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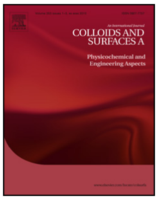

Effect of surfactant concentration and viscosity of outer phase during the coalescence of a surfactant-laden drop with a surfactant-free drop

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HIGHLIGHTS

- Coalescence of drops in oils of various viscosities follows the same power scaling law.
- Marangoni flow induced by the interfacial concentration gradients is observed.
- Coalescence of dissimilar drops is accompanied by a considerable bulk convection.
- Convective patterns depend on the viscosity of the outer phase.
- Asymmetric bridge meniscus is due to local differences in interfacial tension.

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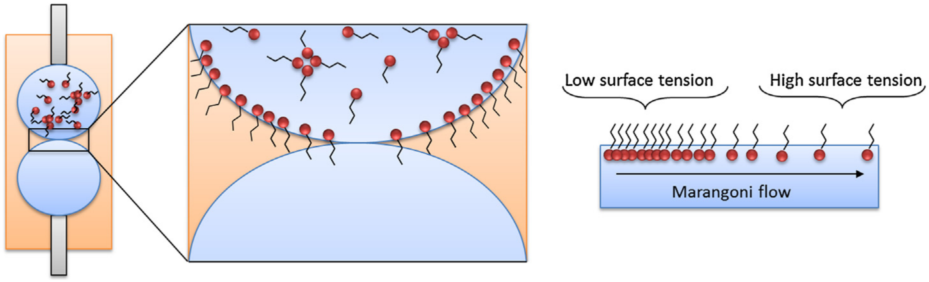
GRAPHICAL ABSTRACT



ABSTRACT

This work focuses on the coalescence of two water drops, one of which contains surfactant. The coalescence was carried out in surrounding silicone oils of various viscosities. It has been found that, in all the studied cases, the outward motion of the liquid neck follows the power scaling law with exponent ~0.5 with the pre-factor dependent upon the surfactant concentration and viscosity of outer phase. Interfacial Marangoni flows arising at coalescence were visualised and quantified. Considerable convective bulk motion was observed by coalescence of surfactant-laden and surfactant-free drops with patterns depending on viscosity of outer phase. No noticeable convection was observed during the coalescence of two surfactant-free drops or similar surfactant-laden drops. It was confirmed that the rate of growth of the liquid bridge was reduced when the surfactant was present in the drops due to the lower interfacial tension in the bridge. Dependence of the reduction on surfactant concentration and viscosity of surrounding liquid is discussed. For the coalescence of a surfactant-free drop and a surfactant-laden drop, the curvature of the meniscus was different on either side of the growing bridge.

1. Introduction

Rapid expansion of formulated products signifies a need to understand the development of bespoke drop designs. For example, recent developments in microfluidics convey new possibilities and precise control of drop coalescence that can be exploited for a plethora of functional products and processes. For instance, aqueous drops in oil can be considered as independent reactors, relevant for many applications [1], hydrogel bead generation [2] or nanopar-

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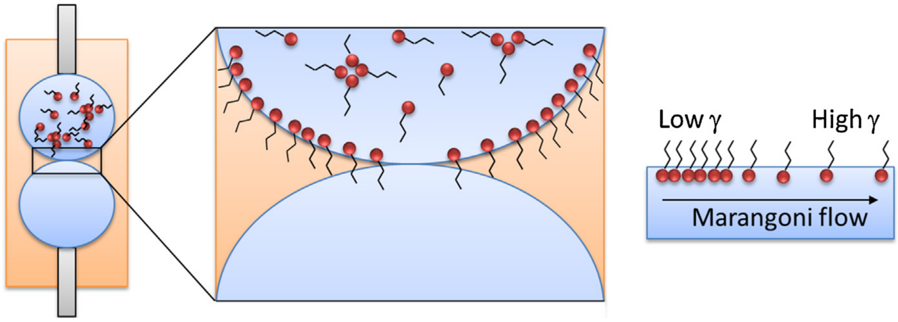

Fig. 1. Schematic representation of induced Marangoni stresses in the coalescence of drops with different composition.

ticle synthesis [3]. These applications and processes are not limited to the coalescence of drops that have similar composition, on the contrary, the possibility of merging dissimilar drops to initiate mixing, fusion, polymerisation or any kind of reaction in a highly controlled manner results in formulation of bespoke multiphase structures which deliver specific functions via novel manufacturing routes. Understanding of the detailed dynamics of such complex multiphase flows is of crucial importance for process development and optimization.

When the fluid film separating two drops ruptures, coalescence occurs spontaneously to form a bigger drop. The coalescence is driven by the capillary force and balanced by the viscous forces at early stages (or highly viscous drops) and inertial forces at longer timescales (or low viscosity drops) [4–6]. However, a few recent studies can be found that employ these theories developed for the dynamics of coalescence in inviscid surrounding liquid to the case where outer liquid is present [7,8].

Most studies on the coalescence of surfactant-laden drops in a surrounding liquid focus on the liquid film drainage just before the drops make contact [9,10]. In this case, a viscous surrounding liquid is present and the flow type and rate of the liquid film drainage from in-between the drops is considered [11,12]. However an open question remains on how the surfactant affects the coalescence after the drops make contact. Presence of the surfactant on the interface reduces the surface tension, γ, and non-uniform surfactant concentration results in surface tension gradients, i.e. the tangential stresses on the liquid interface. These tangential stresses cause surface flow which propagates into the liquid bulk (Marangoni effect, Fig. 1). Marangoni flow results in an additional bulk mixing, which is of importance for many industrial applications. Surface flow causes redistribution of surfactant and changes in the local capillary pressures affecting the kinetics of coalescence. The experimental study by Blanchette et al. [13] describes the effect of surface tension gradients on the coalescence in air of liquid drops with a reservoir of miscible but different liquid having a distinct surface tension. It was observed in [13] that the regime of coalescence depends crucially on the drop/reservoir surface tension ratio. The presence of capillary waves during the coalescence of two drops made from two different miscible liquids that had different surface tension was observed in [14]. Note, both above mentioned studies have been performed employing pure liquids. To the best of the authors' knowledge there are no studies reported on the coalescence of surfactant-laden drops in surrounding liquids bearing different surfactants and with different surface tensions, despite the obvious practical importance of such studies.

Therefore, the aim of this study is to fill this gap and to understand the dynamic processes i.e. the kinetics of bridge expansion as well as surface and bulk motion during the coalescence of two liquid drops, one of them having a much lower interfacial tension due to dissolved surfactant. It should be stressed that this study is devoted to the processes which occur after the fluid film separating the two drops is ruptured. As a plethora of applications deals with the drops merging in an immiscible liquid, this study considers aqueous drops coalescing in silicone oils of various viscosities.

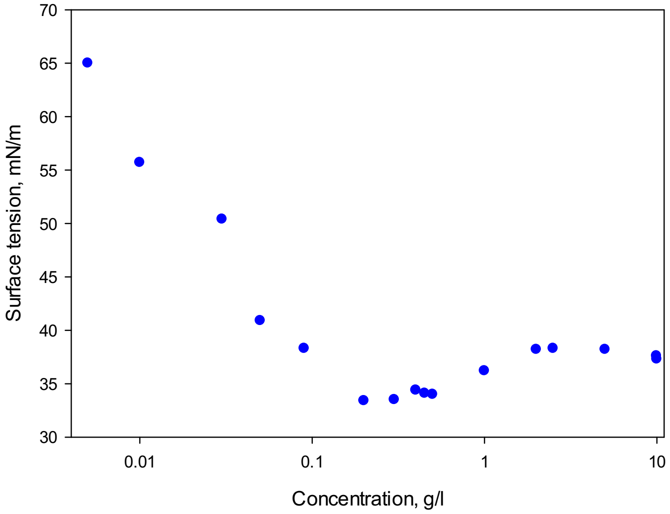

Fig. 2. Surface tension isotherm of sodium lauryl ether sulphate (SLES).

2. Materials and methods

The aim of this work is to investigate the coalescence of drops with an induced interfacial tension gradient along the joining liquid bridge. The gradient was created by contacting two drops, one of which was composed of pure or dyed water and the other was an aqueous solution of sodium lauryl ether sulphate (70%, ES-70, R&D Laboratories Ltd), an anionic surfactant commonly used in industry. The critical micelle concentration, CMC, of SLES was found from the surface tension isotherm presented in Fig. 2 as CMC $\sim$0.2 g L$^{-1.}$ The minimum on the curve is due to impurities always present in industrial grade surfactants. The CMC in this case correspond to the minimum in surface tension, after which impurities solubilise in micelles and the surface tension increases. The concentration of surfactant, c, used in experiments, c = 0.84 g L^{-1} was essentially above cmc. Solutions were prepared in double distilled water produced by Aquatron A 4000 D, Stuart. Nigrosin (Alfa Aesar, Johnson Matthey Company) was used at concentration 0.1 g L^{-1} as a dye to visualise the bulk flow. Hollow glass spheres with average particles diameter of 10 μm, purchased from Dantec were used to visualise the surface flow. Surface and interfacial tensions were measured with Wilhelmy plate method, using a Krüss K100 tensiometer. The interfacial tensions between water and silicone oil was $\sim$32 mN m^{-1}, that of Nigrosin solution, $\sim$25 mN m^{-1}, both are significantly higher than the interfacial tension between aqueous SLES solution and silicon oil, $\sim$9 mN m^{-1} for c = 0.84 g L^{-1}. The coa-

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lescence experiments were performed in silicone oils of various viscosities (0.82, 4.565, 9.3, 19, 48, 96, 339, 485, 970 mPa s) purchased from Sigma-Aldrich.

Fig. 3 shows the sketch of the experimental setup used to study the drop coalescence. The experiments were performed as follows: a transparent cuvette, 45 mm height, 10 × 10 mm cross-section was filled with silicone oil. The aqueous drops of volume ~30 μL were formed at the tips of metal capillaries (1.81 mm outer diameter) using two micro syringes connected to syringe pumps (World Precision Instruments, model AL-1002X). The drops were brought into contact by a micromanipulation rig (THORLABS, Model BSC101 and Longshore Systems Engineering) with controlled constant velocity of 0.01 mm/s. The coalescence process was recorded with a high-speed camera (Photron SA3 or SA5) with varying frame rates depending on the phenomena investigated (2000–10,000 fps). The additional objective (Navatar, 2X F-mount) was used for zooming the coalescing event. The measuring cell was illuminated with cold light source (Krüss Optronic, model KL5125). Image processing was performed using ImageJ free software and Matlab.

3. Results and discussion

3.1. Interfacial/Marangoni flow

An interfacial tension gradient occurs during contact of drops of different compositions. Under the action of this gradient, Marangoni flow develops in the system directed at the interface from the surfactant-laden drop (lower interfacial tension) to the surfactant-free drop (higher interfacial tension) as depicted in Fig. 1. The flow transfers surfactant from the interface of the surfactant-laden drop to the interface of the pure water drop. As there is no surfactant in the bulk of the surfactant-free drop, surfactant desorbs from the interface and transfers to the bulk phase in the drop. At the same time, the surfactant removed by convection from the interface of surfactant-laden drop is replenished by the mass transfer from the bulk phase of the surfactant-laden drop. That is why the surface tension gradient and Marangoni flow is present for a relatively long time.

The interfacial flow penetrates to both bulk phases (drop and surrounding) with viscosity being a drag factor. Therefore the intensity of interfacial flow and the rate of surfactant transfer depend on the viscosities of both aqueous and oil phases. It can be expected that the interfacial flow is slower in the presence of more viscous surrounding phase. This is confirmed by visualisation of the interfacial flow as shown in Fig. 4. Snapshots taken at the same time, 5 ms, from the initial contact time, t = 0, show clear differences between the extension of the interfacial flow in 4.565 mPa s and 48 mPa s surrounding oils (sf. Fig. 4c and e). When two similar drops (either surfactant-free or composed of the same surfactant with the equal concentrations) coalesce, no interfacial motion occurs (Fig. 4a and b). In the asymmetric case of coalescence of surfactant-laden and surfactant-free drops the particles initially present only the drop containing surfactant are convected towards the water drop of larger interfacial tension (Fig. 4c and d). The propagation of the front of particles with time obtained by the image processing is shown in Fig. 5a. The zero distance corresponds to the position on the particles front at the moment when the drops come into contact. The slope of lines in Fig. 5 gives the propagation velocity, v, shown in the graph Fig. 5b. The interfacial velocity can reach up to 0.25 m/s for 4.565 mPa s surrounding oil, but it decreases considerably with the increase of viscosity surrounding oil being only 0.08 for the oil of 96 mPa s.

3.2. Effect of the surfactant asymmetry on the bridge shape

The evolution of the shape of the bridge between two surfactant-laden drops of the same composition coalescing in silicone oil is shown in Fig. 6, which confirms that in this case the bridge remains symmetrical about the horizontal middle plane during the coalescence.

If surfactant is present only in one drop, the bridge becomes highly asymmetrical in low viscosity surrounding oils (Fig. 7). The curvature of the interface on the side of surfactant-laden drop is much higher than that on the side of the pure water drop. This asymmetry is not related to the action of gravity, because the larger curvature is observed for surfactant-laden drop independently of its position (sf Fig. 7a and b). This asymmetry can be related to the capillary pressure $P_c = \gamma k$, where k is the local curvature. The capillary pressure determines the difference in the pressure between the inner and the outer liquids. If the pressures in the drops are different, there should be flow from one drop to another until the pressure equilibrates. The interfacial tension in the surfactant-laden drop is smaller: therefore at the same pressure the curvature should be higher. Comparison between Fig. 4c–e shows that the asymmetry decreases with the increase of the surrounding oil viscosity. This may be because the pressure equilibration occurs slower in highly viscous surroundings. A previous study [14] on the coalescence of miscible liquids that have different surface tension (water and ethanol drop) in air reported presence of capillary waves, hence asymmetrical shape, on the drop with higher surface tension. This was ascribed to the flow of the liquid film on the surface of the drop with higher surface tension.

3.3. Kinetics of bridge expansion

The bridge expansion after the merging of two drops is caused by the difference in the capillary pressure in drops and in highly curved meniscus around the bridge. The higher pressure in the drops drives the liquid into bridge resulting in an increase of bridge diameter, D, with time and is opposed by the viscous and inertial forces [15,16] (Fig. 8). Note, that the pressure in the bridge is determined by the two principal radii of curvature r(t) and D(t)/2 (Fig. 8) which have the opposite signs. In what follows the bridge diameter in both symmetrical and asymmetrical cases presented in Fig. 8 is determined as the minimum diameter.

An example of kinetics of bridge growth is given is Fig. 9. This example shows that both, the presence of surfactant and the properties of surrounding liquid have a considerable influence on kinetics. Kinetics slows down in the presence of surfactant due to a decrease of interfacial tension and therefore a decrease of capillary pressure being the driving force of the bridge growth. An increase in the viscosity of surrounding liquid also slows down the coalescence process.

Depending on the main force counterbalancing the pressure gradient two different regime of the bridge expansion can be observed for the drops merging in an inviscid surrounding, such for example as air. In the viscous regime, the capillary force driving the bridge expansion is opposed by viscous forces. Equating these two forces leads to the linear dependence of the bridge radius on time, t, as [4,6]

$$D/2 \propto \gamma/\eta t \qquad (1)$$

where the η and γ are the liquid viscosity and surface tension respectively. This linear regime can be observed in experiments for highly viscous liquids, such, for example, as glycerol.

Many applications however involve low viscosity liquids such as water, for which the coalescence during the experimentally attain-

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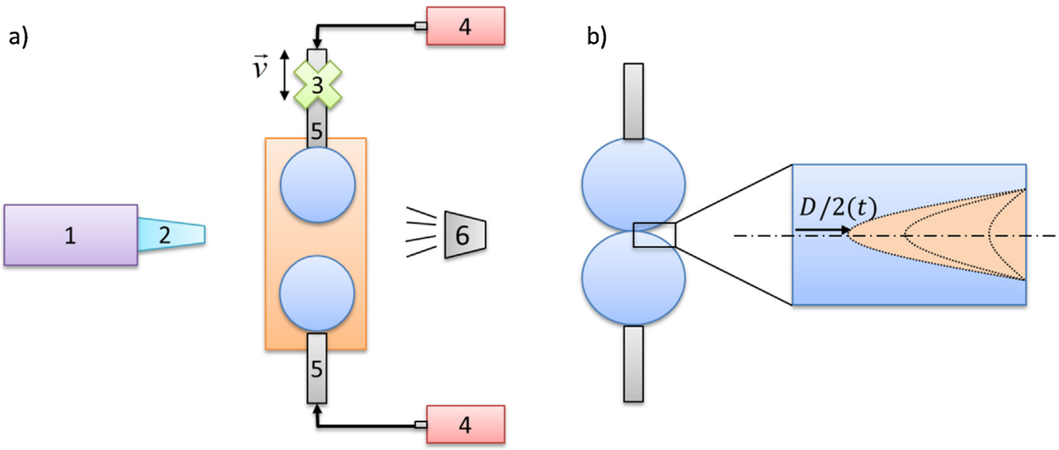

Fig. 3. (a) Sketch of experimental set up: 1—high speed video-camera, 2—zooming objective, 3—outlet of micromanipulation rig, 4—syringe pump, 5—metallic capillaries, 6—light source; (b) the area of interest, growing liquid bridge.

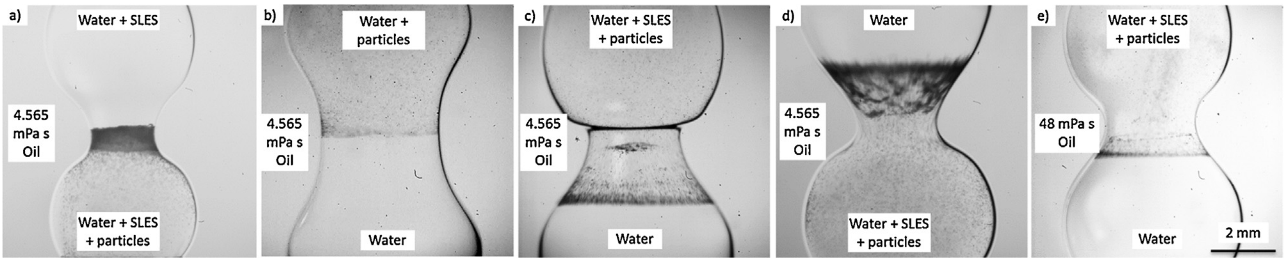

Fig. 4. Propagation of interfacial flow visualised by particles initially added to drops at 5 ms from the initial contact: (a) two surfactant-laden drops in 4.565 mPa s silicone oil, (b) surfactant-free drops, (c) and (d) surfactant-laden and surfactant-free drops in 4.565 mPa s silicone oil, (e) surfactant-laden and surfactant-free drops in 48 mPa s silicone oil.

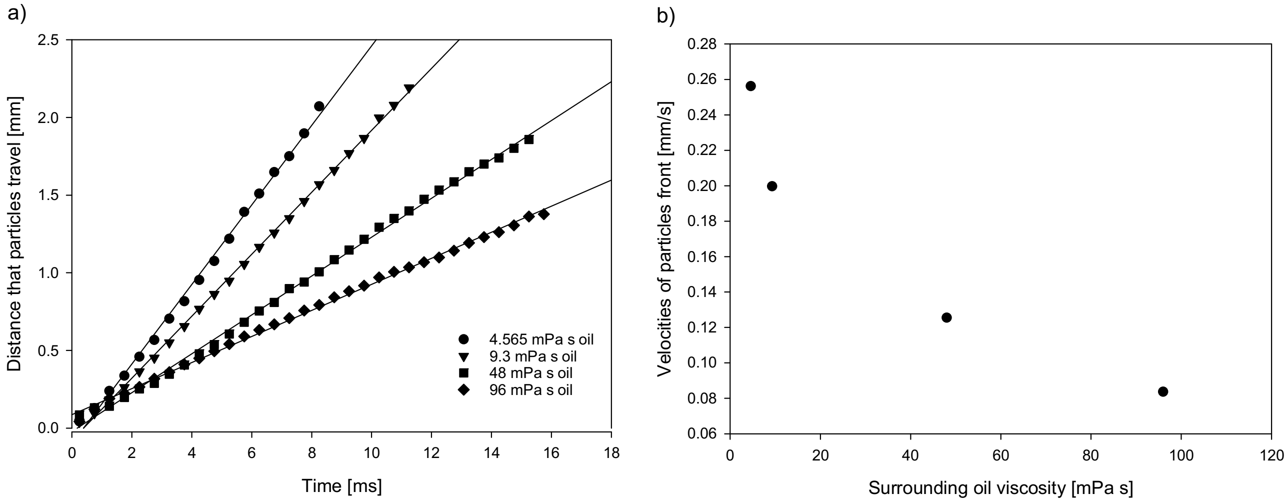

Fig. 5. The propagation of the interfacial flow as visualised by particles present initially in the top drop containing surfactant. The surfactant-laden and surfactant-free drops are brought into contact at t = 0.

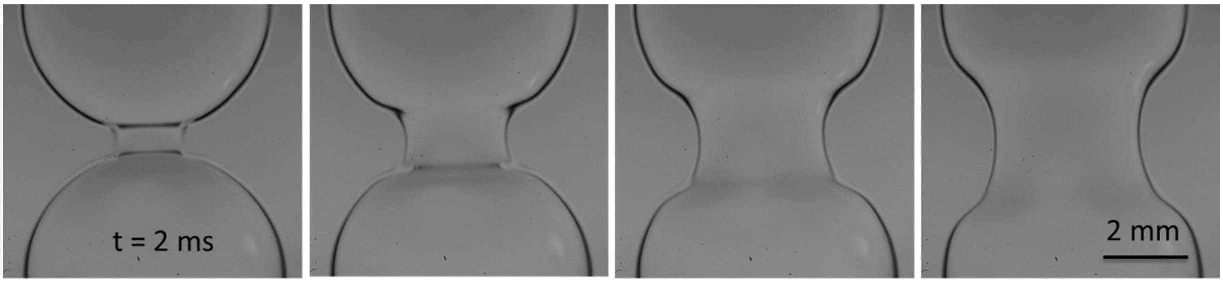

Fig. 6. Images of the coalescing drops of aqueous solution of SLES taken every 2 ms in surrounding 9.3 mPa s silicone oil.

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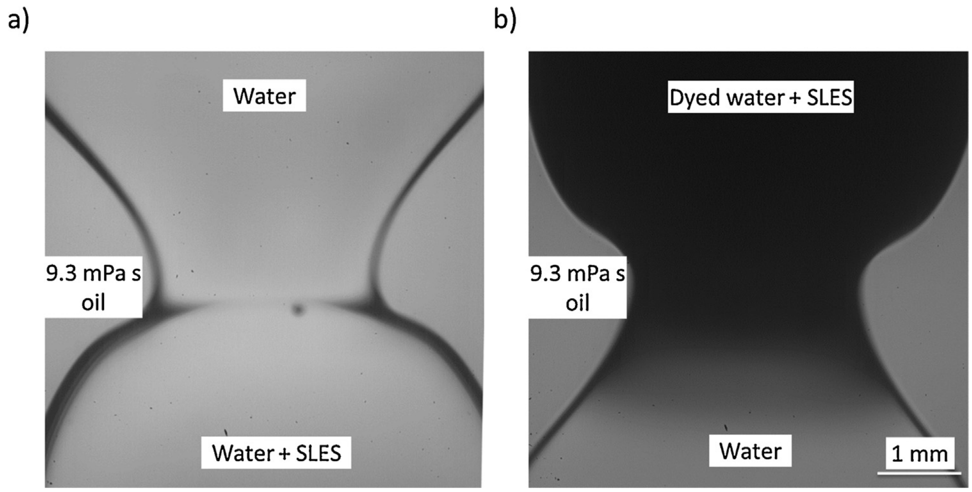

Fig. 7. Images of the coalescing drops of water and 0.84 g L^{-1} aqueous solution of SLES in surrounding 9.3 mPa s silicone oil. The meniscus asymmetry is not due to the gravity. The shape directly reverses when the positions of the two drops swap.

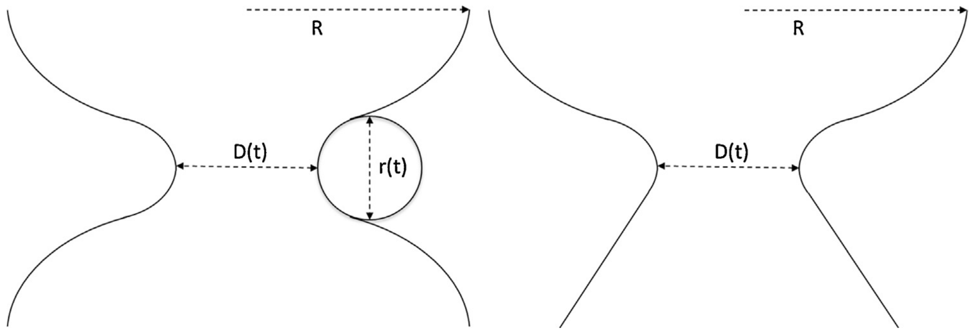

Fig. 8. Scheme of the coalescence of two drops of similar (left) and different (right) compositions.

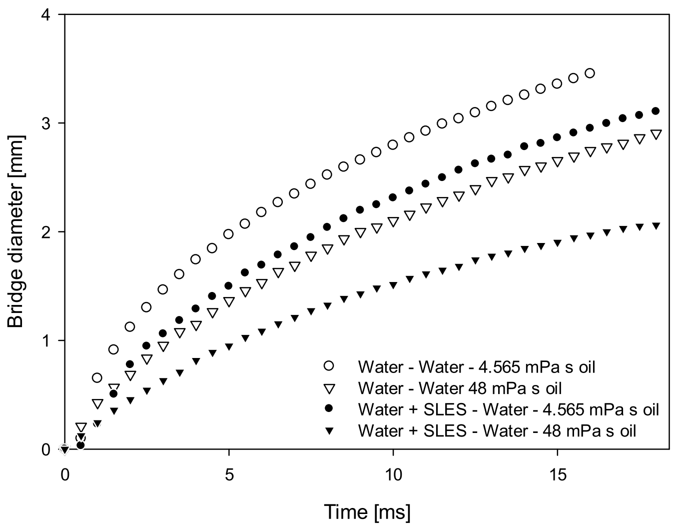

Fig. 9. Comparison of kinetics of coalescence of two drops of pure water and a drop of pure water with a drop of surfactant solution in surrounding oil of 4.565 and 48 mPa s viscosities.

able time scale takes place in the inertial regime with the scaling law [5,17]

$$D/2 \propto \left(R\gamma/\rho\right)^{1/4} t^{1/2} \tag{2}$$

where the R is the initial drop radius and ρ is the liquid density. As it was mentioned above, the literature on the drops merging in surrounding immiscible liquid is rather scarce. According to Ref. [11] in the early stage of coalescence its kinetics are governed by the inner liquid, but after certain time, depending on the properties of both liquids involved, the outer liquid becomes dominating. In the last case Eq. (2) should be replaced by

$$D/2 \propto \left(R\gamma/\rho_{out}\right)^{1/4} t^{1/2} \tag{3}$$

where ρ_{out} is the density of outer liquid, if the inertia of outer liquid is more important than its viscosity or by

$$D/2 \propto \left(R^3\gamma/\eta_{out}\right)^{1/2} t^{1/2} \tag{4}$$

where η_{out} is the viscosity of outer liquid, if the viscosity of outer liquid dominates over its inertia.

In all cases studied here: two drops of pure water, two drops of surfactant solution of the same concentration, a drop of pure water and a drop of surfactant solution bridge diameter was proportional to the square root of time independently on the viscosity of surrounding oil. This is clearly seen from Figs. 10 and 11 where the bridge diameter normalised by the initial drop radius is presented as a function of the square root of time. Though the addition of hollow particles to water does not change surface tension (~72 mN m^{-1}), their presence in one of the aqueous droplets causes reduction of the speed of coalescence, however the difference is very small giving comparable to pure water slopes. The deviations from the linearity can be explained by the fact that the theory was developed for the early stages of the coalescence, when the bridge joining two drops is much smaller that the initial drop radius. Previous studies of the coalescence of different viscosity liquid drops occurring in air revealed that the data could be described by this

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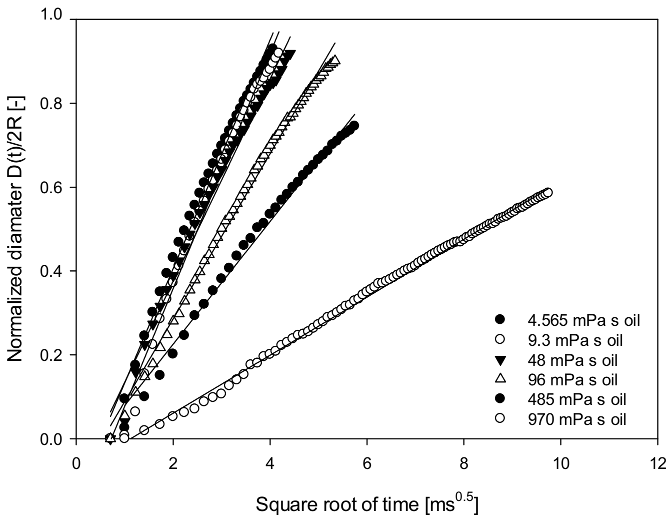

Fig. 10. Kinetics of asymmetric bridge expansion for different viscosities of surrounding silicone oil.

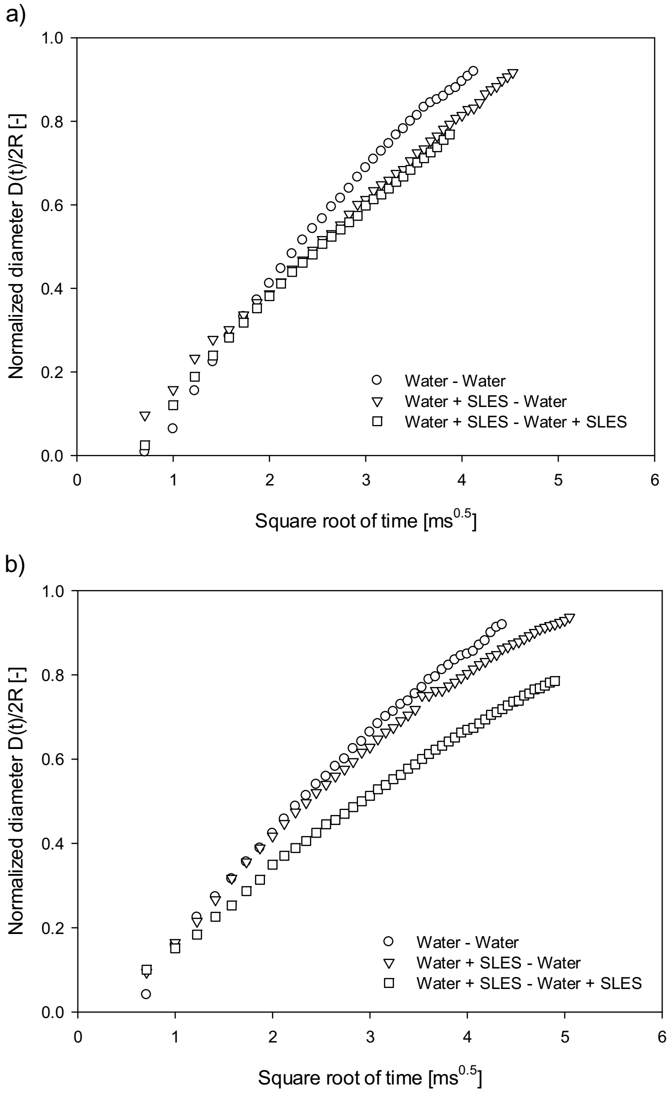

Fig. 11. Dependence of kinetics on surfactant asymmetry in 9.3 mPa s silicone oil (a) and 48 mPa s silicone oil (b).

power law with the exponent oscillating around the value of 0.5 [6,16,18,19]. An earlier study on the coalescence in another liquid reported small effect of the surrounding liquid viscosity (silicone oil) in the range of 0.49–48 mPa s with the unaffected scaling factor slightly oscillating near 0.5 [7]. Therefore the results obtained here for droplets of different compositions including asymmetric case of surfactant-laden and surfactant-free drops are in good agreement with the available data for pure liquids, i.e. the presence of surfactant and Marangoni flow generated at coalescence has no essential influence on the dynamic regime of coalescence.

It is seen from Fig. 10 that there is no noticeable difference in the slope for the two lowest viscosities of surrounding oil. The slope decreases slightly for the oil viscosity of 48 mPa s (sf. Figs. 9 and 10), but starting from the viscosity of 96 mPa s the slope of graph decreases considerably. That is the prefactor in the dependence $D \sim t^{0.5}$ becomes noticeably dependent on viscosity of surrounding liquid. This is in line with the results obtained in [11]. It can be concluded from the results presented in Fig. 10 that the kinetics of a liquid bridge at the viscosity of surrounding liquid below 48 mPa s is described by Eq. (2) or Eq. (3), whereas at higher viscosities there is a gradual transition to Eq. (4). It should be noted that from the results of this study we cannot distinguish between Eqs. (2) and (3) because the densities of silicone oils used are close to each other.

The addition of the surfactant to one of the drops causes a decrease of interfacial tension in the system that subsequently leads to a decrease of the driving force for the coalescence (Fig. 9). Upon the drops making contact the interfacial tension gradients occurs, because the drop containing surfactant has a low interfacial tension ($\sim 10\ \text{mN m}^{-1}$) while the pure water drop has a larger interfacial tension ($\sim 32\ \text{mN m}^{-1}$). The transfer of surfactant with Marangoni flow decreases the effective interfacial tension over the system. As explained in Section 3.1, (Figs. 4 and 5), the intensity of Marangoni flow decreases with the increase of the viscosity of the surrounding oil. That means that the surfactant is supplied slower to the bridge region as compared to lower viscosity surrounding oil. Desorption of surfactant into the bulk is diffusion controlled and depends much less on the intensity of Marangoni flow. Therefore the effective interfacial tension should increase with the increase of the oil viscosity. This assumption is confirmed by Fig. 11, which shows that kinetics of asymmetrical bridge in 9.3 mPa s silicone oil are close to that of bridge between two drops of surfactant solution, whereas in 48 mPa s oil kinetics are close to the kinetics of bridge between two drops of pure water.

3.4. The bulk convection during the coalescence

The use of a dye in one drop allowed tracing the bulk motion during the coalescence as shown Fig. 12. It was discovered that considerable bulk convection develops when a surfactant-laden drop coalesce with a surfactant free one. The bulk convection in the case of asymmetrical drops is affected to the large extent by the viscosity of surrounding oil (sf. Fig. 12a and b). The considerable convective bulk motion occurs only when the two drops have different surfactant concentrations. In the case of the drops of similar composition, convection is absent as it shown in Fig. 12c. With the increase of the oil viscosity the width of the dyed filament becomes smaller, but moves faster. In high viscosity surroundings, formation of a "mushroom" structure of the dyed fluid is observed. It should be stressed that this behaviour is independent of gravity and density differences, as it is unaffected by swapping the positions the two drops.

The observed convective motion and its dependence on viscosity of surrounding liquid can be explained as follows. When two drops of similar size, but different surfactant composition are brought into contact, the capillary pressure is higher in the drop with no surfactant added. This pressure difference drives

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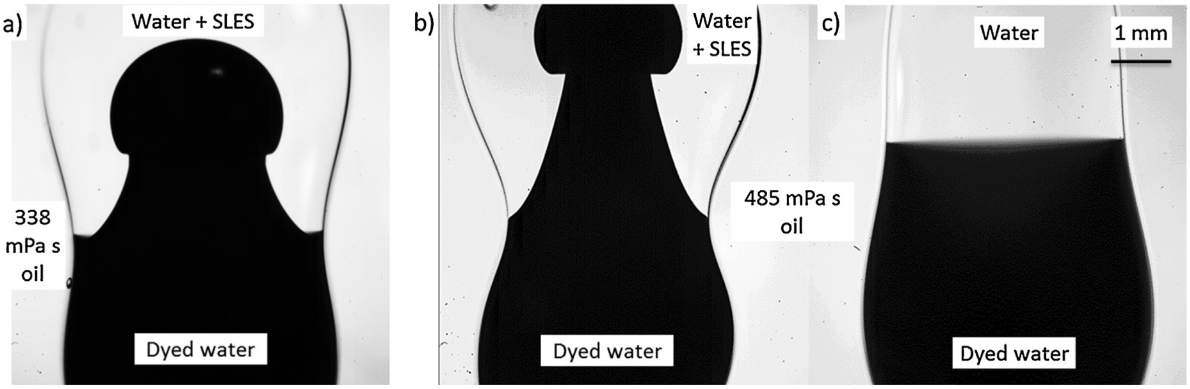

Fig. 12. Effect of the surrounding silicone oil viscosity on the coalescence of drops with different compositions at time 50 ms.

the bulk flow from the surfactant free to the surfactant-laden drop. At the same time, the Marangoni flow develops in the system due to the interfacial tension gradient. This flow is directed from the surfactant-laden to the surfactant-free drop. Obviously the Marangoni flow retards the bulk flow driven by the capillary pressure. The Marangoni flow slows down with the increase of viscosity of the surrounding oil (see Section 3.1). That is why the bulk convection is faster in this case. Due to slower Marangoni convection the surface tension gradient and therefore the conditions of higher pressure in the initially surfactant-free drop retain during the longer time. The last assumption is supported by the smaller asymmetry of the bridge in the surrounding oil of higher viscosity (see Section 3.2 for discussion).

The patterns similar to those shown in Fig. 12 have been observed during the coalescence of two drops of the same pure liquid being of different size [20]. They have been explained by the difference in the capillary pressure due to different curvature of the drop surfaces. This mechanism was confirmed by numerical simulations [21,22].

Note, the convective patterns caused by the difference in the composition of two coalescing drops, such as presented in Fig. 12a and b have been newer reported before, as to the best of our knowledge. The weak tongue of water penetrating into ethanol drop during their coalescence in air was reported in [16], but the depth of penetration was very small. The larger penetration depth was observed in [16] for the water drop coalescing with an ethanol pool. The penetration was explained in [16] by the pressure difference what is in line with the mechanism proposed in the previous paragraph. It can be assumed that the small penetration depth observed in [16] for the two coalescing drops is due to very quick equilibration of surface tension in the inviscid surrounding (air).

The penetration of liquid from one drop into the other was previously observed in the air environment [23]. In this experimental study, the gliding droplet on the wettability gradient solid surface hit the stationary droplet and depending on the surface tension of these droplets (adjusted with Tween 20) the "mushroom" shaped like penetration was observed. However according to [23] the kinetic energy of the moving drop rather than the difference in surface tension was the reason for the structure to appear. The mixing inside coalesced drop as found in [23] was more effective for the cases of convective mushroom formation followed by diffusion. According to our study the presence of viscous surrounding liquid amplify the penetration enormously increasing the contact area of two solutions and improving conditions for the subsequent molecular diffusion.

4. Conclusions

The coalescence of the drops with different compositions was investigated. It was shown that the kinetics of the coalescence follows the power scaling law with a power-law exponent about 0.5 independently of composition of each drop and viscosity of surrounding liquid. At viscosities of surrounding liquid below 48 mPa s inertial kinetics was observed with negligible dependence on viscosity. For higher viscosities of surrounding oil the coalescence slows down with an increase of viscosity. In this case the observed kinetics is in line with the model presented in Ref. [11] for the regime, where the viscosity of outer liquid is dominating.

Upon the contact of surfactant-laden and surfactant-free drops the induced surface tension gradient led to Marangoni flow. The visualisation of surface flow enabled quantifying the flow velocities. It is shown that the increase of viscosity of outer phase results in slower interfacial flow. This results in the higher surface tension and diminishes effect of surfactant. Kinetics of bridge in 9.3 mPa s oil is close to that of two surfactant-laden drops, whereas kinetics in 48 mPa s oil is closer to kinetics of coalescence of two pure water drops.

It is shown that the shape of the bridge joining the coalescing drops is asymmetric relative to the horizontal dividing plane in the case when only one of them is surfactant-laden. This is caused by the inequality of the interfacial tension of the drops.

If two drops of similar composition coalesce there is no noticeable convective mixing in the bulk. At coalescence of surfactant-laden and surfactant-free drops the solution containing surfactant moves into surfactant-free bulk near the water/oil interface due to Marangoni flow, whereas the jet of surfactant-free solution is injected into the surfactant-laden bulk near the axis due to the difference in the capillary pressure between drops. The jet becomes thinner and moves faster with the increase of the viscosity of the surrounding oil.

The results obtained in this study show the way how to improve the mixing during the coalescence of two drops of different compositions: better mixing is achieved in more viscous surrounding as opposed to the more pronounced interfacial motion at lower viscosities.

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