Coalescence of Inner Water Droplets in Double Emulsions Due to Surfactant Transport through Oil

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Dedicated to Prof. Dr. Thomas Hirth on the occasion of his 60th birthday

Double emulsions of the water-in-oil-in-water type are promising encapsulation and delivery systems containing at least one hydrophilic and one lipophilic surfactant. Currently, there are still very few implementations on the market, as these systems are subject to extreme stability problems. This study focuses on stability problems induced by the transport of hydrophilic surfactant molecules through the lipophilic phase to the encapsulated inner water droplets. In particular, a model system was developed to quantify surfactant transport and resulting effects on the coalescence of encapsulated water droplets. Changes in stability of the inner water droplets are demonstrated for different surfactants and compared to the stability of the inner water-in-oil emulsions and corresponding double emulsions.

1 Introduction

Water-in-oil-in-water double emulsions have long been identified as promising systems for the encapsulation of water-soluble ingredients in water-based formulations [1]. Such formulations are especially needed for food, cosmetics, and pharmaceutics [2]. In the first step, an inner water phase with the active substance dissolved within is emulsified in an oil phase. The resulting water-in-oil (W/O) emulsion is dispersed in an outer water phase in an independent emulsification step [3]. As a result, the active ingredient is protected from environmental stresses by an oil layer [4]. In order to distinguish between the two water phases, they are often marked with indices, resulting in the abbreviation $W_1/O/W_2$ for water-in-oil-in-water double emulsions.

Due to the co-existence of three phases in a double emulsion, instability can occur in different ways [5]. These instabilities can be classified into coalescence and diffusional instabilities. Diffusion of water between the inner W_1 droplets and the outer W_2 phase is often observed in double emulsions [6]. It is triggered by the difference in capillary pressure between the two water phases [7]. This challenge can be handled relatively easy when the droplet sizes in the double emulsion are known. The osmotic pressure difference between the water phases can be tailored matching to the capillary pressure and therefore diffusion is hindered [8, 9]. Coalescence occurs in principle between all three phases. The three possible coalescence paths are the following: W_1-W_1, O-O and W_1-W_2. O-O coalescence can be measured by the change of oil droplet size distribution, which is directly accessible by common methods like static laser scattering [10]. W_1-W_2 coalescence is in the focus of many studies, since it is the main mechanism for (undesired) release and therefore defines the main property of a double emulsion [11]. Most commonly, the amount of encapsulated substance in the outer phase is used to describe the encapsulation efficiency of the double emulsion [12]. W_1-W_1 coalescence, however, has been less often examined by systematic investigations up to date.

A possible reason for this research gap is that W_1-W_1 coalescence neither releases the encapsulated substance nor does it change the typical double emulsion properties like viscosity or creaming behavior directly. Still, there are indications that the change of W_1 droplet sizes might increase the release rate [13], since increasing droplet sizes decrease the lifetime of droplets at a flat interface before coalescence occurs [14]. Additionally, the increase in water droplet size decreases the capillary pressure in the W_1 droplets and for osmotic pressure tailored emulsion osmotic swelling will

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result. Osmotic swelling can consequently lead to the complete loss of the double emulsion structure, known as swelling-breakdown [15, 16]. In analyzing W_1-W_1 coalescence in double emulsions, several challenges must be met. The direct measurement of W_1 droplet sizes is only possible via confocal laser scanning microscopy [17] or by nuclear magnetic resonance spectroscopy [18]. Both methods demand high emulsion stabilities since they are time and energy intensive methods. Via optical microscopy, qualitative analysis of the stability of double emulsions against W_1-W_1 coalescence can be made. When the inner droplets coalesce, while there is only little release via W_1-W_2 coalescence, changes in W_1 droplet size can be observed [19].

To prevent or at least slow down coalescence, surfactants are added into double emulsion systems. At least one hydrophilic surfactant is added into the W_2 phase to stabilize the oil droplets. To keep the inner emulsion stable, at least one lipophilic surfactant is dissolved in the oil. The different surfactants are necessary due to the different curvature of the droplets of a W/O and an O/W emulsion [20]. When considering W_1-W_1 coalescence, the lipophilic emulsifier is meant to stabilize inner droplets, while the hydrophilic emulsifier has potentially interfering effects on the stability of inner droplets against coalescence [21, 22]. Since the surfactants are highly interfacial active and partly soluble in the water phase as well as in the oil phase, it can be expected that they distribute at both interfaces over time [5]. While the lipophilic surfactant can go directly to both interfaces, the hydrophilic surfactant is hindered by two reasons. On the one hand, the oil film between the W_2 phase and the W_1/O interface can prevent or at least slow down the migration, dependent on the chemical compatibility of the oil phase and the hydrophilic surfactant [23, 24]. On the other hand, the lipophilic surfactant is already present at the inner interface, when the hydrophilic surfactant is added, due to the two separate steps in double emulsion production. When the inner interface is completely and irreversibly occupied by lipophilic surfactant, there might be less space left for the hydrophilic surfactant to adsorb [25].

In this study, the stability of inner double emulsion droplets is analyzed in different models, considering especially the transport of the hydrophilic surfactant through the oil phase. Between different hydrophilic surfactant types, considerable differences in diffusional speed are to be expected. While non-ionic surfactants should migrate through the oil faster, ionic surfactants and polymeric surfactants should be transported slower or not at all [26]. Additionally, the interactions between the hydrophilic surfactants and polyglycerol polyricinoleate (PGPR), one of the most common lipophilic surfactants in double emulsions, are described. For different hydrophilic surfactants, the stability of the inner emulsion can be different [27]. The interactions between surfactants on a molecular scale are not described, but it was shown that certain surfactant pairings do result in less stable double emulsions [28].

To isolate the stability of the examined formulations, single droplet experiments were performed. Single droplet experiments can in general be used to show effects of small changes in interface composition, since the stability time of two droplets is much more sensitive to a second surfactant than, e.g., the interfacial tension [21]. To understand whether this interaction will occur in a double emulsion the diffusion rate of the hydrophilic surfactant through an oil layer is measured using a pendant drop measurement setup. In the last step W_1/O single emulsion is brought into contact with an outer water phase, containing the hydrophilic surfactant. The main objective of the research is to investigate the impact of the diffusion of hydrophilic surfactants on the stability of the inner emulsion. The approach via single emulsion was chosen to prevent W_1-W_2 coalescence and since the droplet size distribution of a W_1/O emulsion can be measured more easily in a single emulsion than in the double emulsion [29]. It was shown that PGPR could stabilize the inner water droplets less good when alcohol ethoxylates were given into the system, while ionic surfactant in the outer water phase increased the stability of the inner water droplets.

2 Materials and Methods

2.1 Materials

Medium chain triglycerides (MCT) were chosen as oil phase for the experiments. MCT combine the structure of a triglyceride, which are common in life science applications, with a relatively defined chemical composition. The used MCT (WITARIX 60/40, IOI Oleo GmbH, Hamburg, Germany) consists of a mixture of C8 and C10 fatty acids in a ratio of 56:44. For interfacial tension and single droplet experiments the MCT were purified by the method of Dopierala et al. [30] with Florisil (Carl Roth, Karlsruhe, Germany) to remove remaining impurities. The purification step increased the interfacial tension of pure MCT and reduced the stability of single droplets [21]. For the preparation of the water phases for all experiments, ultrapure water was used.

In this study, the commonly used lipophilic surfactant PGPR (Dermofeel PGPR, Evonik Dr. Straetmans GmbH, Hamburg, Germany) was combined with different types of hydrophilic surfactants. As non-ionic surfactants the alcohol ethoxylates (EO) Brij C10 (C16-10*EO) and Brij 58 (C16-20*EO) were chosen. As ionic surfactants CTAB (C16-$C_3H_9N^+$) and SDS (C12-SO_3^-) were used. Brij C10, Brij 58 and CTAB were bought from Sigma-Aldrich (St. Louis, MO, USA) and SDS from Carl Roth (Karlsruhe, Germany). As polymeric surfactant the polypropylene-polyethylene block copolymer Pluronic PE 6800 ($M_W = 8000\,\mathrm{g\,mol^{-1}}$) was kindly provided by BASF SE (Ludwigshafen am Rhein, Germany). The chosen short-chained surfactants cover a wide spectrum of hydrophilic-

lipophilic-balance (HLB) values calculated according to Davies [31]. The HLB values of Brij C10, Brij 58, CTAB and SDS are 2.7, 6.0, 15.8 and 40.0, respectively. Since there is no calculation value available for the ammonium group of CTAB, an experimental value was taken from Miraglia et al. [32]. The more lipophilic the hydrophilic surfactant is, the more soluble in oil it should be and the faster diffusion through an oil phase should occur.

For all experiments, the hydrophilic surfactants were applied at a concentration of 1 wt %, which is within the range of classical applications. In contrast, the selected PGPR concentration of 0.1 wt % was rather low to deliberately speed up emulsion instability and detect stability enhancing surfactant interactions [23, 33]. This also allows for detecting increasing droplet stability. Additionally, the chosen PGPR concentration inhibits spontaneous emulsification of water in oil, which would disturb optical measurements. This effect occurs at PGPR concentrations between 0.5 wt % and 5 wt %, which are used in application [34].

2.2 Double Emulsions

To investigate the stability of double emulsions with the chosen formulation, microscopic pictures of the double emulsions produced with the different hydrophilic surfactants were compared. Ultrapure water was dispersed in 0.1 wt % PGPR in MCT at a disperse phase ratio of 10 vol %. For emulsification, a gear rim disperser (Megatron MT 3000, Kinematica AG, Luzern, Switzerland) at 18 000 rpm (tip speed 24.50 m s^{-1}) was used. In the second step, the inner emulsion was dispersed in a 1 wt % surfactant solution with an Ultra-Turrax (T25 digital, IKA Werke, Staufen im Breisgau, Germany) at 8000 rpm (5.45 m s^{-1}) for two minutes. The initial phase composition of the resulting double emulsion was W_1:O:W_2 = 5:45:50. Microscopic pictures (Axiolab re 450905, Carl Zeiss AG, Oberkochen, Germany) of the double emulsions were taken after a storage time of one week at 25 °C.

2.3 Coalescence Stability of Single Droplets

To describe changes in interfacial composition by competitive adsorption of two surfactants, the coalescence time of individual droplets was measured. In Fig. 1b, a variation of the "Diffusion and Coalescence Analyzer" (DCTA) measurement setup [27, 35] is shown. Two water droplets were placed into a 1.5-mL reaction vial (Carl Roth, Karlsruhe, Germany) filled with 0.7 mL of MCT. The droplet volume was set by a single-channel pipette (0.5–10 μL ergonomic high-performance, VWR International, Radnor,

PA, USA) to 2 μL. The droplets sank down and met at the bottom of the reaction vial. From the first contact of the droplets the time was measured in a 5-s interval until coalescence occurred. In accordance with other authors, the time between contact and coalescence is called coalescence time [35]. For each surfactant combination, the experiment was repeated 24 times in 24 independent reaction vials, resulting in a coalescence time distribution. Since some surfactant formulations produced very stable droplets, the experiment had to be interrupted before coalescence occurred. These measurement values were marked as stable for over 10 000 s (over 2.5 h). As coalescence is a stochastic process [36], the repetitions are plotted in a box plot diagram. This form of plotting can be used for the comparison of coalescence times [21]. The box shows the four quartiles of the measured coalescence times, with the t_{25} to t_{75} area in the box and the median t_{50} marked with a line. The whiskers mark the area of all values, except for the outliers.

2.4 Characterization of the Hydrophilic Surfactant Distribution

For the characterization of the transport of hydrophilic surfactants through an oil phase, the interfacial tension of the two setups shown in Fig. 1c was compared. The interfacial tension was either measured directly at a 1-wt % surfactant solution droplet (left picture) or at a droplet of ultrapure water with the surfactant solution underlaid the oil phase (right picture). The interfacial tension was determined with a pendant drop tensiometer (OCA 15 LJ, DataPhysics Instruments GmbH, Filderstadt, Germany) at 25 °C. For the
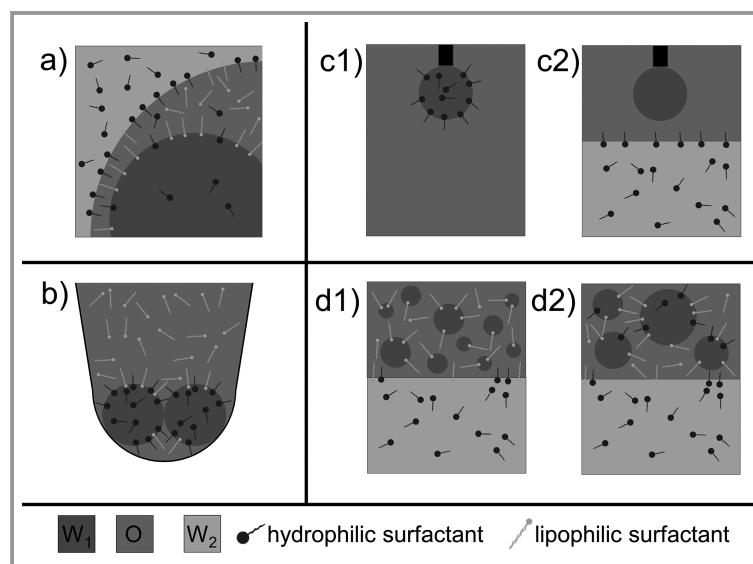

Figure 1. W_1/O/W_2 phases (from dark to bright) in experimental setups with hydrophilic (dark) and lipophilic (bright) surfactants. a) Surfactant distribution in a double emulsion, b) coalescence time measurement with two surfactants in competition, c) interfacial tension in direct measurement (1) and diffusion setup (2), d) single emulsion experiments before (1) and after diffusion (2).

direct measurements, the interfacial tension after one hour was taken. For the diffusion setup, 6 h equilibration time were given before taking the measurements, since longer measurements did not change the described tendencies anymore. Both experimental setups used 1 mm × 1 mm PE photometer cuvettes with 0.9 mL water phase, 0.9 mL purified MCT and a 10-μL droplet on a 0.91 mm outer diameter needle. In the diffusion setup, the distance between the droplet and the interface was set to 1 mm.

2.5 Preparation and Measurements of W/O Single Emulsions

For the W/O single emulsion experiments, the same W/O emulsion as for the double emulsion experiments (Sect. 2.2) was used. Instead of emulsifying the emulsion in the W_2 phase, the emulsion was stored at 25 °C and in contact with different 1-wt % surfactant solutions as shown in Fig. 1d. Of the W_1/O emulsions 20 mL were overlaid over 5 mL 1-wt % hydrophilic surfactant solutions in a glass vial (see Fig. 1d). In the left picture, the emulsion is shown at the beginning of the experiment, when the surfactants are still in their respective phases. In the right picture, a possible surfactant distribution after diffusion of a hydrophilic surfactant is shown. Diffusing surfactants were then able to change the stability of the W/O emulsion. To measure the emulsions' droplet size distributions, the complete oil phase was decanted from the glass vial and stirred prior to the measurement, preventing selective probing from sedimentation of the bigger water droplets. The droplet size distributions were measured by static laser scattering (Horiba LA-940, Retsch Technology GmbH, Haan, Germany). As characteristic value the $d_{90,3}$ was calculated from the measurements, which is the diameter of the droplet in the distribution that is bigger than 90 % of the disperse phase volume in the emulsion.

2.6 Statistical Analysis

All data was measured in triplicate and analyzed and plotted with OriginPro 2021 (OriginLab Corp., Northampton, MA, USA).

3 Results

3.1 Analysis of Double Emulsions

Double emulsions were produced and analyzed via light microscopy. Fig. 2 shows exemplary microscopic images of double emulsion droplets stabilized with different hydrophilic surfactants. A storage time of one week at 25 °C was chosen to allow instabilities to occur and differences

between the formulations to develop. The five images show oil droplets filled with water droplets and dispersed in the outer water phase W_2. The differences in oil droplet size could result from the different interfacial tensions, changing the droplet break-up behavior at the same process conditions [37]. Additionally, coalescence between oil droplets during storage cannot be excluded, but was not further evaluated as it was not within the focus of this study.

When analyzing the inner water droplets of a double emulsion by optical microscopy, only qualitative statements can be made [19]. The use of different hydrophilic surfactants in the different samples did not change W_1 droplet sizes. By comparing W_1 droplet sizes to the initial ones (Sauter mean diameter of 5.8 μm as determined by static laser scattering directly after their production), it was found that W_1-W_1 coalescence was negligible within one week of storage.

However, the amount of encapsulated water varies between the different formulations. Since there are no differences in droplet sizes or osmotic pressure between the formulations, these differences must be a result of W_1-W_2 coalescence. Highest encapsulation efficiency was found for CTAB, while Pluronic led to a nearly complete release of inner water droplets within one week. In double emulsions, W_1-W_1 and W_1-W_2 coalescence may occur simultaneously and are both influenced by the choice of surfactant. W_1-W_1 coalescence leads to larger internal droplet size that may be more prone to W_1-W_2 coalescence [13, 38]. Based on microscopic images (as given in Fig. 2), it is not possible to distinguish whether the missing W_1 droplets coalesced directly into the W_2 phase or first coalesced with themselves (W_1-W_1) and then as larger droplets were preferentially released into the W_2 phase.

As a result of the limitations in this direct measurement, the following models propose measurement models that prevent W_1-W_2 coalescence, making the mechanism of W_1-W_1 coalescence accessible to measurements.
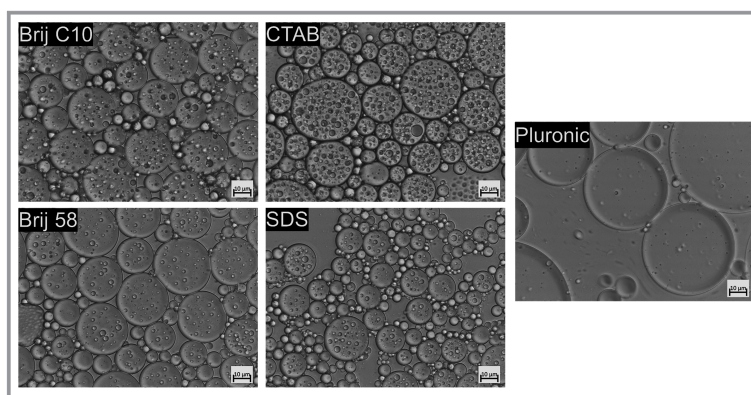

Figure 2. Micrographs of double emulsions after one-week storage at 25 °C. The same inner W_1/O emulsion was dispersed in W_2 phases with five different hydrophilic surfactants.

3.2 Single Droplet Experiments

To isolate the influence of the hydrophilic surfactant on the stability of water droplets stabilized with PGPR, single droplet experiments were performed (see Fig. 1b). The coalescence time of the single droplets is shown in Fig. 3 in a box plot diagram. It represents a characteristic value for the stability of W_1 droplets against W_1-W_1 coalescence. The minimum possible coalescence time in this measurement setup is 5 s. Additionally, the percentage of droplets exceeding a coalescence time of 10 000 s is written over the boxes (representing the number of droplets being stable over a long period of time). Reference values are given for a system with 0.1 wt % PGPR and no hydrophilic surfactant added (first box in Fig. 3).

It can be seen that the coalescence time of the single droplets significantly decreases for both Brij types, while it increases for the ionic surfactants CTAB and SDS. Alcohol ethoxylates are known to destabilize water droplets in double emulsions [39]. Comparing the two ethoxylates, the shorter and less hydrophilic Brij C10 decreased the coalescence time of W_1 droplets more than Brij 58. The same tendency is seen for the two ionic surfactants. SDS (HLB = 40) resulted in significantly increased coalescence times compared to CTAB (HLB = 15.8). The competitive adsorption of the polymeric surfactant Pluronic slightly decreased the coalescence time of the single droplets in this model experiment.

3.3 Characterization of Hydrophilic Surfactant Transport Characterized via Pendant Drop Measurements

In W_1/O/W_2 double emulsions, hydrophilic surfactants may only adsorb at W_1 droplet interfaces if they are able to diffuse through the oil phase. To characterize the diffusion of the hydrophilic surfactants through the oil phase, the interfacial tension was compared in two setups (see Fig. 1c). In Fig. 4 the interfacial tension values for the five hydro-
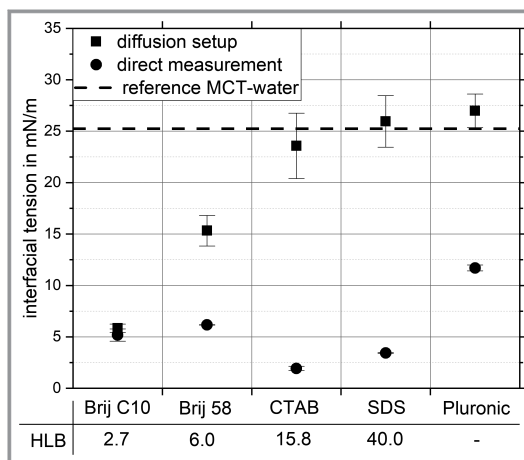
Figure 4. Interfacial tensions at the W_1/O interface for the five different hydrophilic surfactants at 1 wt % either in the W_1 phase (circles) after 1 h equilibration time (direct measurement) or in the W_2 phase (squares) after 6 h equilibration time (diffusion setup). An illustration of the measurement setups is shown in Fig. 1c.

philic surfactants for the direct and the diffusion measurement are shown. The measured values in direct measurement (circles) suggest that all four short-chained surfactants decrease the interfacial tension to about 5 mN m^{-1} from 25 mN m^{-1} for a surfactant free interface (water/MCT, dashed line). The ionic surfactants decrease the interfacial tension even lower than the nonionic ones. Pluronic decreased the interfacial tension to 12 mN m^{-1}. The presence of all hydrophilic surfactants can be clearly detected via interfacial tension measurements.

Comparing these values with the interfacial tensions measured in the diffusion setup (squares), the different diffusion behavior of the hydrophilic surfactants through the oil layer can be derived. The interfacial tension for Brij C10 is nearly the same in both measurement setups. This indicates that the oil layer poses only a minor barrier for this short-chained non-ionic hydrophobic Brij surfactant. Brij 58 only decreases the interfacial tension to 15 mN m^{-1} in the diffu-
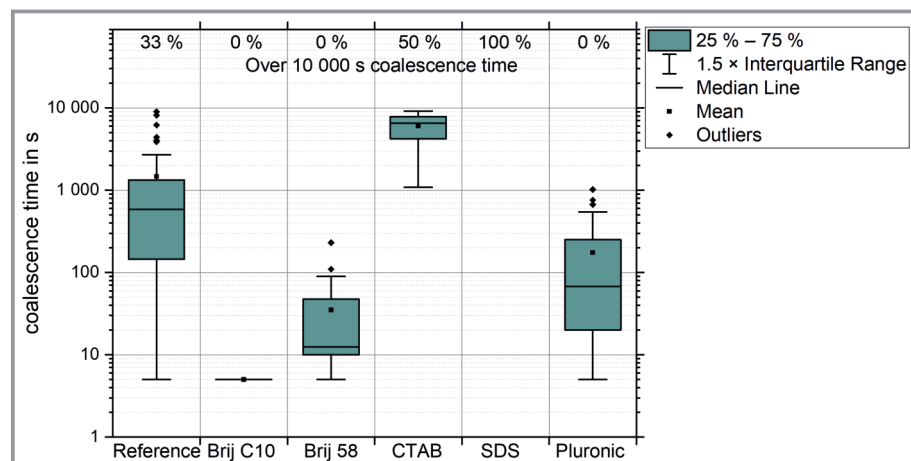
Figure 3. Coalescence times of single droplets with different hydrophilic surfactants. Reference with 0.1 wt % PGPR only, the other values with 0.1 wt % PGPR + 1 wt % hydrophilic surfactant. Corresponding setup, see Fig. 1b.

sion setup, indicating a slower but still notable diffusion of the short-chained non-ionic Brij surfactant of higher HLB value. No significant change in interfacial tension could be seen after 6 h equilibration time for the ionic surfactants in the diffusion setup. This implies that the oil imposes a barrier to the transport of these surfactants to the W_1/O interface. The HLB values of Brij C10, Brij 58, CTAB and SDS shown on the x-axis fit well to the observed diffusion behavior. The more lipophilic the hydrophilic surfactant is, the more probable is a transport through the oil phase to the W_1/O interface.

The polymeric surfactant Pluronic did not change the interfacial tension of the W_1/O droplet in the diffusion setup within the measurement accuracy. The diffusion of Pluronic obviously is completely hindered. Apart from the hydrophilicity, the molar mass is likely to have a large influence on the transport rate through the oil phase. It is widely described in double emulsion literature that polymeric surfactants are especially useful for double emulsion stability [11, 23, 40], which the authors attribute to the presumably slower diffusion of the polymeric surfactant through the oil phase. This hypothesis can be confirmed by the model experiment presented.

3.4 Stability of W_1/O Emulsions with Hydrophilic Surfactant

With the same surfactant combinations, the stability of W_1/O emulsions in proximity of W_2 surfactant solutions was examined. After production, the emulsions were stored over solutions of the different hydrophilic surfactants as seen in Fig. 1d. As a reference, the W_1/O single emulsion was stored over ultrapure water. Changes in W_1 droplet sizes – resulting from W_1-W_1 coalescence – were measured over time. The overlaying itself did not influence the W_1 droplet size (data not shown). The $d_{90,3}$ values of the droplet size distributions were chosen as characteristic droplet size and are shown for the different hydrophilic surfactants in Fig. 5. Due to the low PGPR concentration of 0.1 wt %, W_1-W_1 coalescence was found in the reference system without hydrophilic surfactant. The droplet sizes increased from an initial $d_{90,3}$ of approx. 10 µm to over 20 µm after one day and to over 40 µm after one week.

Adding the Brij surfactants to the second water phase, differences in stability were measured. The characteristic droplet sizes increased faster to $d_{90,3}$ values over 30 µm after one day. Especially with Brij 58, the W_1/O emulsion was highly instable after one week, showing a $d_{90,3}$ of over 130 µm. This increased instability proves that the ethoxylates diffuse through the oil and distribute in the single emulsion, decreasing their stability.

The ionic surfactants also changed the stability of the W_1/O emulsion. As found with the single droplet experiments, the ionic surfactants enhanced the stability of the W_1 droplets. The characteristic droplet sizes in the W_1/O
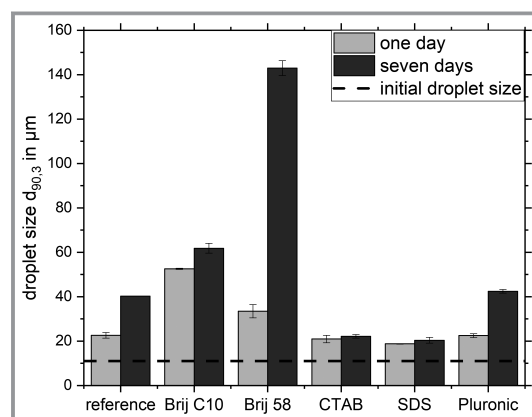

Figure 5. Droplet size $d_{90,3}$ of the W_1 droplets in a single emulsion in contact with different W_2 phases. The dashed line marks the initial droplet size and the bars show the droplet sizes with different hydrophilic surfactants after different storage times (also see Fig. 1d).

emulsion increased slower within the first day of storage than in the reference. Between one day and seven days of storage, practically no difference in the $d_{90,3}$ value was found. The strong impact on the stability of the W_1/O emulsions, even though the surfactants were not added to the droplets but to the second water phase, indicates clearly a transport of ionic surfactants through the oil phase to the W_1/O interface in a real emulsion-based system. The increase of the droplet size within the first 24 h was nearly the same for pure water and a surfactant solution, which means that the transport of both, SDS and CTAB, needed a significant amount of time. Only after a certain stabilization time (which was longer than one day) enough emulsifier had diffused to the drops to prevent further coalescence.

The addition of the polymer surfactant Pluronic to the second water phase did not change the stability of the inner emulsion at all and the droplet sizes were the same as in the reference, after one day and after one week, respectively. This means that the oil phase poses a barrier for Pluronic within the examined time scales.

4 Discussion

Based on the hypothesis that diffusion of the hydrophilic surfactant through the oil phase changes the W_1/O interface, which results in a different stability of the inner water droplets against coalescence, several model experiments were introduced in this work. The model experiments were designed to support the following hypotheses: First: If hydrophilic surfactants in a double emulsion can be transported through the oil phase, they adsorb at the inner W_1/O interface and destabilize W_1/O droplets by inducing W_1-W_1 coalescence. Second: The molecular structure of the hydrophilic surfactant influences their transport through the oil phase. Increased transport is expected with decreasing molar mass and increasing hydrophobicity of the

hydrophilic surfactant. To examine the second hypothesis, five hydrophilic surfactants of different molar mass, HLB values, and intrinsic charge were chosen.

It was expected that short-chained non-ionic surfactants show fast diffusion through an oil layer, while short-chained ionic surfactants are hindered to reach the inner interface of a double emulsion [41]. For polymeric surfactants, diffusion was declared unlikely in previous studies [23]. Whether the interaction between PGPR and the different hydrophilic surfactants would decrease or increase stability of W_1 droplets was not clear before, since these interactions are known to be different for every surfactant combination [5].

When comparing the microscopic images of double emulsions stabilized with the different hydrophilic surfactants no clear growth of W_1 droplets via W_1-W_1 coalescence could be detected. However, it could be seen that W_1 droplets were lost via W_1-W_2 coalescence leaving partially empty oil droplets. The degree of loss of inner droplets depended on the examined formulations. A microscopic description of W_1-W_1 coalescence as described by Ficheux et al. [19] is therefore only possible, if W_1-W_2 coalescence can be excluded or is at least much slower than W_1-W_2 coalescence. Otherwise, the two coalescence mechanisms are superimposed and the loss of W_1 droplets makes the analysis of the inner droplet coalescence difficult.

The single droplet model experiment designed to enforce coalescence and quantify coalescence times revealed clear differences for the different hydrophilic surfactants. When in competition with PGPR, the alcohol ethoxylates decreased significantly the coalescence times of W_1/O droplets, while the ionic surfactants CTAB and SDS increased the stability of W_1/O droplets. The polymeric surfactant Pluronic decreased the coalescence time by one order of magnitude.

The interaction between hydrophilic surfactants and PGPR can only occur at the W_1/O interface, and if the hydrophilic surfactant can diffuse through the oil phase. Here, diffusion of the hydrophilic surfactant through an oil layer was estimated by comparing interfacial tension at W_1/O interface for the cases when hydrophilic surfactant was added directly to the inner aqueous phase (W_1) or delivered through the outer aqueous phase separated from the W_1/O interface by a thin oil layer. It was found that only the alcohol ethoxylates Brij C10 and Brij 58 showed diffusion through a macroscopic oil layer. Diffusion of SDS, CTAB and Pluronic to the W_1/O interface could not be detected within 6 h of diffusion time.

A final model experiment measuring the change in droplet size of W_1/O single emulsions in close proximity to W_2 phases containing hydrophilic surfactants allowed to simulate the situation in W_1/O/W_2 double emulsions with simultaneous diffusion of the hydrophilic surfactant and coalescence of the water droplets. As expected from the other model experiments, the alcohol ethoxylates did diffuse to the inner interface and accelerated the increase of droplet size over time. The ionic surfactants slowed down W_1/O

droplet coalescence especially after within a week of storage time, leading to the conclusion that diffusion of the ionic surfactant through the oil phase occurred in this experiment but it took some time for the surfactant to reach sufficient interfacial concentration. The polymeric surfactant did not change the behavior of the W_1/O emulsion at all because too few polymeric molecules diffused through the oil phase to affect the stability of the W_1/O droplets within one week, which was the duration of measurement.

When discussing the difference in diffusion behavior of the ionic surfactants in the interfacial tension measurement and in the stability of the single emulsions, the limitations of the experimental setups shown in Fig. 1c must be taken into consideration. The interfacial tension diffusion setup experiment is limited in two respects. On the one hand, a comparatively large diffusion distance was covered in a relatively short time in this experiment. On the other hand, the lipophilic emulsifier is not present in this measurement. However, the lipophilic surfactant could enhance the transport of the hydrophilic emulsifier. For instance, it was found by Pays at al. [42] that SDS diffuses to the inner interface when Span 80 is dissolved in the oil phase. When having both surfactants in the interfacial tension measurement setup, the competitive adsorption of PGPR and hydrophilic surfactant makes the interpretation of the results difficult. PGPR as polymeric surfactant has a rather slow adsorption kinetics. The adsorption kinetics of PGPR and the diffusion kinetics of the hydrophilic surfactant can hardly be separated. The significance of the results of the model experiment is therefore limited, but it allows a very fast rough verification of the transport of hydrophilic surfactant through the oil phase.

These results underline the importance of choosing a suitable lipophilic-hydrophilic surfactant pairing when producing double emulsion-based formulations. When two surfactants adsorb at one interface, the influence on droplet stability is difficult to predict. Single droplet model experiments, however, give a fast and easy possibility to estimate stability effects.

Concluding, W_1-W_1 coalescence is an underestimated phenomenon in double emulsions, potentially changing double emulsion stability via triggering W_1-W_2 coalescence or via changes in the osmotic-capillary pressure balance. However, W_1-W_1 coalescence is challenging to isolate in experiments. With the examination of the W_1/O single emulsions in contact with the outer water phase, a good and fast estimation can be made. The results show that not only the release behavior but also the stability of the inner emulsions depend strongly on the choice of surfactants. We could find that diffusion of the hydrophilic surfactant could be minimized more successfully using high molecular weight surfactants than using charged surfactants. The transport of short-chained high-HLB surfactants through the oil phase was slower, yet clearly visible in the experiments. When diffusion occurred, the stability of the inner water droplets changed. In our experiments with low PGPR concentra-

tions, the stability of W_1/O droplets was increased by the short-chained high-HLB surfactants. For polymeric surfactants, diffusion can be prevented at least for moderate time periods and with low lipophilic surfactant concentrations examined in this study. It can be confirmed by the results that high molecular weight surfactants have advantages for the production of double emulsions, also in regards of W_1-W_1 coalescence.

Whether W_1-W_2 coalescence is a direct follow-up mechanism to W_1-W_1 coalescence is a next step to examine. Using microfluidic techniques to produce double emulsions could help producing monomodal double emulsion droplets, where both W_1-W_1 and W_1-W_2 coalescence could be seen directly and the influence of the two mechanisms on each other could be described. This approach could answer the hypothesis that W_1-W_1 coalescence could not be seen in the real double emulsion, because once the inner droplets grew due to coalescence they are released faster into the W_2 phase.

Abbreviations

CTAB	cetrimonium bromide
DCTA	diffusion and coalescence time analyzer
EO	ethoxy group
HLB	hydrophilic-lipophilic-balance
MCT	medium chain triglycerides
M_W	molecular weight
O	oil phase
O/W	oil-in-water
PGPR	polyglycerol polyricinoleate
SDS	sodium dodecyl sulfate
W_1	inner water phase
W_2	outer water phase
W/O	water-in-oil
W_1/O/W_2	water-in-oil-in-water

References

[1] D. J. McClements, *Adv. Colloid Interface Sci.* **2015**, *219*, 27–53. DOI: https://doi.org/10.1016/j.cis.2015.02.002

[2] G. Muschiolik, E. Dickinson, *Compr. Rev. Food Sci. Food Saf.* **2017**, *16 (3)*, 532–555. DOI: https://doi.org/10.1111/1541-4337.12261

[3] A. Schuch, A. N. Tonay, K. Köhler, H. P. Schuchmann, *Can. J. Chem. Eng.* **2014**, *92 (2)*, 203–209. DOI: https://doi.org/10.1002/cjce.21834

[4] H. Lamba, K. Sathish, L. Sabikhi, *Food Bioprocess Technol.* **2015**, *8 (4)*, 709–728. DOI: https://doi.org/10.1007/s11947-014-1468-6

[5] N. Leister, H. P. Karbstein, *Colloids Interfaces* **2020**, *4 (1)*, 8. DOI: https://doi.org/10.3390/colloids4010008

[6] F. Leal-Calderon, S. Homer, A. Goh, L. Lundin, *Food Hydrocolloids* **2012**, *27 (1)*, 30–41. DOI: https://doi.org/10.1016/j.foodhyd.2011.09.004

[7] J. Jiao, D. G. Rhodes, D. J. Burgess, *J. Colloid Interface Sci.* **2002**, *250 (2)*, 444–450. DOI: https://doi.org/10.1006/jcis.2002.8365

[8] V. Eisinaite, P. Duque Estrada, K. Schroën, C. Berton-Carabin, D. Leskauskaite, *Food Res. Int.* **2018**, *106*, 722–728. DOI: https://doi.org/10.1016/j.foodres.2018.01.042

[9] S. Iqbal, M. K. Baloch, G. Hameed, D. J. McClements, *Food Res. Int.* **2013**, *54 (2)*, 1613–1620. DOI: https://doi.org/10.1016/j.foodres.2013.09.035

[10] A. Schuch, P. Deiters, J. Henne, K. Köhler, H. P. Schuchmann, *J. Colloid Interface Sci.* **2013**, *402*, 157–164. DOI: https://doi.org/10.1016/j.jcis.2013.03.066

[11] K. Pays, *J. Controlled Release* **2002**, *79 (1–3)*, 193–205. DOI: https://doi.org/10.1016/S0168-3659(01)00535-1

[12] J. O. Regan, D. M. Mulvihill, *Food Hydrocolloids* **2009**, *23 (8)*, 2339–2345. DOI: https://doi.org/10.1016/j.foodhyd.2009.06.009

[13] C. H. Villa, L. B. Lawson, Y. Li, K. D. Papadopoulos, *Langmuir* **2003**, *19 (2)*, 244–249. DOI: https://doi.org/10.1021/la026324d

[14] E. S. Basheva, T. D. Gurkov, I. B. Ivanov, G. B. Bantchev, B. Campbell, R. P. Borwankar, *Langmuir* **1999**, *15 (20)*, 6764–6769. DOI: https://doi.org/10.1021/la990186j

[15] B. Khadem, N. Sheibat-Othman, *Chem. Eng. J.* **2020**, *382*, 122824. DOI: https://doi.org/10.1016/j.cej.2019.122824

[16] B. Khadem, M. Khellaf, N. Sheibat-Othman, *Colloids Surf., A* **2020**, *585*, 124181. DOI: https://doi.org/10.1016/j.colsurfa.2019.124181

[17] S. Schuster, R. Bernewitz, G. Guthausen, J. Zapp, A. M. Greiner, K. Köhler, H. P. Schuchmann, *Chem. Eng. Sci.* **2012**, *81*, 84–90. DOI: https://doi.org/10.1016/j.ces.2012.06.059

[18] X. Guan, K. Hailu, G. Guthausen, F. Wolf, R. Bernewitz, H. P. Schuchmann, *Eur. J. Lipid Sci. Technol.* **2010**, *112 (8)*, 828–837. DOI: https://doi.org/10.1002/ejlt.201000022

[19] M.-F. Ficheux, L. Bonakdar, F. Leal-Calderon, J. Bibette, *Langmuir* **1998**, *14 (10)*, 2702–2706. DOI: https://doi.org/10.1021/la971271z

[20] A. Kabalnov, H. Wennerström, *Langmuir* **1996**, *12 (2)*, 276–292. DOI: https://doi.org/10.1021/la950359e

[21] N. Leister, H. P. Karbstein, *Colloids Interfaces* **2021**, *5 (2)*, 21. DOI: https://doi.org/10.3390/colloids5020021

[22] D. J. McClements, S. M. Jafari, *Adv. Colloid Interface Sci.* **2018**, *251*, 55–79. DOI: https://doi.org/10.1016/j.cis.2017.12.001

[23] E. Dickinson, *Food Biophys.* **2011**, *6 (1)*, 1–11. DOI: https://doi.org/10.1007/s11483-010-9188-6

[24] F. Michaut, P. Hébraud, P. Perrin, *Polym. Int.* **2003**, *52 (4)*, 594–601. DOI: https://doi.org/10.1002/pi.995

[25] M. Kanouni, H. Rosano, N. Naouli, *Adv. Colloid Interface Sci.* **2002**, *99 (3)*, 229–254. DOI: https://doi.org/10.1016/S0001-8686(02)00079-9

[26] F. Michaut, P. Perrin, P. Hébraud, *Langmuir* **2004**, *20 (20)*, 8576–8581. DOI: https://doi.org/10.1021/la048715t

[27] S. M. Neumann, U. S. van der Schaaf, H. P. Karbstein, *Colloids Surf., A* **2018**, *553*, 464–471. DOI: https://doi.org/10.1016/j.colsurfa.2018.05.087

[28] T. Schmidts, D. Dobler, C. Nissing, F. Runkel, *J. Colloid Interface Sci.* **2009**, *338 (1)*, 184–192. DOI: https://doi.org/10.1016/j.jcis.2009.06.033

[29] S. M. Neumann, I. Scherbej, U. S. van der Schaaf, H. P. Karbstein, *Colloids Surf., A* **2018**, *538*, 56–62. DOI: https://doi.org/10.1016/j.colsurfa.2017.10.073

[30] K. Dopierala, A. Javadi, J. Krägel, K.-H. Schano, E. P. Kalogianni, M. E. Leser, R. Miller, *Colloids Surf., A* **2011**, *382 (1–3)*, 261–265. DOI: https://doi.org/10.1016/j.colsurfa.2010.11.027

[31] J. T. Davies, A quantitative kinetic theory of emulsion type, I. Physical chemistry of the emulsifying agent, in *Proc. of the 2nd International Congress Surface Activity (1957)*, Butterworth, London **1957**, 426–438.

[32] D. B. Miraglia, J. L. Rodríguez, R. M. Minardi, P. C. Schulz, *J. Surfactants Deterg.* **2011**, *14 (3)*, 401–408. DOI: https://doi.org/10.1007/s11743-010-1239-y

[33] A. L. Márquez, A. Medrano, L. A. Panizzolo, J. R. Wagner, *J. Colloid Interface Sci.* **2010**, *341 (1)*, 101–108. DOI: https://doi.org/10.1016/j.jcis.2009.09.020

[34] J. Bahtz, D. Z. Gunes, A. Syrbe, N. Mosca, P. Fischer, E. J. Windhab, *Langmuir* **2016**, *32 (23)*, 5787–5795. DOI: https://doi.org/10.1021/acs.langmuir.6b00425

[35] S. M. Neumann, U. S. van der Schaaf, H. P. Schuchmann, *Food Struct.* **2017**, *12*, 103–112. DOI: https://doi.org/10.1016/j.foostr.2017.02.002

[36] J. Kamp, J. Villwock, M. Kraume, *Rev. Chem. Eng.* **2017**, *33 (1)*, 1–47. DOI: https://doi.org/10.1515/revce-2015-0071

[37] P. Walstra, *Chem. Eng. Sci.* **1993**, *48 (2)*, 333–349. DOI: https://doi.org/10.1016/0009-2509(93)80021-H

[38] A. Kabalnov, *Curr. Opin. Colloid Interface Sci.* **1998**, *3 (3)*, 270–275. DOI: https://doi.org/10.1016/S1359-0294(98)80071-X

[39] A. Schuch, L. G. Leal, H. P. Schuchmann, *Colloids Surf., A* **2014**, *461*, 336–343. DOI: https://doi.org/10.1016/j.colsurfa.2013.11.043

[40] A. Schuch, C. Helfenritter, M. Funck, H. P. Schuchmann, *Colloids Surf., A* **2015**, *475*, 2–8. DOI: https://doi.org/10.1016/j.colsurfa.2014.06.012

[41] R. Dinarvand, S. H. Moghadam, A. Sheikhi, F. Atyabi, *J. Microencapsulation* **2005**, *22 (2)*, 139–151. DOI: https://doi.org/10.1080/02652040400026392

[42] K. Pays, J. Giermanska-Kahn, B. Pouligny, J. Bibette, F. Leal-Calderon, *Langmuir* **2001**, *17 (25)*, 7758–7769. DOI: https://doi.org/10.1021/la010735x

Coalescence of Inner Water Droplets in Double Emulsions Due to Surfactant Transport through Oil

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Research Article: The coalescence of the inner water droplets in a double emulsion is difficult to measure. With simplified models of double emulsions, the stability of the inner emulsion can be described and the influence of diffusion of the hydrophilic surfactant through the oil phase can be discussed. ·· ■