduces interfacial energy and the rate of coalescence, making it possible to produce droplets that are stable over long periods. It has been shown that the addition of surfactants increases the time required for the film drainage before rupture [53], while here we have shown that this addition increases the time interval between the moments of the first droplet contact and when the two droplets fully merge. This means that the stability of individual droplets generally increases over the whole coalescence process. The effect of the stearic acid concentration on the interfacial tension can be modeled by the Gibbs-Langmuir adsorption isotherm,

\[ \gamma_0 - \gamma = -RT \Gamma_m \ln(1 + K_f C) \]  

(4)

Here \( \gamma_0 \) is the interfacial tension between pure toluene and water; \( \gamma \) is the interfacial tension between toluene with a certain amount of stearic acid and water (so that \( \gamma_0 - \gamma \) is the surface pressure); \( R \) is the gas constant; \( T \) is the temperature; \( \Gamma_m \) is the maximum surface concentration; \( C \) is the concentration, and \( K_f \) is the adsorption equilibrium constant relating the rate of adsorption and desorption from the interface as well as the energy of adsorption. The equilibrium surface pressure was fitted to the concentration of stearic acid in toluene. The values of surface excess (\( \Gamma_m \sim 10^{-6} \text{ mol/m}^2 \)) and the equilibrium constant (\( K_f = 5.9 \text{ m}^3/\text{mol} \)), obtained by regression to our data, are in good agreement with the values reported in the literature [54][55]. It has been observed that for small droplets the size has an impact on the value of the surface pressure. This happens because for small droplets accumulation of the surfactant on the surface affects its concentration in the volume due to high surface-to-volume ratios [56]. Therefore, it may be hypothesized that the coalescence of very small drops may lead to significant changes in the interfacial tension. In our experiments toluene containing stearic acid flows in the middle channels prior to the droplet formation. It contacts the water phase upon meeting close to the flow-focusing junction, where the water-toluene interface is formed. A droplet grows and becomes filled by toluene and stearic acid. The characteristic convection time is \( t_c = l/\nu \), where \( l \) is the length of the narrow channel (see Figure 4); \( \nu \) is the flow rate. On the other hand, a characteristic time \( t_f \) for the formation of a droplet of a diameter \( d_d \) equals to the ratio of the droplet volume, \( \pi d_d^3/6 \), to the liquid flowrate \( q \). A computation shows that \( t_f \) is several times smaller than \( t_c \). Hence, the convective mechanism may be sufficient for the transfer of stearic acid to the surface of the droplet. Further redistribution of the stearic acid from the bulk to the interface inside the droplet proceeds by diffusion. The characteristic time for such redistribution, \( t_D = d_d^2/D \) (here \( D \) is the diffusion coefficient), has a value of a few seconds. It is much larger than the observation time for droplet generation and coalescence. The adsorption time of surface-active components may additionally contribute to the formation of the droplets [57]. Hence, the surface concentration of the surfactant on each droplet and the interfacial tension for an individual droplet may be assumed to remain invariable during the experiment.

Fatty acids tend to form dimers in the non-aqueous phase [58]. The aggregation numbers gradually increase with the concentration of the surfactant [59]. Consequently, at higher concentrations, there may be more monomer stearic acid molecules adsorbed to the interface, which could be an additional reason for the increase of the coalescence time. In the presence of a small amount of water, which may appear during switching the liquid reservoir from water to toluene, there may even be inverse micelles in the toluene phase [60].

Unlike the addition of surfactants, the addition of salts, e.g. NaCl, CaCl₂, Na₂SO₄, increases the interfacial tension between hydrocarbons and water. A higher salt concentration increases the interfacial tension to a larger extent [61]. This would decrease the coalescence times, contrary to our results. Therefore, interfacial tension is not responsible for the increase of the coalescence time in the presence of salts examined in our experiments. The salt effect on interfacial properties is usually evaluated by accounting for the electrical double layer forces, with the DLVO theory. This theory works well for low salt concentrations and the fluid-surface
separation higher than a few nanometers. For the concentrations exceeding 0.1 M, as in our experiments, the range of the electrostatic interactions is greatly reduced and the specific ion effects dominate. Wang et al. investigated the effect of different halide ions on bubble coalescence and showed that the coalescence time increased in similar concentration ranges as in our experiments. They stated that the electric double layers at the bubble surfaces become weak with the increasing salt concentration due to compression of the double layers and that the inhibition of bubbles coalescence at high salt concentration is not well understood [62]. The role of specific ions may be understood through their adsorption and hydration. The ions attached to the surfaces of the droplets create repulsion between the two merging droplets and resist the coalescence at short distances where the Van der Waals attraction forces prevail. The surface of a toluene droplet has a negative zeta potential [63], so that the outer surface has a positive charge. Therefore, the surface tends to attract negatively charged ions. When in our experiments we changed the cations, while the anion Cl\(^-\) remained the same, this did not affect the coalescence times. On the contrary, when the anion was switched to the hydrated sulfate possessing a significantly larger diameter than the hydrated chloride [64], the repulsion due to hydration increased. The ionic strength of SO\(_4^{2-}\) is twice that of Cl\(^-\) at the same concentration. The addition of SO\(_4^{2-}\) stabilized the interface and significantly increased the coalescence time. With the presence of stearic acid (0.1 wt%), the coalescence was rarely observed at very small concentration (0.1 mM) of NaCl. No coalescence was observed for the NaCl concentrations higher than 0.1 M. The surface charges of the droplets are screened by electrolytes, inducing a denser packing of stearic acid molecules at the interface. Thicker and more rigid interfacial films may form with saline solutions compared to distilled water, which may be the reason for such stabilization effect. For higher concentrations of the non-pH-determining ions, the Debye screening length decreases and contributions from the diffuse double layer become apparent, which leads to lower surface potentials. This, in turn, reduces the surface concentration of hydronium ions and promotes the dissociation of additional carboxylic acid groups creating larger repulsion forces. The relative proportion of uncharged COOH groups at the interface decreases, which increases the stability of the interface with regard to the droplet coalescence. Density and viscosity of the continuous phase may also influence the stability of oil droplets and delay their coalescence [65]. However, the change of density and viscosity of water within the concentration range of salts adopted herein is not significant compared to the intermolecular interactions.

Dudek et al. studied the effect of salts and surfactants on the coalescence of hydrocarbon droplets in a saline environment, similarly to our study [39]. Their results seemingly contradict ours, in that the reported coalescence times are reduced by the increase of the salinity. A reason for the difference is that their definition of coalescence times includes the time required for the liquid film between the two droplets to drain out, while we exclude this stage and only consider the merging times since the first droplet contact. Our definition is less dependent on the geometry of the space where the coalescence is studied. Dudek et al. studied the coalescence in a larger space compared to the droplet sizes. There was enough space for the two droplets with a negatively charged surface to keep a distance from each other. Hence, the times required for the droplets to approach each other dominated in the total coalescence time. High salinity neutralized the surface charges and decreased this time. In our case, the drainage times were largely shortened due to hydrodynamic flows in the confined space. This gives us an easier way for comparison separating the physicochemical effects from the contribution of a particular flow geometry. With well-controlled hydrodynamic conditions, we could get well repeatable results. Moreover, the directed movement of droplets in capillaries resembles the flows in the pores of petroleum reservoirs or the filters, in correspondence to our applications.

The pH plays an important role in the presence of stearic acid, as the interfacial activity of RCOOH is pH-dependent [66][67]. As pH becomes higher, the RCOOH groups are gradually deprotonated into RCOO\(^-\) anions. The stability of the oil droplets is ensured by the repulsive electrostatic interactions between the stearate RCOO\(^-\) head groups present at the interface, leading to a larger excluded area of the individual molecules.
A strong correlation exists between the RCOO⁻ formation and interfacial tension [68]. We performed measurements of interfacial tension between toluene (0.1 wt% stearic acid) and water at different pH. The interfacial tension did not exhibit a significant change at pH values lower than 8.3. When the pH value reaches the pKa of stearic acid (around 10.15 [69]), all the RCOOH is deprotonated into RCOO⁻. Then the interfacial tension becomes much lower due to maximum adsorption of RCOO⁻ at the interface. At very high pH (pH ~ 12), the interfacial tension drops dramatically to a rather low value of ~ 7.5 mN•m⁻¹ compared to ~ 34 mN•m⁻¹ at lower pH values. Similar viscous-like interface as that in Figure 9 is formed. The change of interfacial tension cannot effectively account for the stability of droplets at increased pH. It should be mentioned that there has been significant controversy around the actual pKa's of fatty acids at interfaces and the effects of both micellization in the aqueous phase and the dimerization in the oil phase as mechanisms affecting the equilibrium conditions across the oil-water interface.

A very high pH is connected with an increase in Na⁺ concentration as the pH is adjusted with NaOH solution. The Na⁺ cations screen the electrostatic repulsion between the carboxylate polar heads and thereby reduce their specific area. At low interfacial tensions, the droplets may change shapes in the flow and collapse into stable interfacial films. The generation of the droplets may fail. Kanichy & Shah investigated the pKa of fatty acids and found that hydrogen bonds are easily formed when the pH was near the pKa [69]. Stearic acid molecules may stack together driven by hydrophobic interaction and hydrogen bonding. Vesicles or planar sheets may form due to the collapsing of the spherical shape and shortening of the distance between carboxyl headgroups by hydrogen bonding and counterions, leading to stable aggregates in the microchannel. The mechanical properties and viscoelastic properties of the oil-water interface may also vary, contributing to the formation of plastic-like interfaces.

5. Application to oil recovery

The above results may contribute to the explanation of the role of oil and brine compositions and their interactions on the interfacial properties of crude oil-brine systems, with implications for the production and processing of crude oil, especially in the application of waterflooding of petroleum reservoirs. The oil in a reservoir exists in contact with a high salinity formation water. Seawater with a lower salinity is usually injected under waterflooding. Improved oil recovery by waterflooding involves modification of the salt composition of the injected water, which is the so-called smart water injection. Calcium, magnesium, and sulfate ions have been reported to be most advantageous for the recovery [70][71][72][73].

The residual oil exists in the form of separate droplets. Common knowledge is that such dispersed oil cannot be recovered unless the droplets merge into larger “spots” that can move in the flow. On the other hand, stable droplets may be captured by the pore constrictions and plug them for the water flow. This diverts the flow towards unswept zones. This mechanism is called the microscopic fluid diversion [74][75]. In a heterogeneous reservoir, the injected water may break through the high-permeable zones, causing non-uniform sweep. If the oil droplets in such zones become stable, emulsions are formed and plug the water-bearing zones. Water will then be diverted to other positions, producing a more uniform oil displacement. Therefore, stability and coalescence of oil droplets is an important factor for the success of waterflooding. The size of our microchannel is close to reservoir pore sizes, and the experimental results may help understanding the underlying mechanisms for smart waterflooding.

Higher salt concentrations stabilize the oil droplets to a higher degree, as observed in our experiments. This may be one of the reasons why flooding with brines of a lower salinity may increase the recovery. However, the mechanism may also be different. For example, it has been reported that the cations of calcium and magnesium in the injected water may increase recovery [76]. Our experiments show that these cations do not affect the coalescence differently from
the sodium ions. The mechanism of increasing the recovery must be different in this case. Probably, this is related to the formation of the emulsions or reactions on the rock-fluid interface [74][77]. On the contrary, our experiments show that the sulfate ion may contribute via the coalescence or fluid diversion mechanisms. Oil-water-solid emulsions may form in the presence of solid fine particles, which may be an additional mechanism facilitating microscopic flow diversion [74][75].

Our results indicate that the residual oil droplets are highly stabilized in the reservoir if the pH is higher than 8.5. Dudek et al. performed similar coalescence experiments with crude oil and found that coalescence is more likely to happen at a lower pH of the saline solutions [37]. Any technique allowing for lowering the pH of the reservoir brine may help to avoid the formation of naphthenates and induce coalescence of the stabilized oil droplets, thereby increasing the recovery rate. The interactions between oil, brine, and surface of reservoir rocks, e.g. wettability or surface charge, should also be taken into account when the pH effect on oil recovery is considered [78][79]. Aksulu et al. showed that brines with a lower salinity increase the local pH in a sandstone reservoir and affect the adsorption/desorption of organic components. The clay becomes more water-wet and the recovery is promoted [80]. However, we have shown that under high pH the oil-water interfaces are stabilized. The mechanism of blocking narrow pores and subsequent fluid diversion is more likely to account for the improvement of the recovery in this case [74].

Salinity increase causes an increase in coalescence time, corresponding to more stable droplets. Therefore, injection of the low salinity brine may facilitate the recovery. The ionic effect was mostly attributed to the influence on the surface-active asphaltenes and resins. However, our experiments indicate that salinity and ionic species may also have an impact on the stability of the droplets consisting of pure toluene. Calcium and magnesium have been shown to be the most effective cations that promote the emulsification of crude oil [81]. Here we have shown that for the pure toluene droplets, the cation species have a limited impact on their stability. This confirms that emulsions are stabilized through adsorption on the water-oil interface of some strong surface-active components like naphthenic acids, asphaltenes, and resins; and through complexation of acidic groups with cations in the brine in the case of cations.

6. Conclusions

We have studied the generation and coalescence of model oil (toluene) droplets in a microchannel under brine flow. Four main stages can be resolved in the coalescence process: 1. Two droplets approach each other and the liquid between the two droplets drains out; 2. The collision of the two droplets occurs; 3. The interfacial film ruptures; 4. Merging/fusion of the two droplets into a larger droplet happens. A head-on collision is faster than a glancing collision. Larger droplets that are formed from coalescence travel faster than smaller ones in the microchannel, which suggests a ‘domino effect’ escalating the droplet coalescence in the flow.

The effects of salinity and ion species were studied by adding NaCl, CaCl2, MgCl2, and Na2SO4 into the water phase. Adding salts increased the coalescence time. Cations examined in our experiments did not affect the times significantly, while sulfate ions increased the coalescence times about threefold at a concentration of 0.6 M, compared to the chloride ions.

When surface-active component stearic acid is present in the system, coalescence is slowed down. A higher concentration yields a longer coalescence time. This is caused by a decrease of interfacial tension between toluene and water in the presence of stearic acid.
A pH higher than 8.5 stabilizes the interface by forming RCOO⁻ groups. The coalescence time increases correspondingly. The values of pH higher than the pKₐ (~10) of stearic acid induce very stable toluene-water interfaces and the generation of the droplets is stopped.

Changing parameters of the injected brine (smart waterflooding) may improve the residual oil recovery when the oil exists in the form of oil-in-water droplets. Coalescing the droplets may promote the recovery. Our experiments indicate that coalescence may be facilitated by injection of the lower salinity brine and decrease of the pH. Potential determining cations (Ca²⁺, Mg²⁺) do not seem to affect this mechanism significantly, while anions (SO₄²⁻) hinder coalescence to a great extent. The presence of the natural surfactants increases the coalescence time and prevents the drops from coalescing in the presence of salts. We believe that coalescence, along with different mechanisms (e.g. microscopic diversion or reactions on the rock-fluid interfaces) is among the mechanisms for oil recovery.

Acknowledgments

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Appendix A. Supplementary material

References


Table 1. Physical properties of stearic acid.

<table>
<thead>
<tr>
<th>Name</th>
<th>Stearic acid/Octadecanoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C\textsubscript{17}H\textsubscript{35}CO\textsubscript{2}H</td>
</tr>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>284.48</td>
</tr>
<tr>
<td>Density (g/cm\textsuperscript{3})</td>
<td>0.9408</td>
</tr>
<tr>
<td>pKa</td>
<td>10.15 [69]</td>
</tr>
<tr>
<td>Solubility in toluene</td>
<td>15.75 g/100g</td>
</tr>
<tr>
<td>Log(K\textsubscript{ow}) (heptane/aqueous phosphate buffer)</td>
<td>7.6×10\textsuperscript{3} [42]</td>
</tr>
</tbody>
</table>
Figure 1. (a) Chemical structure of stearic acid; (b) Stearic acid exists on the interface between toluene and water, with its hydrophilic carboxyl group facing the bulk water and the hydrophobic hydrocarbon tails dissolved in toluene.
Figure 2. Schematic illustration of the flow control system. The pressure is supplied to the pressure controller by purified nitrogen gas at around 2 bars. The desired pressure can be modulated and supplied to the sealed liquid reservoirs to compress the air inside and drive the fluid flow into the microfluidic chip. The generation and coalescence of the droplets are visualized with an inverted microscope with a 10X objective. The inset shows the schematic illustration of the microfluidic chip for droplet generation. All channels have a depth of 50 μm.
Figure 3. Different flow regimes at different pressure ratios for the flow of toluene and water. 
(a, b) 1.08:1; (c) 1.03:1; (d) 1.015:1; (e) 1:1.
Figure 4. Different stages captured in the coalescence process of toluene (0.05 wt% stearic acid) in water: (a) Two droplets approach each other, and the thin interstitial film drains. (b) (c) Two interfaces overlap and interact. (d) The interfacial film ruptures, and a rapid flow of liquid between the two droplets occurs. (e) (f) (g) (h) (i) (j) (k) (l) Merge of interfaces leading to the coalescence of the two droplets and subsequent adjustment of the new droplet shape.
Figure 5. Schematic illustration of head-on (left) and glancing (right) collisions between two toluene droplets. The arrow represents the direction of the water flow.
Figure 6. Coalescence time for head-on collision and glancing collision with toluene droplets in water and in 0.1 M NaCl solution.
Figure 7. Average coalescence time for toluene droplets in water with different salt species at increasing concentrations.
Figure 8. (a) Coalescence time for toluene droplets in deionized water (○) and surface pressure (□) versus concentration of stearic acid dissolved in toluene. (b) Coalescence time plotted
against the surface pressure of toluene (with different concentration of stearic acid) in water. The dashed line represents a linear fit of the data.

Figure 9. (a) Plasticized interfacial films forming between toluene/0.1 wt% stearic acid and water. The generation of droplets was stopped and the microchannel was filled with stabilized oil-water interfaces. (b) The behavior of toluene/stearic acid droplets at different pH of the water phase.
Figure 10. (a) An example of larger droplets catching up smaller droplets ahead. (b) Schematic illustration of the fluid flow around droplets. Blue circles represent two droplets with different sizes, and the grey shadows represent water that flows around the droplets.