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Polish Journal of Chemical Technology, 26, 1, 51—63, 10.2478/pjct-2024-0006

Liquid-liquid two phase-system stabilized by tween 40 and 80 surfactants: multiparametric study

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The purpose of this study was to investigate the impact of process parameters such as interfacial tension, type of surfactants, and their concentration on simple oil-in-water dispersion. Explored systems were prepared with 5% liquid paraffin oil and aqueous phase with emulsifiers Tween 40 of concentrations from 0.008325 mM to 0.025 mM and Tween 80 with concentrations ranging from 0.00375 mM to 0.011 mM. All systems were characterized in terms of their density and interfacial tension. In the next step analysis of droplet size distributions and mean droplet diameter was performed. The results showed that the size of paraffin droplets decreased as the concentration of surfactants grew. This trend is accompanied by decrease in the interfacial tension between phases. The correlation between mean drop size and the energy input and physical properties of both liquids was developed. The last step provides scientific evidence for the formulation of stable droplets of liquid paraffin.

Keywords: two-phase liquid system, interfacial tension, surfactants, stirred vessel, stable droplets.

INTRODUCTION

Oil-in-water (O/W) systems (called occasionally emulsions when surface-active component is used) can be found in a range of food and beverage products, including creams, desserts, dressings, soft drinks, and others[1]. But they are not only appealing to the food industry. Application of stabilized O/W system or emulsion as delivery agents for vitamins, supplements, and other nutraceuticals[2] have attracted attention of many researchers. They are widely present in our daily life, in products such as personal and home care[3] and more. For instance, emulsions and microemulsions have been applied in environmental technologies such as subsurface remediation and biofuel production[4]. They may facilitate some processes, for example, transportation of heavy oil, storage of milk, synthesis of chemicals or materials and also lead to serious upgrading or environmental issues (e.g., pipeline plugging, corrosions to equipment, water pollution, soil pollution).

The two-phase liquid phase or emulsions are generally formed by mixing two naturally immiscible fluids where the oil phase is made of organic liquids insoluble in aqueous phase[5]. They were found to be thermodynamically unstable with the tendency to breakdown over time due to numerous physicochemical mechanisms such as gravitational separation, flocculation, coalescence, particle coalescence, Ostwald ripening, and phase separation[6]. On the basis of the above-mentioned state, an emulsifier is necessary to be added to achieve desired stability of emulsion. Non-ionic surfactants[7] are known as the most important groups of surfactants that are applied as detergents or emulsifiers. A representatives of this group of surfactants might be Tween 40 or Tween 80. Generally, non-ionic surfactants pay attention to scientist due to their efficiency at low concentrations and comparative low toxicities. Recently it was proven that a mixture of two or more different emulsifiers may improve the formulation, performance, and stabilization of O/W rather than an individual surfactant[6, 8]. The result of O/W dispersion or emulsion varies depending on the volume fraction of both phases and the kind of emulsifier utilized. Nevertheless, the type of emulsifiers applied allows to simplify formation of stabilized liquid dispersion or emulsion and influences the functional features of the final product.

Liquid stabilized dispersion or emulsion in different industries can be formed intentionally to meet required applications, for instance in a reaction process they are widely used to increase the reaction efficiency and control mass transfer process between phases[9]. Hence, precise prediction of the interfacial area is crucial to set mass transfer and reaction rates[10]. However, emulsions occurrence in many cases is undesired and it may cause serious problems, for instance, in the oil and gas industry causing serious corrosion and increasing the operational cost of crude oil production[4]. Then again, emulsions can intentionally be formed for application in some upstream operations such as enhanced oil recovery (EOR), hydraulic fracturing, and emulsified acids[4, 11].

Emulsions can be formed using rather high-energy[11] than low-energy methods[11]. High-energy methods are currently the most used in the food industry because they are already well-established and capable of large production while low-energy methods are of growing interest due to their low cost and ease of implementation[11]. Agitated vessels (low-energy equipment) were often selected to produce stabilized O/W dispersion in the wide range of the drop size[12, 13] but less than rotor stator mixers like Silverson[14, 15] those are found to be used in process industries such food processing, fine chemicals, and medicines[16–18]. But mechanical stirring is very frequently employed to produce rather the stabilized liquid dispersion with the controlled-drop size than emulsion.

Available investigations in emulsion (sometimes also called as stabilized liquid-liquid dispersion) production in such mixers are mostly focused on the effect of the following factors: type of surfactants[19–23], dispersed phase fractions[24, 25], viscosity[25], type of impellers[24–26] on drop size distributions and mean drop size (mean Sauter diameter)[10, 12, 27]. Mostly the organic phases such as toluene or chlorobenzene[12, 19, 23], silicones oils[27] and others[28] were selected as dispersed phase (their density is rather close to a continuous phase) to be dispersed in aqueous phase

supplemented with surface-active components[19, 28–32]. For instance, Tween 80 and Tween 40 were commonly used as stabilized agents in formulation of liquid-liquid dispersion or O/W emulsion. Roldan-Cruz et al.[20] has studied the stability of O/W emulsions made with the nonionic surfactant Tween-80 by cyclic voltammetry and electrical impedance spectroscopy (EIS). It has been shown that the double-layer capacitance increased as the amount of Tween-80 grew up to about 2% v/v. Similarly, Udomrati et al.[33] have investigated the stabilization mechanism of oil-in-water emulsion by a combination of esterified maltodextrin (EM) and Tween 80. The interfacial tension, ζ-potential, non-adsorbed Tween 80 in centrifuged-serum of emulsion, and fluoresced microstructure were determined to examine the stabilization mechanism. The ζ-potential changed to small negative charge as EM was added into Tween 80-stabilzed emulsion while ζ-potential of sole Tween 80-stabilzed emulsion had a small positive charge. Authors[33] have concluded Tween 80 was mainly adsorbed at the oil surface and esterified maltodextrin interact with Tween 80 to form a double stabilization layer without competitive replacement.

Atarian et al.[34] have investigated stable sunflower O/W Pickering emulsion stabilized by chitosan (CS)-stearic acid (SA) nanogels and have compared the oxidative stability with sunflower oil emulsion stabilized by Tween 80 using the peroxide and thiobarbituric acid tests. The comparison has implied that the O/W emulsion stabilized by CS-SA nanogels had a higher oxidative stability than the O/W emulsion stabilized by Tween 80. The same emulsifier and others (Tween 20 and Lecithin) were used to stabilize oil-in-water emulsions containing varying percentages of ethanol and sunflower oil[35]. It was found that a droplet size of emulsions decreased with the addition of ethanol to the aqueous phase showing a minimum at a concentration of ethanol around 40%. This tendency was related to a decrease in the interfacial tension between water and oil as the ethanol concentration increased. Authors have proven that addition of the ethanol has influenced on solubility of the surfactants. On the other hands, Tween 80 and myofibrillar protein (MP) were used as stabilized agent for camellia seed oil emulsions[36] and they were utilized to prepare composite gels. The investigation has shown that the oil droplet size of the Tween 80-stabilized emulsion was significantly smaller ($p < 0.05$) than that of the MP-stabilized emulsion with the same homogenization speed. However, a polymerization of Tween 80-stabilized emulsions occurred during the preparation of the composite gels.

Tween 80 as a non-toxic surfactants has found application in bioengineering or food industries. Nielsen et al.[37] have investigated how Tween 80 influences the growth and antimicrobial sensitivity of bacteria existed on human skin, in intestine, and in food products. The addition of 0.1% Tween to the growth media caused the growth rate of specific bacteria and increased of biomass. Their finding suggest that Tween 80 in cosmetics and food products could affect the composition of skin and intestine microbiota, and the effect of emulsifiers on the human microbiome should therefore be explored to uncover potential health effects. Dias et. al[38] have shown another example of applying Tween 80 and 40 as stabilizing agents. Authors have investigated their effect on the stability, rheology and encapsulation efficiency of W/O/W multiple emulsions, which contain avocado oil (as great potential as a food ingredient) and NaCl encapsulated. The primary emulsion contained 5 or 6 wt.% polyglycerol polyricinoleate (PGPR) and 3 or 4 wt.% gelatin, and the secondary emulsion contained 2 wt.% Tween 40 or Tween 80. It was shown that emulsions containing Tween 40 had a higher stability than those containing Tween 80, however, the use of Tween 40 combined with PGPR and gelatin has great potential to form stable multiple emulsions. Also, Fuller et al.[39] have investigated the effects of Tween emulsifier fatty acid chain length on the shear stability and crystallization behavior of 35 wt.% partially crystalline oil-in-water emulsions prepared with and without 1 wt.% sodium caseinate. They found that emulsifier Tween 80 was the most shear sensitive followed by the saturated emulsifiers Tween 20, 40 and 60 in order of increasing fatty acid chain length. Long chain saturated Tween emulsifiers (40 and 60) improved shear stability and formed more robust interfacial films compared to the saturated short chain length Tween 20 and Tween 80. Their findings offer guidance on how combinations of proteins and emulsifiers can be used to modify and control the stability of partially crystalline oil-in-water emulsions through their combined effects on the properties of the interfacial film and fat crystallization. In another paper, emulsifier Tween 40 was used to prepare nanoemulsion of flaxseed oil and water that is of interest to a beverage industry[40]. Emulsions with a mean droplet size as low as 135 ± 5 nm were achieved by ultrasonic power generated at 20–24 kHz and they were comparable in size to those for emulsions prepared with a microfluidizer operated at 100 MPa. Authors have shown that ultrasound method can be effective in producing nanoemulsions of potential application as food ingredients.

To conclude the literature review dedicated to the application of both surfactants it should be noted that they are successfully used as stabilized agents in a variety of systems. The cited literature shows that the main focus is rather put on the stability of emulsion and its improvement than on the impact of process parameters used for liquid-liquid dispersion formulation and their effect on drop size distribution.

For industrial applications of liquid dispersions or emulsions it is necessary to accomplish two goals: i) obtain the narrow drop size distribution (DSD) and ii) obtain uniform spatial drop size distribution in a mixer. Those characteristics guarantee that the entire volume of liquid is involved in the mass transfer between phases[41]. The following properties of the emulsion in aspect of long-term stability[5, 6, 42], degradation rates, resistance to creaming[5, 6] texture and optical appearance[42], viscosity[5, 6, 43], and chemical reactivity[44] depend on droplet size distribution. Therefore, it is crucial to adjust the appropriate process parameters of a stirred tank to control the droplet size within an acceptable range and narrow distributions which is key for any emulsion-based products.

Beside the type of apparatus used for the liquid-liquid/emulsion formulation, generally, in both case, the process is not a simple task due to its complex nature where features such as components, structures, phenomena,

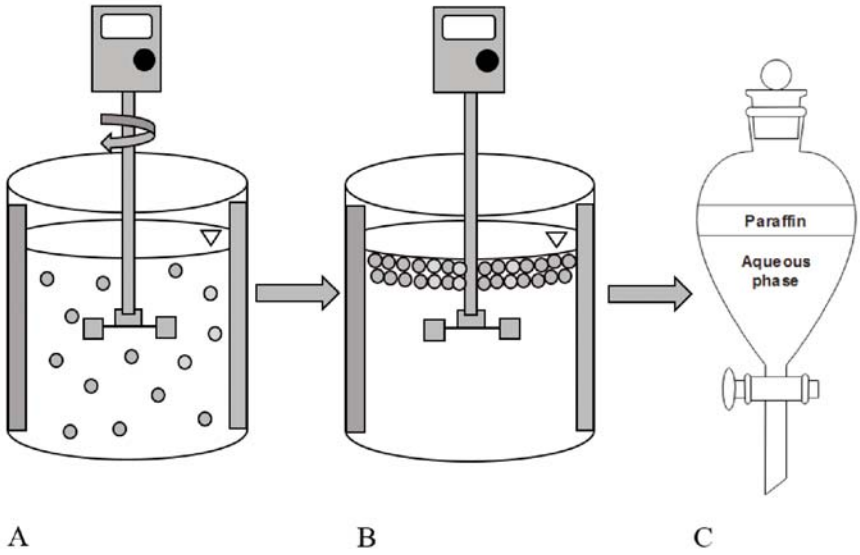


Figure 1. Scheme of experimental rig used for preparation of liquid stable dispersion: A) Formulation step of liquid dispersion in stirred vessel fitted with RT at adjusted impeller speed; B) Separation of the system immediately after impeller has stopped; C) Separation process was conducted in the separation funnel into stabilized paraffin oil droplets- top phase and continuous phase supplemented with the required concentration of surfactant – bottom phase

and processes are strongly interconnected. Consequently, any decision must be made at the experimental design stage having its numerous effects on the final product's properties in mind. Hence, in this work, the effect of process parameters, type of emulsifier and its concentration on simple O/W dispersion or emulsion prepared by mechanical stirring is investigated. To this end, two surfactants – Tween 40 and Polysorbate 80 (commercially called Tween 80) were selected as they are both non-ionic surface-active components with relatively close the hydrophilic–lipophilic balance (HLB) values and they are extensively use in food and polymer industries. However, to the authors' best knowledge, no complementary studies have been yet published where the above-mentioned problem was addressed. Obtained results can help in better understanding of mechanisms occurring in liquid-liquid dispersion formulation, allowing manufacturers to adjust their processes or formulation of products containing stabilized dispersion.

MATERIALS AND METHODS

Materials

Two non-ionic surfactants were selected to conduct this research: Tween 40 (Polysorbate 40, also known as olyoxyethylene sorbitan monopalmitate) and Tween 80 (Polysorbate 80, also called as polyoxyethylene (80) sorbitan monooleate). Tween 40 (CAS number: 9005-66-7) was purchased from Carl Roth GmbH (Karlsruhe, Germany) whereas Tween 80 (CAS number: 9005-65-6) from Alfa Aesar Chemicals – Thermo Fisher Scientific (Kandel, Germany). Both surfactants are structurally different: Tween 40 has palmitic acid in the fatty acid side-chain while Tween 80 has oleic acid. They both are more hydrophilic and tend to make an oil-in-water emulsion due to high values of HBL. Tween 40 has a slightly higher hydrophilic–lipophilic balance value (15.6) than Tween 80 (15.0). Therefore, they both are suitable to be used as paraffin in water emulsifiers. Liquid paraffine oil (CAS number: 8042-47-5) was purchased from Merck KGaA (Darmstadt, Germany). All chemicals were of analytical grade and used without further purification or modification. The water used in the preparation of all systems was passed through a milli-Q water system. All aqueous phases were supplemented with the required concentration of surfactant (c) and left for a few hours while mixing to allow surface-active components to dissolve and create a well-mixed solution. Preliminary experiments with Tween 80 revealed that using an unfresh solution caused drop size to increase with higher impeller speed. Thus, all solutions with Tween 80 were prepared daily.

Experimental set-up

Oil-in-water (O/W) dispersion was prepared by combining an aqueous phase – the continuous phase with paraffin oil dispersed on agitated mixing glass vessel (T = 0.128 m) equipped with four identical baffles and standard Rushton turbine (RT) impeller at room temperature. The RT impeller of 0.064 m diameter was located at 1/2 of the liquid height. Total volume of the system used in all experiments was 1 L. The experimental rig is depicted in Fig. 1 A followed by the image of a stopped impeller (Fig. 1 B) and the separation process of the oil-in-water dispersion (Fig. 1 C).

The continuous phase was prepared by mixing milli-Q water and emulsifier of the required percentages of Tween 40 or Tween 80. Three different concentrations for both types of surfactants were selected that corresponded to 25%, 50%, and 75% of critical micelle concentration (CMC) estimated at T=298 K equals $CMC_{Tween40}$= 0.033 mM and $CMC_{Tween80}$= 0.015 mM[45], respectively. The value of CMC for Tween 80 is similarly close to result shown by Bąk and Podgórska[23]. Surfactant concentrations have corresponded to the following values summarized in Table 1.

The vessel was first filled with milli-Q water supplemented with Tweens as the continuous phase and the

Table 1. The values of surfactants concentration used in the experiment corresponded to 25%, 50%, and 75% of critical micelle concentration (CMC)

Surfactant	Concentrations, mM		
	25% of CMC	50% of CMC	75% of CMC
Tween 40	0.00835	0.01665	0.025
Tween 80	0.00375	0.0075	0.011

required amount of paraffin oil (equivalent to 5% v/v) was added near to the impeller region as suggested by EL-Hamouz et al.[25]. They[25] have found that narrower drop size distributions and smaller Sauter mean diameters, d_{32}, were obtained when the oil was injected into the impeller region. It was also allowed to attain equilibrium in a shorter time. The range of impeller speed was determined experimentally for each of the investigated systems in range of 225 rpm to 530 rpm with 100 rpm increment. It was equivalent to Reynold's number ranged from 12 300 to 28 850. The minimum speed necessary to completely disperse paraffin oil in the whole volume of the vessel was determined by visual observation, and the maximum speed was selected to avoid aeration and prevent creaming during the experiment. Each of the investigated systems was stirred at four impeller speeds. At each speed system was mixed for 60 min to reach equilibrium. After that time the sample was taken to measure the DSD by laser diffraction technique.

Droplet size measurements

The mean Sauter diameter and drop size distributions (DSD), supported by the calculated span defining the width of distributions, were measured by a Malvern Mastersizer 3000 (Malvern Panalytical, Malvern, UK), with a Hydro SM manual small volume sample dispersion unit attached. This measurement technique allows to obtain the range of 0,01–3500 μm with the accuracy of ± 0.6%, repeatability of ± 0.5% variation and reproducibility better than ± 1% variation. Sample of the dispersed phase was taken from the constant location near to the impeller region where the breakage rate is indicated to be high and directly transferred to the measurement unit to minimize influence of additional environmental stresses on droplets. Then, the sample was diluted in the same continuous phase (until required obscuration rate was achieved) used in the formulation stage to prevent coalescence, washout of absorbed surfactant from droplets' surface and oil deposition on the optical windows of the measurement cell. Liquid-liquid dispersion samples were measured immediately after preparation and the mean Sauter diameter and drop size distributions are reported as the average of twenty or more independent measurements. The standard deviation, σ, was ranged from 0.5 to 10 μm.. Particle size measurements were taken immediately after collection and no meaningful differences in $d_{32,}$ and DSD were observed over 48 h and after the month of storage. The drop size distributions were characterized by the common parameters used and they are: mean Sauter diameter, d_{32}, skewness, width, and uniformity of DSD.

Density measurements

Density of surfactant solutions was measured at room temperature using the portable density meter Densito 30PX (Mettler-Toledo, Poland). All measurements were repeated ten times to calculate the average value of density, along with the standard deviation.

Interfacial tension measurements

The interfacial tension, σ, between paraffin oil and the surfactant solutions was measured at room temperature on a goniometer OCA 15 (DataPhysics Instruments GmbH, Germany), with drop pendant method. This analysis measures the shape of a liquid drop suspended from the end of a dosing needle in another liquid or air medium. The shape of the hanging drop of liquid is determined by competition between two forces: surface tension and gravitation. The gravity force pulls the drop into the typical pear-like shape, whereas the surface tension minimizes the surface area and tries to maintain a sphere[7]. The Young-Laplace equation is used to examine the drop shape. All measurements of σ were made in triplicates and the average value of interfacial tension, as well as the standard deviation, was calculated.

RESULTS AND DISCUSSIONS

Density and interfacial tension

Properties such as viscosity, temperature, surface tension, and density have significant impact on the drop size and distribution[42, 43, 46]. An increase of the fluid temperature causes a decrease of interfacial tension and then the droplet size[46]. The mean Sauter diameter gradually increases with a viscosity of the dispersed phase and surface tension[23, 28, 43]. Thus, it is important to determine how properties such as surface tension and density affect the d_{32} and DSD.

Figure 2 shows the effect of concentrations of surfactants on the density of continuous phase. As was expected, the value of density gradually increased with concentration of surface-active components. This trend coincides with the results given by Perinelli et al.[47]. Subsequently, the increment of this physicochemical property is less distinct for a concentration in which micelles are present considering also the error associated with the measurement. It can be explained by the difference between volume fraction in the solution of monomer and micelles. Monomer have higher volume fraction than micelles due to their greater hydration. It causes water to be more bounded in monomeric form compared to micelles form. The micellization process is, in fact, a dehydration process, where a greater increment of free water regarding bounded water is observed. Consequently, for monomers the growth of volume per unit mass of the surface-active component is lower than for micellar form. Apparently, as shown in Fig. 2, the concentration dependence of density follows the same trend for both surfactants. Growth level of density in the monomeric form relies on different grades of hydration and molecular weight of the surfactant. Therefore, a slightly higher value of density was observed for Tween 80 due to a greater molecular weight (MW) of this surfactant and the possible negligible differences in hydration of monomeric form between both surfactants. According to the literature[47], density at very low surfactant concentrations is practically equivalent to that of pure water.

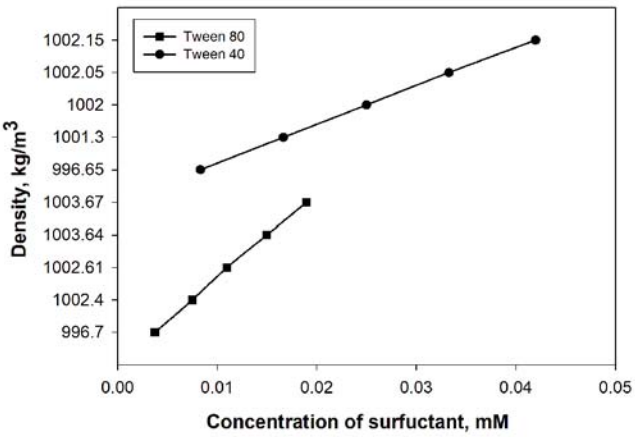


Figure 2. Density of continuous phase as a function of concentration of surfactants Tween 40 and 80 at room temperature

Figure 3 illustrates the influence of concentrations of analyzed surfactants on interfacial tension (IFT). The profile for both surfactants is representation of a pure surfactant where two regions are indicated: the sharp decrease of interfacial tension with the concentration of the surfactant and then the plateau. The boundary of these changes is the value of CMC (CMC for nonionic surfactants is generally below 1 mM) estimated at T=298 K for both surfactants: $CMC_{Tween40}$= 0.033 mM and $CMC_{Tween80}$= 0.015 mM[45], respectively, as is presented in Fig. 3. The reduction of interfacial tension with concentration is ascribed to an increase in the number of molecules of surfactants at the interface. In contrast, the plateau region, above CMC, corresponds to the concentrations of surfactants that do not affect the interfacial tension, and results presented in Fig. 3 have shown a characteristic behavior of interfacial tensions in the proximity of CMC. At those concentration surfactants start aggregating into micelles (Tweens form a normal micelle), therefore, it causes the surface free energy to decrease by reducing the contact area of hydrophobic parts of the surfactant with water[7]. Here, the oil-water surface is saturated by surfactant molecules/amphiphile. Generally, the change in the slope of interfacial/surface tension raw data can be applied for the calculation of CMC (empirical approach), where the intercept between the two lines fitting the data allows to approximate the value of CMC[7, 47]. The knowledge of CMC value is important since is known as a representative of the most important chemical–physical parameters (surface characteristics) of surfactants that influence the other mixture properties involving conductivity, density, viscosity, osmotic coefficient, water activity, and surfactant activity coefficient[7]. For concentrations higher than CMC, the Marangoni stresses acting on the drop's surface are minor since the diffusion time of surfactant from the bulk to the droplet interface decreases causing a reduction of the Marangoni stresses (this phenomenon is also observed in non-surfactants and at high surfactant concentrations systems). Nevertheless, the presence of the surfactant still alters the rheology of the interface, causing the increase of the effective viscosity of the water[7]. However, for surfactant concentrations even far below a critical micelle concentration, Marangoni stresses play a key role in a liquid dispersed system and can drastically change the flow[7, 42]. In such systems, interfacial tension gradients form on the droplet surface when the droplet is deformed, which results in Marangoni stresses that resist the droplet against disruption. Nevertheless, fast adsorbing surfactants can repopulate promptly any interface that is stretched and should not allow occurring any interfacial gradients and Marangoni stresses and consequently, both: the effective elasticity or viscosity related to exchanges with the bulk should disappear for such surfactants. Measured interfacial tension value between paraffin and pure water is 49.31 mN/m ±0.20 and it is slightly lower than the reported value of 51.7 mN/m[48]. The differences in the value of interfacial tensions may be attributed to that of a paraffin containing a small amount of impurities. The eventual presence of impurities can be assessed by adopting appropriate mass spectrometry techniques; however, it is beyond the scope of this paper. Adding the required amount of surfactant caused the reduction of interfacial tension from 48.69 mN/m ±0.06 (the lowest concentration) to 39.40 mN/m ±0.12 (the highest concentration) for all solutions with Tween 80. In the case of Tween 40, the interfacial tension was reduced from 46.46 mN/m ±0.10 to 36.85 mN/m ±0.11 with increasing concentrations. It is clearly shown that slightly higher values for interfacial tensions are for all systems supplemented by Tween 80. This can be explained by a slightly higher value of MW for this surfactant.

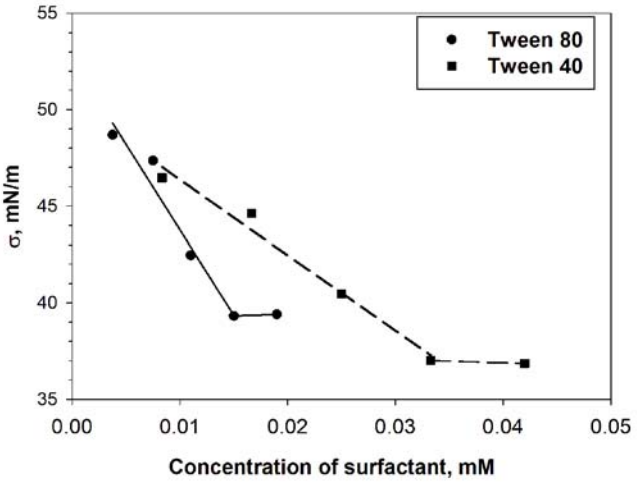


Figure 3. Surface tensions as a function of concentration of surfactants: Tween 40 and 80

Droplet size measurements

The measurement of the droplet size distribution requires adding the information on the refractive index (RI) of both phases in. Here, the value of 1.333 was taken for all continuous phases (the same value of RI as for water) and 1.467 for paraffin oil dispersed phase. Surprisingly, the RI value for all aqueous phases was the same but it was expected that an increase in the length of the alkyl chain will lead to rise of the thickness of the resulting film, and then to decrease the speed of light transmission, and consequently to increase of the refractive index. Thus, RI for Tween 80 should be higher than for Tween 40. However, the presence of one unsaturated carbon-carbon double bond in the alkyl

fragment in Tween 80 makes RI values for both Tweens approximately the same.

The structure of prepared systems was also observed under the microscope and representative examples of captured images are shown in Fig. 4. It seems that slightly bigger droplets are obtained for the system with Tween 80 as the interfacial tension for all those systems is marginally higher. It was also proven by studying DSD (volume) presented in Fig. 5, Fig. 6 and particularly the comparison of DSD shown in Fig. 7. All figures show volume drop distribution as a function of step-increasing impeller speed.

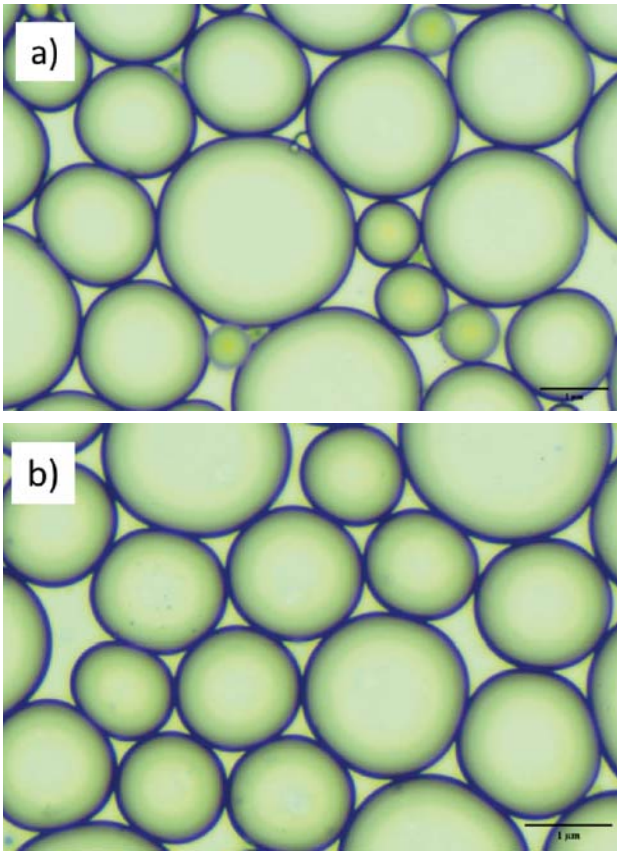


Figure 4. Exemplary microscopic images of the system paraffin and water supplemented by a) 0.01665 mM of Tween 40 and b) 0.0075 mM of Tween 80 at similar impeller speed (N = 425 rpm for Tween 40 and N = 430 rpm Tween 80)

All distributions for Tween 80 and Tween 40 are rather predominantly monomodal with one characteristic peak and generally the entire distribution shifted towards smaller droplets as the impeller speed increased. First, the size frequency augments at a higher impeller speed causing smaller and finer droplets. Second, it happens as a result of an increase in drop breakage rate with power input to the system. For instance, the mean Sauter diameter at c_{Tween40} = 0.025 mM was 240 μm, 193 μm, 133 μm and 92 μm at impeller speed increased from 225 rpm to 525 rpm, respectively. The same trend was observed for system with Tween 80 at comparable concentration, c_{Tween80} = 0.011 mM, where d_{32} changed from 286 μm to 102 μm for N increasing from 230 rpm to 530 rpm. The obtained results for Tween 80 are to some extent correlated with those presented by Bąk and Podgórska[49] who studied 0.0012 – 0.8 mM Tween 20 and 0.006 and 0.9 mM Tween 80 aqueous solution/toluene systems in breakage and coalescence mode. At the impeller speed N = 350 rpm and 0.006 mM Tween 80 the drop size was 85 μm whereas in our study d_{32} is 235 μm for N = 330 rpm and 0.0075 mM Tween 80. The difference is almost three times the size. In contrast, Liu et. al.[19] investigated experimentally and numerically the effect of Tween 80 concentration on the evolution of drop size distribution in Exxsol oil-deionized system. For the concentration of Tween 80 equals 0.00758 mM, d_{32} was roughly 64 μm at N = 500 rpm. Comparison with data obtained for similar concentration (0.0075 mM) and impeller speed (N = 530 rpm) has revealed about 40 μm variance in the size of droplets. All differences in the drop size can be addressed to the following aspects: the physical properties of the dispersed phase, varying conditions of experiments (e.g. longer agitation time), differences in the applied measurement techniques, i.e Bąk and Podgórska[49] utilized the video-techniques method (a high-resolution digital camera mounted on a stereomicroscope objective) but Liu et. al.[19] used focus beam reflectance measurements (FBRM) and measurement position of DSD.

In general, the mean Sauter diameter values for all investigated systems were decreasing as the concentration of surfactants was increased and the impeller speeds, as clearly shown in Fig. 8. The higher surfactant concentrations are, the lower IFT until a CMC value is reached and thus lowers the mean diameter of a droplet. As expected, the intensification of the mixing process leads to an increase in shear and energy dissipation rate and in turbulent pressure fluctuations which are the main external forces that govern drop breakup process. Similar findings were reported by El-Hamouz[46], Hohl et al.[29], Zainal Abidin[27], Liu et al.[19] and others[50, 51]. The experimental results showed that DSDs are rather narrowed, as typical for the system with surface-active components when compared to those for non-surfactant systems. As expected, smaller droplets were found for all systems with higher concentrations of surfactants and mean droplet size decreased with increasing surfactant concentrations, wherein, interfacial tension value decreased. It happens since lower interfacial tension is causing diminishing the surface force which keeps droplets from break-up. Analogous conclusion was posted by Hecht et al.[52], Pichot et al.[53] or Politova et al.[54]. The span value was changing from 0.592 to 1.335 for all systems with Tween 80 whereas for systems with Tween 40 span was varied between 0.515 to 1.492. These results confirm the above-mentioned statement that all distributions are considered for all surfactant systems, and they were rather log-normal, with positive value of skewness. For all cases, the tail appeared on the right side of DSDs. However, the lowest value of span was found for the impeller speed N = 425 rpm for Tween 40 and N = 430 rpm for Tween 80 which indicates the smaller width of distribution. This trend was repeatable for all examined systems. It was observed that the value of span increases with concentration of surfactants. It should be noticed that the physical stability of liquid dispersion/emulsions depends not only on mean diameter but also on span values[55]. Besides, as the general picture (Fig. 5 and Fig. 6), at the constant impeller speed, the volume percentage decreased with increasing concentration of surfactant, except for the system of c_{Tween80} = 0.011 mM

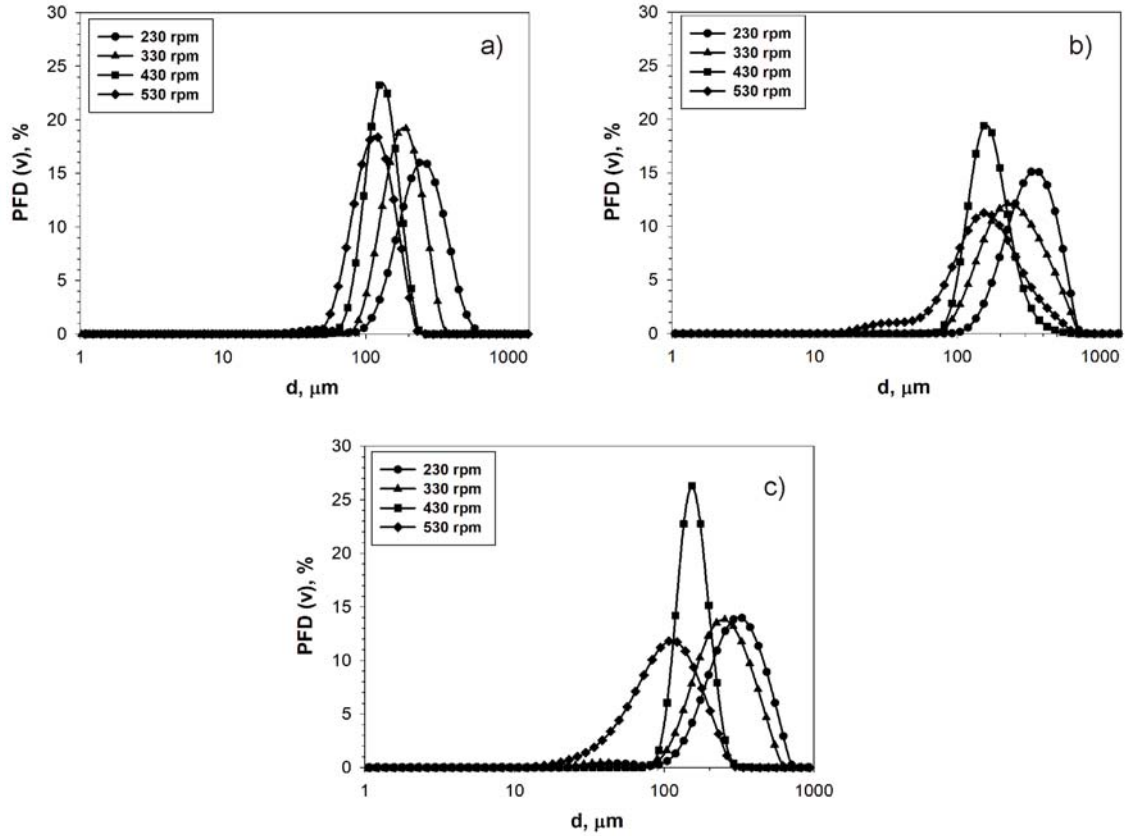


Figure 5. Drop size distribution for 5% v/v of paraffin in A) 0.00375 mM Tween 80, B) 0.0075 mM Tween 80 and C) 0.011 mM Tween 80

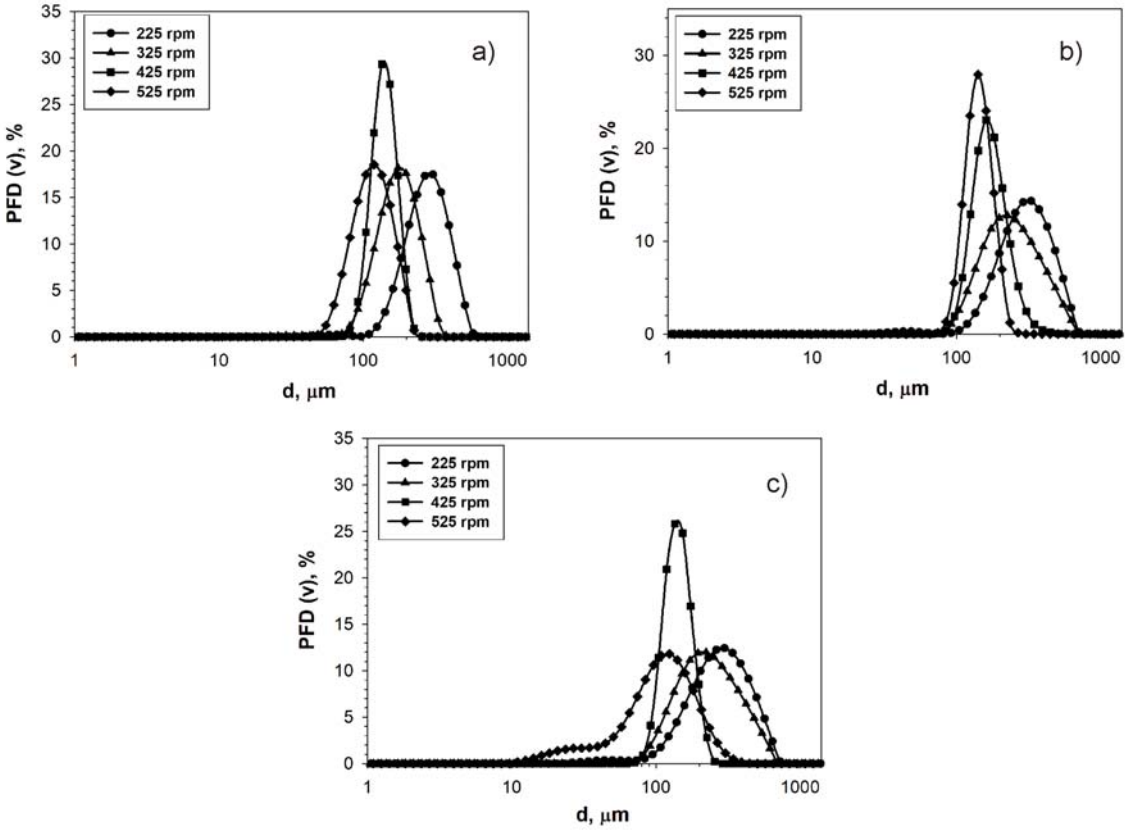


Figure 6. Drop size distribution for 5% v/v of paraffin in A) 0.008325 mM Tween 40, B) 0.01665 mM Tween 40 and C) 0.025 mM Tween 40

and $N = 430$ rpm which consistently does not follow this trend. The comparison of DSDs for both surfactants is depicted in Fig. 7 and allows us to observe that for the system with Tween 40 at similar conditions the same trend can be found. In addition, Fig. 7 can help to disclose any differences in DSDs for both surfactants used in experiments. It is known[28] that the surfactant type and concentration significantly affect the droplets morphology besides dispersed phase composition.

The investigated DSDs, at similar impeller speed, for two concentrations that corresponded to 50% and 75% of critical micelle concentration (CMC) of Tween 40

and 80 that are presented in Fig. 7 clearly show that the DSDs are rather very good agreement in shape, span and positive skewness of distributions between 0.405 to 0.685. Analysis of DSD evolution at the similar surfactant concentrations and at the same energy dissipation rate shows that, generally, slightly bigger droplets were produced in all systems with Tween 80. This can be attributed to the slightly higher value of IFT for Tween 80. For example, the mean Sauter diameter at similar impeller speed is 301 μm and 260 μm for $c_{Tween80}$ = 0.0075 mM and $c_{Tween40}$ = 0.01665 mM, respectively, whereas for higher concentration of both surfactants d_{32} equals to 286 μm and 240 μm. But for higher impeller speeds those differences in the value of d_{32} are minimal. Both surfactants have similar values of HLB, and also, they may demonstrate similar mechanics of absorption of molecules of Tween 80 and Tween 40 on the oil surface, which results in the production of comparable DSDs and less pronounce changes in d_{32} between surfactants. The assessment of uniformity of DSDs, presented in Fig. 7, has shown that for lower impeller speed of all investigated concentrations, the value of uniformity is between 0.295 to 0.381. As impeller speed increased the value of uniformity decreased. The analysis of the influence of the concentration of surfactants clearly shows that also the composition of the continuous phase greatly influences the homogeneity of distributions following the same trend as was found for impeller speed. The higher concentration of surfactants is, the lower the interfacial tensions are, and then smaller droplets in the system which results in narrower distributions. At the higher concentrations of surfactant, there is enough surfactant present in the solution to fully cover all the newly formed interfaces and immobilized oil droplets, causing coalescence to be completely suppressed or slowed down[7, 23, 50]. In general, the smaller uniformity is, the narrower droplet size range is, indicating that the homogeneity of the droplet size distribution is better. Therefore, for lower values of N, distributions are broader, with the value of span higher than 1 for all DSDs while for higher impeller speed the span value is around 0.65. It can be concluded that uniformity depends on both: mean specific energy dissipation rate (impeller speed) and the concentration of surfactants.

The evaluation of DSD at $c_{Tween80}$ = 0.011 mM and N = 430 rpm with relevant concentration and impeller speed for Tween 40 ($c_{Tween40}$ = 0.025 mM and N = 425 rpm) has shown that both DSDs overlapped. The value of d_{50} is 140 μm for Tween 40 and 160 μm for Tween 80. The change in d_{50} is less pronounced for this system and the similar trend was noticed for other systems where values of d_{50} are close to each other. Therefore, it can be stated that practically both surfactants give comparable results in DSDs and in other variables that are used to describe distributions since they are characterized by the similar value of HLB. This is important information while the selection of appropriate surfactants is made to obtain a certain distribution or mean Sauter diameter. In this case, it seems that mainly the economic aspect plays a key role, and before the stability of an emulsion. Dias et al.[38] have also proven that Tween 40 can be a good alternative to Tween 80 as a stabilized agent in O/W dispersion or emulsion. The results also have proven that the observed deviation of DSD for the Tween 80 system should be accepted as correct.

In general, these figures (Fig. 5, Fig. 6 and Fig. 7) show very good agreement in the shape of the distributions between the surfactants, and as expected, smaller drops are produced in a dispersion of the higher concentration of surfactants which results in lower value of interfacial tension. The maximum drop sizes in all systems (for a given impeller speed and concentrations of surfactant) are rather similar, demonstrating that drop breakage mechanisms are also similar.

Sauter mean diameter as function of impeller speed, energy dissipation rate and Weber number

Figure 8 shows the effect of impeller speed on the mean Sauter diameter for tested systems for both surfactants. As it was mentioned above, the mean Sauter diameter decreased with increasing impeller speed, and it is clearly shown in Fig. 8. It means that impeller speed has a strong influence on the droplets size. At the same impeller speed, slightly higher value of d_{32} was observed for all systems with Tween 80 which is attributed to the higher interfacial tension. It was also seen that the value of the mean Sauter diameter diminished with the concentration. Those outcomes have been already

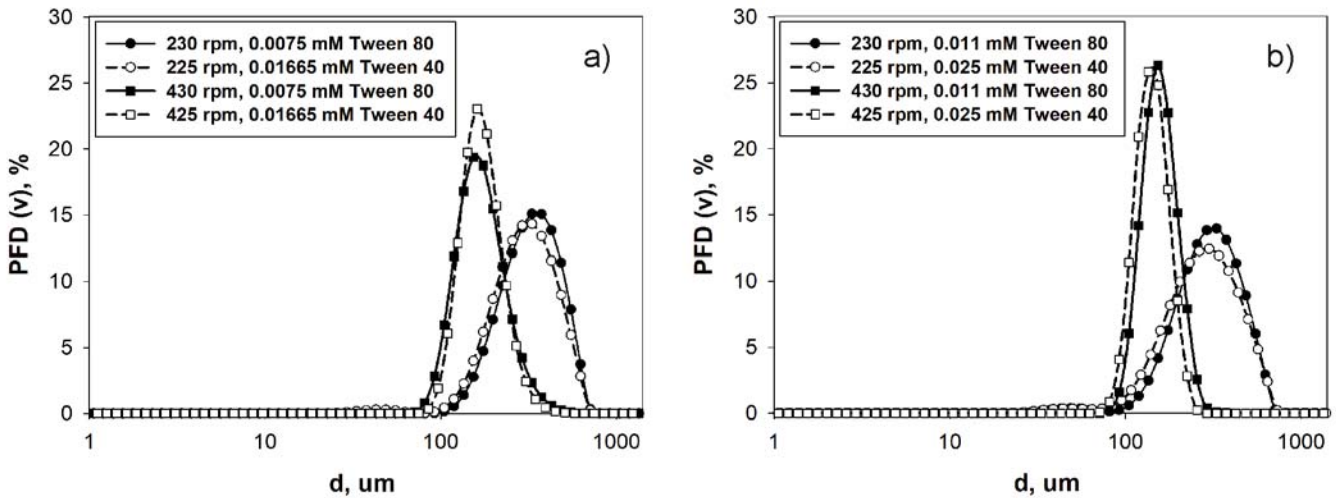


Figure 7. Comparison of DSD obtained at similar impeller speed for 5% v/v of paraffin in A) 0.0075 mM of Tween 80 and 0.01665 mM Tween 40 and B) 0.011 mM of Tween 80 and 0.025 mM Tween 40

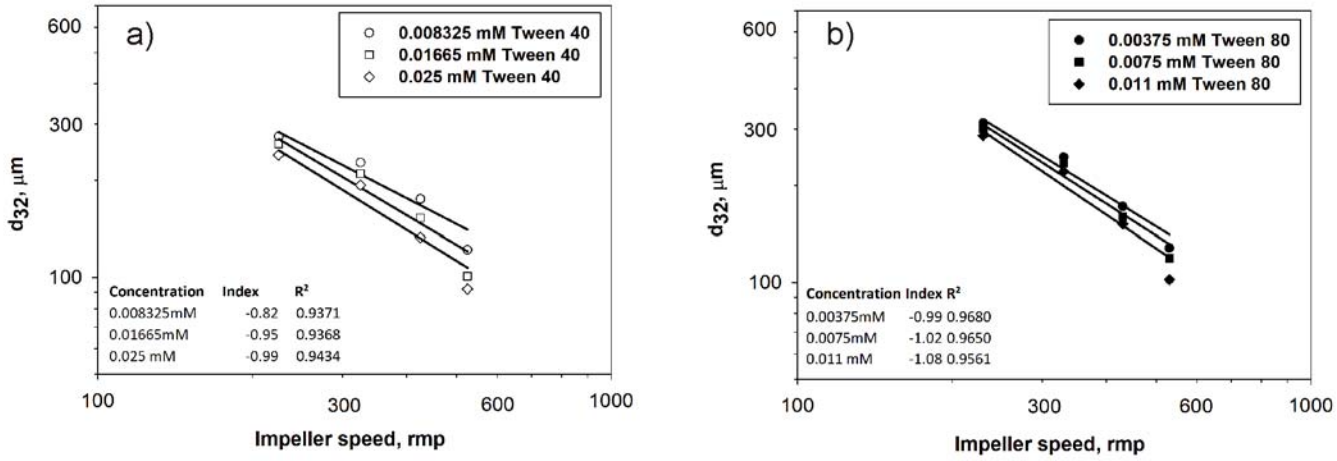


Figure 8. Effect of impeller speed on mean Sauter diameter for all concentrations of: A) Tween 40 and B) Tween 80

mentioned in the previous section and Fig. 8 evidently verifies them.

The value of d_{32} is proportional to impeller speed to the power b (N^b) and results from this experiment cover the range of exponents from –1.08 to –0.99 for systems with Tween 80 and from –0.99 to –0.88 for Tween 40 with the value of $R^2 > 0.93$. The exponent b decreases as concentration increases and slightly higher slopes were obtained for the lowest concentration of surfactants. All systems with low c generate bigger droplets compared to that of higher concentration. The differences in slopes can be explained by the varied influence of the size of droplets on breakage. Maaß et al.[56] have found that small droplets resist against N better than large ones. For the bigger droplets the region of breakage is large causing an increase in the probability of breakup. Therefore, all systems with lower IFT produce smaller droplets and changes in mean Sauter diameter with impeller speed augmentation are smaller. In general, for turbulent inertial regions of breakup, exponent b should equal to –1.2 for the droplet sizes higher than Kolmogorov length scale (η_k). But, Shinnar[57] suggested the value for $b = -1$ for all droplets of size lower than η_k. Here, the Kolmogorov length scale is of the order of 21–40 µm for all systems and mean droplets size are above this range. This suggests that exponent b should be around the value of –1.2. As was assessed by Atiemo-Obeng and Calabrese[17] stirred vessels usually do not operate at enough high-power draw to produce droplets of the length of the Kolmogorov scale. The results from this study show that values of b are close to the criterion of –1.2. It still suggests that turbulent inertial stresses control the breakage process more likely than viscous stresses since all droplets are above η_k. The value of viscosity of liquid paraffin is 32 mPas (it is classified into the group of low viscosity system) thus the viscous stresses should not govern the breakage process since the effect of viscous forces is less pronounced for low viscosity system[14, 17]. Even so, the b was increased to –0.82 at 0.008325 mM Tween 40 and this value is relatively close to –0.75 as suggested by Leng and Calabrese[58] for viscous dispersed phase. This inconsistency found in this study for the value of b may be due to the fact that the inertial viscous stresses can, by some means, affect the breakage process.

In general, liquid-liquid systems have been extensively investigated and it helps to derive theoretical correlations for maximum stable drop size (d_{max}) in fully developed, homogeneous turbulent flow. In such system, correlations rely on mechanistic models proposed by Hinze[59] who stated that breakage of droplets occurs when the disruptive stress is greater than the cohesive stress[58]. It is commonly known, that for dilute liquid-liquid systems with low viscosity of dispersed phase the disruptive stress is associated with energy dissipation and the cohesive force is related with interfacial tension which resist the droplet against breakage. In this case, internal viscous stresses are negligible. There are many works where this theoretical background is explained in detail[56–59]. For turbulent flow when the following assumption is applied that ratio of d_{32}/d_{max} stays constant and all drops are greater than Kolmogorov's length scale, the average stable drop size (d_{32}) can be associated to the local energy dissipation rate[58] by following formula:

$$d_{32} = C_1 \varepsilon_T^{b_1} \quad (1)$$

or Weber number:

$$\frac{d_{32}}{D} = C_2 We^{b_2} \quad (2)$$

The above equations and other models[58, 59] were developed and commonly used for stirred vessels, wherein eq. (2) is frequently applied in the scaling of emulsification processes. Theoretical values of exponent b_1 and b_2 for the above conditions are –0.4 and –0.6, respectively. The experimental constants C_1 and C_2 depend on the type of impeller and Po number[12, 50] and literature shows that constant C_2 can vary between 0.09 and 0.125[12]. All proportionality constants C, exponents b and coefficients of determination R^2 were calculated by using non-linear regression from the experimental data for the different continuous phases and the results are summarized in Table 2 and shown in Fig. 9 and Fig. 10.

Fitting experimental data to the eq. (1) allowed to find the constant C_1 and exponent b_1 and obtained results are presented in Fig. 9 and Table 2. The exponents on mean specific energy dissipation rate () from the data are relatively close to the theoretical value of -0.4 (dedicated to the turbulent flow) for all systems with Tween 80 with fit of $R^2 > 0.96$. Slightly weaker fitting and shallower gradients on mean specific energy dissipation rates were found for systems of Tween 40. The differ-

Table 2. Coefficients from non-linear regressions for correlations of mean Sauter diameter, d_{32}, with scale-up terms (d_{32}/D with We) of paraffin oil droplets for all investigated systems

Results from regression						
Continuous phase	C_1	b_1	R^2	C_2	b_2	R^2
0.008325 mM Tween 40	200	–0.28	0.937	0.021	–0.36	0.923
0.01665 mM Tween 40	180	–0.32	0.937	0.027	–0.42	0.926
0.025 mM Tween 40	164	–0.33	0.943	0.028	–0.44	0.933
0.00375 mM Tween 80	217	–0.33	0.968	0.035	–0.45	0.961
0.0075 mM Tween 80	206	–0.34	0.965	0.037	–0.47	0.958
0.011 mM Tween 80	192	–0.36	0.956	0.042	–0.49	0.949

ence in the gradients indicates rather that drops are still broken by similar mechanisms, in this case, by turbulent inertial forces. Fig. 9 shows that the function of drop size and mean specific energy dissipation rate falls into three distinctive lines that depend, as expected, on the different values of interfacial tension and different properties of the interface (concentration of surfactants). As expected, at a similar energy dissipation rate, the smallest drops were formed in the systems with the highest concentrations of surfactants as a result of the lowest interfacial tension. For all systems with lower values of concentrations, large droplets were formed which can be explained by the highest interfacial tension. The effect of interfacial tension on drop size is discussed in Section Droplet size measurements. In general, the effect of surfactant concentration on mean drop size was found to be rather insignificant. As it was mentioned above, the comparison between two surfactants has revealed that at the same for all systems with Tween 80 forms systematically slightly larger drops which can be explained by the higher value of interfacial tensions. Fig. 9 indicates that the mean specific energy dissipation rate in this case is not probably an accurate variable to correlate mean Sauter diameter since the scattering of experimental data is observed. El-Hamouz et al.[25] suggested that tip speed is a better correlating parameter for dispersion/emulsification in stirred vessels than mean specific energy dissipation rate. A similar conclusion was found by Hall et al.[14] who suggested that tip speed gives a better approximation of the maximum energy dissipation rate which is significant for droplet breakup[14]. However, the correlation of tip speed with mean Sauter diameter is out of the scope of current work.

Proportionality constant C_2 was found by expressing dimensionless drop size as a function of Weber number and results are summarized in Table 2 where the different effects of continuous phase on constant C_2 can be indicated. The experimental constant of C_2 varies between 0.021 to 0.042 and it is lower than suggested in the literature[58, 60] value of $C_2 = 0.056$ for similar impeller. Here, fitting of eq. (2) to the experimental data provided almost two times smaller value of constant for all system with Tween 40. In the case of Tween 80, the differences in C_2 between literature and experimental data are less noticeable. Nevertheless, the increase of volume fraction of dispersed phase commonly causes changing of C_2 at quite different rates in pure coalescing systems; and even with non-coalescing systems since the dispersed phase is considered to suppress the turbulence[58]. The results shown in Table 2 clearly indicate that both the volume fraction of the dispersed phase and the composition of continuous phases (the presence of surface-active components there) can affect the extent of coalescence and thus the constant C_2. The goodness of fitting for all systems is higher than 0.92 and all systems with Tween 80 give a slightly better fit.

Dimensionless Sauter mean diameters as a function of Weber number are presented in Fig. 10. The results practically collapse in one line, but the experimental data are scattered, which is particularly evident for Tween 40. The overall correlation for all systems was obtained as shown below:

$$\frac{d_{32}}{D} = 0.04We^{-0.49} \tag{3}$$

with goodness of fitting and root-mean-square deviation (RMSE) equals 0.91 and 0.00031, respectively. The exponents on Weber numbers are –0.51 and –0.46 for Tween 80 and 40, respectively, with a value of coefficient of determination that is better for Tween 80 ($R^2 = 0.960$) and worse for Tween 40 ($R^2 = 0.919$). The value of b_2

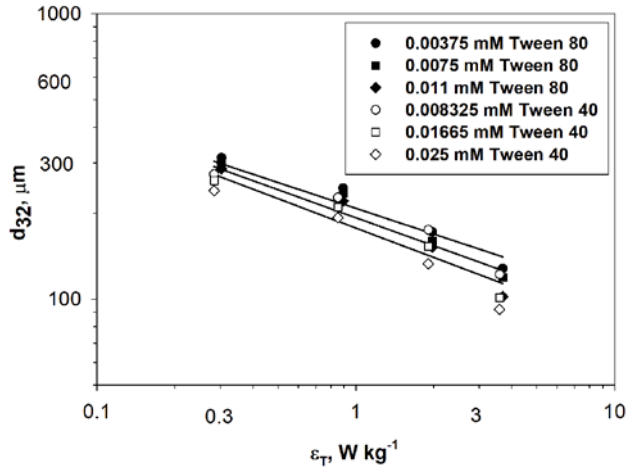


Figure 9. Mean drop size of 5% paraffine oil as a function of specific energy dissipation rate for Tween 40 and Tween 80

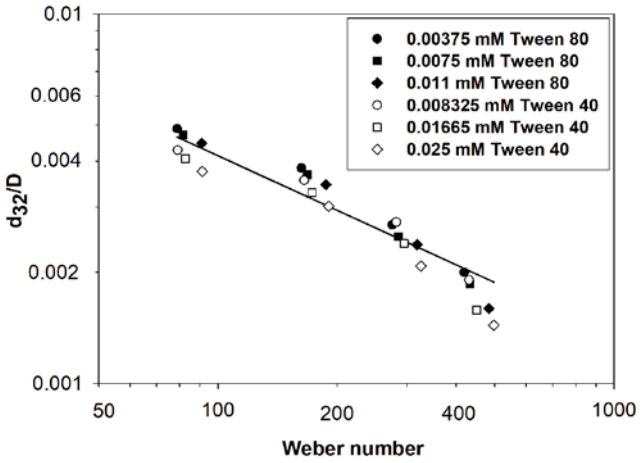


Figure 10. Dimensionless drop size as a function of Weber number for both systems: Tween 40 and Tween 80

is slightly higher than the theoretical value of –0.6 suggested for turbulent inertial break-up. Results depicted in Fig. 10 account well for the effect of interfacial tension in the surfactant system. Again, the smallest droplet size was found for the smallest value of interfacial tension (the highest concentration of surfactants) because a lower interfacial tension diminishes the surface force which keeps droplets against break-up. It was found that the value of Weber number increases with surfactant concentrations and it is in good agreement with results published by Janssen et al.[61].

Stabilization test

As was mentioned above, dispersions/emulsions are known as thermodynamically unstable systems and rapidly separate into individual phases of oil and water[5]. It occurs because the density of oil and aqueous phases are different and the unfavorable contact between oil and water molecules[6]. In general, the stability of an dispersion/emulsion is defined as its ability to sustain its properties in such a way that phases are capable of remaining mixed together[5, 6]. The level of stability depends on many factors and they are particle size, particle size distribution, density between the dispersed and continuous phases and the chemical integrity of the dispersed phase[5]. The disintegration of systems can happen when several phenomena such as coalescence, flocculation, Ostwald ripening or other above-mentioned. Here, the observation of the stability of dispersions was based on values of d_{32} because droplet size has an important role in defining the stability and rheological properties of the dispersions and emulsions[5]. The mean Sauter diameter for all systems was monitored for up to 30 days. Following their preparation, samples of the collected dispersed phase were stored at room temperature in a dark room to eliminate exposure of the sample to sunlight. Each systems was again measured via Mastersizer 3000 after 24 hours, 7, and 30 days to obtain DSD and value of d_{32}. Stable oil dispersions were dispersed in the same continuous phases as used while their formulation. The example of the results of the value of mean Sauter diameter for impeller speed 425 and 430 rpm are summarized in Table 3.

The collected dispersion for each concentration revealed that for concentrations of surfactants higher than 0.0166 mM for Tween 40 and 0.0075 for Tween 80 they remained stable during 30 days of storage. Qualitatively similar values of mean Sauter diameter were found between fresh and aged dispersions. As expected, a higher surfactant concentration of Tween 40 and Tween 80 allowed to stabilize the droplets slightly better against partial coalescence which is the one possible phenomenon causing destabilization of dispersion/emulsion[5, 53]. At higher surfactant concentrations there was enough surfactant to fully cover a newly formed surface, help immobilize it and cause small droplets to act as rigid spheres[23]. In this condition, the film drainage becomes more hampered, so the rate of coalescence slows down or completely suppresses. In fact, absorbed surfactant on an oil-in-water interface can form an interfacial layer that causes the increase of the electrostatic and/or steric repulsion between droplets, and so the stability of dispersion/emulsion is improved, and droplets are partly protect against coalescence. The development of a highly charged interfacial layer also helps in the improvement of dispersion/emulsion stability because the electrostatic and/or steric repulsion between droplets is increased[5, 8].

The worst stability was observed for the lowest concentrations of surfactant of 0.008325 mM for Tween 40 and 0.00375 mM for Tween 80 and all lower impeller speeds for other systems. For both systems, the value of the mean Sauter diameter increased with time which indicates that the concentration of surfactant is too low to keep droplets from coalescence. It was possible to observe from the collected samples that extensive destabilization in the form of phase separation occurred in those systems, the film of separated paraffin was built up with time and the layer of dispersion was reduced. However, no complete separation was observed but meaningful reduction in stable droplets layer over investigated time. In general, the stability of dispersion against coalescence becomes the poorest for all systems of low interfacial tension value[6] and others of lower impeller speeds therefore the strong phase separation was observed for the lowest concentration of both surfactants.

CONCLUSION

This study helps in understanding the effect of nonionic concentrations of Tween 40 and Tween 80 on drop size distribution and mean Sauter diameter. This information is important for industrial applications of liquid dispersions or emulsions to control and optimize mass or heat transfer processes. Drop size distributions affect many properties of liquid dispersion or emulsion, and thus quality of any emulsion-based products.

It has been found that the lowest value of interfacial tension was for the highest concentrations of both surfactants and its value decreased with concentration up to the CMC. After that concentration interfacial tension values were independent of concentration.

It has been shown that the liquid-liquid dispersion is characterized by a narrowed distribution, typical for non-coalescing systems and it is practically similar for both types of surfactant. It suggests that the droplets break up under a similar mechanism. The stable droplets of required, adjustable size and interfacial area could be produced in a standard stirred vessel, from concentrations 0.01665 mM and 0.0075 mM of Tween 40 and

Table 3. The mean Sauter diameter for fresh and storage liquid dispersion at 425 and 430 rpm

Continuous phase	Mean Sauter diameter, μm			
	Fresh	*24 hours*	*7 days*	*30 days*
0.008325 mM Tween 40	175±1.7	193±1.05	238±1.62	350±2.0
0.01665 mM Tween 40	153±1.5	155±0.67	158±1.02	160±0.82
0.025 mM Tween 40	133±0.5	136±1.5	140±1.0	143±0.67
0.00375 mM Tween 80	172±0.35	190±0.5	221±0.62	327±1.75
0.0075 mM Tween 80	160±0.32	164±1.0	167±1.05	170±0.5
0.011 mM Tween 80	152±0.65	155±0.5	159±1.0	164±0.95

Tween 80, respectively. A correlation relating the mean Sauter diameter to the impeller speed and physical properties of the continuous phase has been developed. The experimentally determined exponent on mean specific energy dissipation rate and on Weber number is rather associated with theoretical models derived for turbulent flow.

In fact, long-term stability tests have shown that the dispersion remained stable after 30 days, with no significant change in droplet size. Despite the type of surfactant used, dispersions proved to be stable for all systems with the higher value of surfactant concentration and impeller speeds. All dispersions become unstable at the lowest value of concentrations of both surfactants and all stirrer speeds (lower impeller speeds give large droplets size which accelerates the coalescence process) and strong phase separation was observed.

Importantly, some limitations in this study were acknowledged. First, tip speed should be used instead of specific energy dissipation rate as it is considered to be a much better correlating parameter. Secondly, interfacial tension included in the Weber number should be replaced by effective interfacial tension containing an elasticity term which is suggested for surfactant systems as it gives better correlation with experimental results. Future research should attempt to gain a deeper understanding of the processes when the following limitations will be examined.

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