

**Analysis of droplet expulsion in stagnant single water-in-oil-in-water double emulsion globules**

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## **Abstract**

Double emulsions created by phase inversion can be used for fast liquid-liquid separation; therefore, the coalescence behaviors of these types of multiple emulsions need to be predictable for different physical properties and drop size ratios. The aim of this study is to determine the influence of the effective overall drop diameter and the internal droplet size on the coalescence time and the coalescence behavior. Experimental investigations on the physical stability of single stagnant water-in-oil-in-water ( $W_1/O/W_2$ ) double emulsion globules are performed. For this investigation, a formation device to inject one water droplet into an oil drop inside a water bulk phase is developed. The coalescence process of the sole internal water droplet floating on the  $O/W_2$  interface with the water bulk phase, often termed droplet expulsion or external coalescence, is recorded with a high speed camera. Based on image analysis, the diameters of the effective overall drop  $D$ , containing the oil and entrapped water volume, and the internal water droplet  $d$  are determined. Additionally, the coalescence time  $\tau$ , including the time from the first contact of the internal droplet and the drop-bulk interface to the film rupture is measured. A large increase in coalescence time with increasing water droplet diameters is found. For the investigated paraffin oil-water system and initial drop sizes, partial coalescence occurs. In this case, the diameter ratio of daughter-to-mother droplet  $\psi$  is determined.

*Keywords:* double emulsion; separation; droplet expulsion; partial coalescence; coalescence time; multiphase flow

## 1. Introduction

Since their initial description (Seifriz 1925), double emulsions, of either the water-in-oil-in-water ( $W_1/O/W_2$ ) or oil-in-water-in-oil type ( $O_1/W/O_2$ ), have obtained a wide range of industrial applications (Khan et al. 2006). In this nomenclature, index 1 is used for the internal liquid phase; whereas, index 2 indicates the bulk phase. A maximum lifetime is required in most applications, for example in pharmaceuticals (Brodin et al. 1978; Garti 1997), cosmetics (Tadros 1992), foods (Lobato-Calleros et al. 2006), and membranes (Raghuraman et al. 1994). In the crude oil industry, however, fast water and crude oil separation of complex crude oil-water-multiple emulsions is required (Kokal 2005). Double emulsions are also formed as an intermediate step during phase inversion (Pacek et al. 1994), where droplet inclusion (Jahanzad et al. 2009; Sajjadi et al. 2002) and droplet expulsion (Klahn et al. 2002) occur. For liquid-liquid separation in chemical engineering (Hadjiev and Paulo 2005) and the petroleum industry (Vu 2005; Vu et al. 2009), double emulsions are formed by dispersing a water-in-oil ( $W_1/O$ ) emulsion into a water bulk phase. Once the  $W_1/O/W_2$  emulsion is formed, external coalescence of the internal water droplets with the surrounding water phase leads to fast phase separation. The main advantages compared to a settler are increased interfacial area and decreased separation distance.

In this study, only destabilization mechanisms related to film rupture are considered, because the coalescence times in absence of any surfactants and, therefore, the lifetimes of the internal water droplets, are short. Diffusion and Ostwald ripening are not taken into consideration. The steps involved in the external coalescence process are most likely the same as for the binary and interfacial coalescence processes. After reaching the interface, the internal droplet will deform. This deformation depends mainly on the physical properties density difference and interfacial tension. As a result of the gravitational force, the interfacial film drains and decreases in thickness (Hartland 1967a). When the critical film thickness is reached, the random process of film rupture will occur (Hartland 1967b). Even though these phenomena

are investigated intensely for binary and interfacial coalescence, film rupture phenomena in double emulsions are mostly unexplored (Bibette et al. 1999). Experimental investigations on the coalescence of double emulsions are available for stabilized double emulsions (Garti 1997). Internal coalescence of the  $W_1$  water droplets in  $W_1/O/W_2$  emulsions is described for varying hydrophilic and lipophilic surfactant concentrations (Villa et al. 2003). Experiments regarding the external coalescence in  $W_1/O/W_2$  double emulsion with liposomes in the  $W_1$  phase were performed by Wang et al. (2010). In addition to these investigations, Wang et al. compared the external coalescence without emulsifiers in the internal water phase. In both cases, Span 80 is added to the oil phase and Tween 80 concentrations from 0 to 0.01 mol/L are adjusted in the external water phase. Very little has been reported on  $W_1/O/W_2$  double emulsion stability in the absence of surfactants. These configurations were found to be intrinsically unstable (Hou and Papadopoulos 1996). No data regarding coalescence times or partial coalescence in unstabilized  $W_1/O/W_2$  systems are available.

Predicting the coalescence time  $\tau$ , defined as the time from the first contact with the interface to the moment when the interfacial film ruptures (Basheva et al. 1999), is difficult, but critical for double emulsion stability. The shape and the dimension of the interfacial film entrapped between the internal water droplet and the external water phase greatly affect the film drainage velocity, and therefore, the coalescence time (Wang et al. 2010). The interfacial film shape is determined by the ratio of the internal droplet to the effective surrounding drop diameter.

Partial coalescence has been found and described for both the interfacial coalescence case (Charles and Mason 1960; Chen et al. 2006) and the binary one (Zhang et al. 2009), but no detailed investigations of this phenomenon for double emulsions are available. After the hole nucleation in the interfacial film, secondary droplets are formed when the rate of horizontal collapse of the forming water column preponderates the vertical one. Different size ratios  $\psi$ , of the daughter and mother droplet diameters, mostly in the range of 0.3 to 0.5, are reported

(Aryafar and Kavehpour 2006; Charles and Mason 1960; Gilet et al. 2007). Two dimensionless numbers are used to predict partial coalescence (Blanchette and Bigioni 2006; Gilet et al. 2007): The Ohnesorge number

$$Oh = \eta_d \rho_m^{-0.5} \sigma^{-0.5} d^{-0.5} \quad (1)$$

which relates the viscous force to the interfacial force and the Bond number

$$Bo = (\rho_1 - \rho_2) g d^2 \sigma^{-1} \quad (2)$$

which relates the gravitational force to the interfacial force. The dynamic viscosity of the dispersed phase is given by  $\eta_d$ , the mean density of the both liquids by  $\rho_m$ , the interfacial tension by  $\sigma$  and the droplet diameter by  $d$ . The density difference of the liquids is  $(\rho_1 - \rho_2)$  and  $g$  the acceleration due to gravity.

It is reported that partial coalescence takes place in a specific range of drop diameters and, therefore, critical Bond and Ohnesorge numbers are used to predict this effect (Chen et al. 2006). Evidently, since partial coalescence slows down liquid-liquid separation, it plays an important role in process design.

## 2. Materials and methods

### 2.1. Model system

The experiments are performed with paraffin oil (Fauth+Co. KG, Germany) and ultra-purified water with a specific resistance of 18.3 M $\Omega$  cm. To avoid mass transfer during the experiments, the oil and water phases are saturated.

The liquids are saturated by first mixing, and then intensely shaking, oil and water in a 500 mL separation funnel. Both phases are subsequently separated and used for the experiments. Table 1 shows the physical properties of the saturated phases. No emulsifiers are added, and it is important that the system be of highest purity to avoid undefined influences.

Table 1

Both liquids show Newtonian behaviour, and the viscosity of the paraffin oil is determined with an Anton Paar RheolapQC rotational viscometer using a DG42 measurement system. A pendant drop device is used to determine the interfacial tension. The index of refraction is measured with a Krüss DR201-95 refractometer.

For all components in contact with liquids, a thorough cleaning procedure was followed in order to obtain liquids of high purity and to avoid undetermined influences. First, Extran MA 03 (Merck) and hot tap water are used for rough cleaning. After flushing with deionized water, all parts are dried in a fume hood, cleaned with acetone and dried again. Finally, the components are flushed with ultra-purified water and dried in the fume hood before usage.

## *2.2. Experimental setup*

To observe the droplet expulsion processes in a water-in-oil-in-water system, a drop formation device is developed (see Fig. 1). The complete setup in contact with the liquid phases consists only of glass, PTFE, and stainless steel. A covered glass cuvette with a square cross section of 100 mm and a depth of 20 mm is filled with 160 mL saturated ultra-purified water. In order to minimize contact with air and impurities, saturated oil and saturated ultra-purified water for the drop formation are stored in airtight sealed glass bottles.

One cannula with an external diameter of 1.8 mm and a wall thickness of 0.1 mm is used to create the oil drop and also to inject the internal water droplet. With this setup, the disturbance of the interfaces is minimized for a fixed drop configuration. Oil and water are fed in an alternating fashion with two Hamilton PSD/2 precision pumps, each equipped with a 25  $\mu\text{L}$  volume syringe. The water volume is injected into the oil stream through a PTFE T-fitting. Since PTFE is hydrophobic, it is wetted by oil, and water does not get into contact with the PTFE-tubes. The water volume forms a bead inside the oil bulk liquid. Thus, equidistant

segments of water-in-oil are formed inside the tube downstream of the T-fitting. The water-in-oil droplets are formed at the tip of the cannula, inside the continuous water leg. The oil phase does not wet the stainless steel, but rather it forms a drop attached to the PTFE-surface inside the cannula. The drop is kept in position due to buoyancy. It is important to adjust the inlet moment of the water droplet into the oil drop for reproducible experiments. The water droplet should be injected right before the complete oil drop is formed. This can be initialized by changing the length of the PTFE-tube from the T-fitting to the tip of the stainless steel cannula. The stroke speed is set to a low value to reduce internal flow inside the drops. The small water droplet exits the PTFE-tube, falls inside the oil drop, and settles to the lowest position. It floats on the oil-in-water ( $O/W_2$ ) interface until the critical film thickness is reached and the film ruptures. Once the separation process is complete, a water jet generated by a second cannula detaches the remaining oil drop. An insignificant oil meniscus is left on the tip of the cannula. The cycle restarts with the creation of a new  $W_1/O/W_2$  drop with fresh, and therefore clean, interfaces. The experiments are performed at ambient conditions, and since the temperature only ranges from 22 to 24 °C, no thermostat is used.

Fig. 1.

A computer controls the drop formation and image acquisition. Many parameters, including the effective overall diameter  $D$ , water droplet diameter  $d$ , stroke speed, elapsed time before oil drop removal, and the total number of events can be set by the software.

The high speed camera (Photonfocus MV-D752-160) is equipped with a 16 mm 1:1.4 monofocal lens (Pentax C31630KP) and an additional 10 mm spacer. One pixel represents 16  $\mu$ m. The camera is focused on the symmetric axis of the drop. A triggered LED flashlight (CCS Inc. LDL FP-100/100-R) with a square area of 100 mm, the same cross-section as the cuvette, is used to backlight the coalescence cell. The frame rate of the camera and the

synchronized flashlight can be adjusted. The coalescence time  $\tau$ , and the drop diameters  $D$  and  $d$ , are measured with a frame rate of 4 frames per second (fps). Frame rates of up to  $10^4$  fps are used to record the detailed phenomena of film rupture, capillary wave propagation, and coalescence.

Experiments with different overall diameters and internal water droplet diameters are performed. The effective oil drop diameter  $D$ , for the drop including the oil volume and the initial water volume is varied between 2.8 and 3.0 mm. The diameter of the injected water droplet  $d$  is set between 0.9 and 1.5 mm. The maximal and minimal values are restricted by experimental conditions. Therefore, the initial drop size ratio  $d/D$  is between 0.30 and 0.54, which includes the size ratio of  $0.4 \pm 0.05$  used by Wang (2010). For each parameter set, 100 sequences showing the steps of  $W_1/O/W_2$  double emulsion globule formation, water droplet lifetime, and coalescence are performed. The large number of repetitions is necessary to obtain valid data for the stochastic process of interfacial film rupture leading to coalescence. The reproducibility of the formed effective oil drop and internal water droplet diameter has a standard deviation below 0.02 mm, which is close to the resolution of the camera of 0.016 mm per pixel.

### *2.3. Image analysis*

The drop diameters of the effective drop  $D$ , and the internal water droplet  $d$ , as well as the coalescence time  $\tau$ , are determined with the image analysis software. To calibrate the image, the known external diameter of the cannula  $D_c$ , is used and the resolution of the image is determined. A threshold is set with a macro to transform the grey scale images into binary ones. The area of interest is reduced from the original size of 256 by 250 to 2 by 250 pixels. This reduced area includes the symmetrical axis of the drops. The boundaries of the drops and the cannula are recognized as individual objects. The distances between the centers of the

objects in the image are used to determine the internal and external drop diameters. From the recorded frame rate, and the number of frames representing the different stages of the coalescence process, the coalescence times  $\tau_i$ , of the different internal water droplets are calculated. Fig. 2 gives an exemplary result showing the drop formation process, water droplet injection and partial coalescence steps for one experiment.

Fig. 2.

For this representative sequence, the vertical dotted lines indicate the coalescence times of the initial, first and second secondary water droplet  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ . As can be seen, the position of the cannula appears to change within the first seconds. In fact, this drift is caused by the shadow of the forming oil drop. The oil drop interface becomes an individual object after 3 s. Once the oil drop has a certain size, the cannula position stays constant. Caused by a short time delay between the water and oil pump, the position of the oil drop remains unchanged between 5 and 8 s. The lower edge of the overall drop moves to its lowest position within 41 s; by this time the internal water droplet is injected, settles inside the oil drop, and rests at the O/W<sub>2</sub> interface. The distance  $d_{im,1}$  corresponding to the initial water droplet diameter is determined. After about 59 s, corresponding to a coalescence time  $\tau_1 = 18$  s, the initial water droplet coalesces partially and a first secondary droplet with a smaller diameter remains inside the oil drop. The distance  $d_{im,2}$  is obtained and the effective overall diameter decreases as a result of the water volume loss. The secondary water droplet has a lifetime  $\tau_2 = 6$  s. After the second partial coalescence step at about 65 s, a second secondary droplet, represented by  $d_{im,3}$ , remains. This water droplet has a coalescence time of  $\tau_3 = 1.5$  s before the water phase is completely removed by a final coalescence step.

The results for all recorded experiments are exported to a spreadsheet program for further evaluation. To calculate values for the coalescence time of one set of effective overall drop and water droplet diameters, 100 sequences are analyzed. The stochastic nature of the moment of film rupture causes the data to be highly scattered. Arithmetic averages are calculated from this data. To determine a highly reproducible size ratio  $\psi$ , only a few experiments would be required, but all recorded events are analyzed.

#### 2.4. Diameter corrections

The different refractive indices of the saturated water phase  $n_w$ , and the saturated oil phase  $n_o$ , cause optical distortion at the O/W<sub>2</sub> interface to appear. The oil drop acts like a lens and distorts the picture of the internal water droplet; therefore, a correction of this effect is needed. It is assumed that the beams of light are parallel outside the coalescence cell, and that they are not distorted as they pass through the glass wall into the continuous water phase. The flashlight and the camera are installed along an axis perpendicular to the glass surfaces of the cell. Spherical shapes of the external drop and the internal water droplet are assumed for the calculation of the correction term for the optical distortion. An axisymmetric geometry is used. As can be seen in Fig. 3, the upper part of the overall drop is hidden inside the cannula. The effective overall drop diameter  $D$ , enclosing the water droplet and the oil volume, is calculated from the distance  $D_{im}$ , present on the image and the known inner diameter of the stainless steel cannula  $D_{c,inner}$ .

The diameter of the internal water droplet  $d$  is larger than the droplet diameter displayed on the images  $d_{im}$ , because the beam of light tangent to the internal water droplet interface is refracted at the O/W<sub>2</sub> interface.

Fig. 3.

A correction term based on Snell's law

$$\frac{\sin \alpha}{\sin \beta} = \frac{n_o}{n_w} \quad (3)$$

with  $\alpha$ , the angle of incidence of the light beam at the O/W<sub>2</sub> interface, and  $\beta$ , the angle of refraction, is developed. The angle of incidence  $\alpha$  is larger than the angle of refraction  $\beta$ , due to the higher index of refraction of the oil phase,  $n_o$ . The angle  $\alpha$  is calculated by

$$\alpha = \arcsin\left(\frac{(D/2) - d_{im}}{D/2}\right) \quad (4)$$

while angle  $\beta$  follows by equation (3). When the internal droplet is smaller, the influence of curvature increases and the need for a mathematical correction, therefore, becomes more important. Inside an oil drop with an effective overall diameter  $D = 3$  mm a water droplet with a diameter of  $d = 1.0$  mm appears to be only 0.95 mm in diameter. A distance  $d_{im} = 0.5$  mm given on the image represents a droplet with a corrected diameter of  $d = 0.59$  mm. The distortion of the width, or the horizontal size, of the internal droplets is smaller because the curvature near to the symmetrical axis is diminished.

### 3. Results and discussion

#### 3.1. Partial coalescence

For the investigated paraffin oil-water system with the initial diameters of the internal water droplet and the effective overall diameter, partial coalescence occurs. There are three coalescence steps before the complete internal water phase is removed. A detailed sequence of one partial coalescence event is shown in Fig. 4. An internal water droplet with a primary diameter of 1 mm is entrapped inside an oil drop with an effective diameter of 3 mm. The

water droplet floats on the O/W<sub>2</sub> interface. The last image recorded before the interfacial film rupture is visible is selected to be  $t = 0$  ms.

Fig. 4.

Within one millisecond after hole nucleation, the interfacial film flattens and part of the water droplet volume merges with the water bulk phase. Capillary waves propagate over the water droplet interface towards its top. These waves cause an uplift of the droplet apex above the original level. Between 2 and 3 ms, a water column is formed inside the paraffin oil drop. A neck forms and capillary pinch-off occurs, because the horizontal collapse of this liquid column exceeds the vertical one. The secondary droplet is formed within 4 ms after film rupture. These 4 ms are the time of coalescence, defined as the time from the beginning of film rupture to the formation of the secondary droplet (Aryafar and Kavehpour 2006). The O/W<sub>2</sub> interface that had flattened while the hole in the interfacial film was growing, curves back when the film closes again. About 7 ms after the coalescence process started, the secondary water droplet comes to rest on the O/W<sub>2</sub> interface. During this partial coalescence event, no satellite droplets are observed. All recorded partial coalescence events proceed in a similar way as shown in Fig. 4 and as described above.

The size ratio of daughter-to-mother droplet  $\psi$ , is important in predicting how many partial coalescence steps will happen before complete coalescence removes the remaining internal water phase. The internal water droplet size before and after each partial coalescence step is determined by means of image analysis. For the subsequent coalescence events, the daughter droplets are considered the mother droplets. Fig. 5 gives the mother droplet diameter  $d_i$ , and the resulting daughter droplet diameter  $d_{i+1}$ .

Fig. 5.

The diagram should be read in the following way. An initial mother droplet with a diameter of 1.35 mm coalesces partially and a daughter droplet with a diameter of 0.60 mm is left over. This droplet is considered as the new mother droplet and coalesces again partially and a second secondary droplet with a diameter of 0.26 mm remains, that finally coalesces completely. Error bars of the individual data points are not shown in Fig. 5, because the standard deviation of the 100 sequences used for the average values is below 0.01. When partial coalescence occurs, a linear dependence on both water droplet sizes is found. The droplet size ratio  $\psi$  is 0.41 with a standard deviation of 0.06 over the range of the investigated mother droplet diameters. This means that 6.9 % of the initial water volume remains inside the oil drop when partial coalescence occurs. The found size ratio fits to the values presented in various references (Aryafar and Kavehpour 2006; Charles and Mason 1960; Gilet et al. 2007). Mother droplets with a diameter above 0.27 mm do not coalesce completely. With the presented setup and pair of liquids, it is not possible to generate water droplet diameters with a size above the specific range needed for partial coalescence, as proposed by Chen (2006). Therefore, only the lower value of the water droplet diameter for partial coalescence can be given. The presence of an upper critical value for partial coalescence in  $W_1/O/W_2$  double emulsions, meaning a critical droplet diameter above which complete coalescence does always occur, remains unknown at this point of research. Varying the overall diameter between 2.8 and 3.0 mm has no observable effect on the droplet size ratio  $\psi$ . The shown coalescence map (see Fig. 6) introduced by Chen (2006) is used to predict critical values of the Bond and the Ohnesorge number for partial coalescence.

Fig. 6.

In the case of the investigated paraffin oil-water system the critical Bond number is about  $2.5 \times 10^{-3}$  and the critical Ohnesorge number is  $10^{-2}$ . Below this Bond number, and above this Ohnesorge number, complete coalescence takes place. The critical water droplet diameter is about 0.27 mm. All data for the investigated paraffin oil-water system are on one line in the coalescence map, because  $Bo Oh^4$  is constant for one set of physical properties. The critical value of both dimensionless numbers is expected to change for different pairs of liquids.

### 3.2. Coalescence time

The coalescence time  $\tau$  of the internal water droplets is of great importance for the design of liquid-liquid separation processes. In the case of separators working on the principle of phase inversion, the height of the vessel must be large enough to allow complete removal of the internal water phase. In this study the influence of the size ratio between internal water droplet diameter  $d$  and effective overall diameter  $D$  on the coalescence time is investigated. The average times of 100 sequences for one set of parameters are given in Fig. 7.

Fig. 7.

All secondary droplets with diameters below 0.75 mm show an increase in the coalescence time with increasing diameter. While droplets with a diameter of 0.09 mm coalesce within 0.4 s after contact with the O/W<sub>2</sub> interface, droplets with a diameter of 0.6 mm remain at the interface for 10.6 s on average. The delay of the coalescence events is caused by a slowing down of film drainage with increasing interfacial film area. For the water-in-oil-in-water double emulsion globules the interfacial oil film is in between the W<sub>1</sub>/O and the O/W<sub>2</sub> interface. It should be pointed out that for the double emulsion geometry, the curvature of the

$W_1/O$  and the  $O/W_2$  interface are in the same direction. The opposite is true for binary coalescence, where the curvatures are antipodal. The interfacial film drainage for droplet expulsion processes in  $W_1/O/W_2$  systems is, therefore, hindered to a higher extent.

The coalescence times of the initial internal water droplets, having a diameter above 0.86 mm, do not show a consistent dependency on the diameter. These droplets come into contact with the  $O/W_2$  interface with a certain velocity. Therefore, the interfacial film drains not only by gravitational forces, but also by an additional momentum. Accordingly, the coalescence times of the initial water droplets show no clear trend compared to the lifetime of the secondary droplets.

From the representative error bars giving the standard deviation, it can be seen that the coalescence time measurements have more scattered data than the determination of the daughter-to-mother droplet size ratio (see Fig.5). For smaller water droplet diameters the standard deviation decreases. The huge variations of the coalescence time for equally sized droplets are well known (Hartland 1967b). One reason could be impurities in the system influencing the physical properties and, therefore, the coalescence time. The high reproducibility of the droplet size ratio  $\psi$  in the same experiments proves the physical properties remain constant.

## **5. Conclusions**

A formation device for stagnant single water-in-oil-in-water double emulsion globules is developed. Oil drops with a specified volume are generated, and a sole water droplet with a certain diameter is injected into the oil volume. Automation of the experiments is achieved to allow large numbers of repetitions. Therefore, an image analysis procedure is developed to analyze the drop diameters of the internal water droplets and the effective overall drop. For each internal water droplet the coalescence time is measured by means of image analysis software.

It is shown that partial coalescence occurs in coalescence processes of water droplets entrapped inside a paraffin oil drop in an aqueous bulk phase. As a result of the capillary wave propagation on the water droplet interface after film rupture, capillary pinch-off happens. As partial coalescence takes place, the daughter-to-mother droplet size ratio is found to be 0.41. Only droplets with a diameter above 0.27 mm coalesce partially; below that value complete coalescence is observed. This value corresponds with a Bond number of  $2.5 \times 10^{-3}$  and an Ohnesorge number of  $10^{-2}$ . The separation process slows down when partial coalescence occurs, because the single coalescence times add up until the complete internal water phase is removed.

For the secondary water droplets, an increase of the coalescence time with increasing droplet diameters is found. For the initial water droplets that settle inside the oil drop, no clear trend of the coalescence time is observed. Because of their settling velocity, the droplets reach the interface with a certain momentum. Accordingly, the film drainage is influenced and does not follow the same mechanisms as for the smaller drops that are generated close to the interface, and that have no initial velocity.

## Notation

$Bo$	Bond number ( $=(\rho_1 - \rho_2) g d^2 \sigma^{-1}$ )
$D$	effective overall drop diameter enclosing oil and initial water volume, m
$D_c$	diameter of the cannula, m
$d$	water droplet diameter, m
$g$	acceleration due to gravity, $\text{m s}^{-2}$
$n$	index of refraction
$Oh$	Ohnesorge number ( $=\eta_d \rho_m^{-0.5} \sigma^{-0.5} d^{-0.5}$ )
$t$	time, s
$T$	temperature, °C

## Greek letters

$\alpha$	angle of incidence
$\beta$	angle of refraction
$\eta$	dynamic viscosity, Pa s
$\rho$	density, $\text{kg m}^{-3}$
$\rho_m$	mean density, $\text{kg m}^{-3}$ , ( $=(\rho_1 + \rho_2)/2$ )
$\sigma$	interfacial tension, $\text{N m}^{-1}$
$\tau$	coalescence time, s
$\psi$	droplet size ratio

## Subscript

$c$	cannula
$d$	internal water droplet

<i>i</i>	index
<i>im</i>	displayed on the image
<i>m</i>	mean
<i>o</i>	oil
<i>w</i>	water

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Fig. 1. Experimental setup for the formation of stagnant single water-in-oil-in-water double emulsion globules with defined diameters.

Fig. 2. Representation of the different process steps formation, settling, resting, and three coalescence steps and the dimensions after the image analysis. The distances of the objects  $d_{im,i}$ , recognized by software are given with their individual coalescence times  $\tau_i$ . A threshold is applied to the corresponding overlaid images for visualization of the different coalescence steps.

Fig. 3. Geometrical correction of the effective overall drop diameter  $D$ , based on the distance displayed on the image  $D_{im}$ . The water droplet diameter  $d$  is distorted by a change of the index of refraction from  $n_w$  to  $n_o$  and is calculated from the droplet diameter pictured on the image  $d_{im}$ .

Fig. 4. Exemplary partial water droplet expulsion process out of a paraffin oil drop to the water bulk phase.

Fig. 5. Daughter droplet diameters  $d_{i+1}$ , remaining after a coalescence event involving different mother droplet sizes  $d_i$ . The effective overall drop diameter  $D$  is between 2.8 and 3.0 mm.

Fig. 6. Coalescence map relating the Ohnesorge number  $Oh$ , and the Bond number  $Bo$  for the investigated water-in-paraffin oil-in-water double emulsion globules. The effective overall drop diameter  $D$  is between 2.8 and 3.0 mm.

Fig. 7. Coalescence time  $\tau$  of different internal water droplet diameters  $d$  entrapped in a paraffin oil drop in a water bulk phase. The effective overall drop diameter  $D$  is between 2.8 and 3.0 mm. Representative error bars for the different coalescence steps giving the standard deviation are shown.

Table 1

Physical properties of the saturated liquids at  $T = 23\text{ }^{\circ}\text{C}$