A multi-probe non-intrusive electrical technique for monitoring emulsification of hexane-in-water with the emulsifier C10E5 soluble in both phases

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Abstract

This work measures the variation of local water fraction during emulsification of hexane-in-water by an electrical conductance technique employing multiple non-intrusive ring electrodes. The emulsifier, C10E5, was initially dissolved only in water although it is highly soluble in both phases. This gives birth to interesting emulsification kinetics. Experiments were conducted at four emulsifier concentrations (from 1 × 10^{-4} to 1 × 10^{-3} M) and three hexane-to-water ratios (from 40/60 to 5/95, v/v). Emulsification was conducted by intense mixing with a Rushton turbine. CFD calculations were employed to estimate the distribution of turbulent dissipation rate in the mixing vessel. Furthermore, measurements of interfacial tension (static and dynamic) and interfacial dilatational elasticity and viscosity were conducted. An effort was made to explain the observed phase’s distribution during emulsification by invoking arguments with respect to interfacial properties and turbulent dispersivity.

1. Introduction

Emulsification is the process of making fine dispersions of immiscible liquids. The emulsification process is widely used in the food, pharmaceutical, cosmetic, agrochemical and chemical industry. In order to form an emulsion of given characteristics (dispersed phase volume fraction, droplet sizes, functional properties etc.) the process of emulsification has to be monitored and controlled. To appraise processing uniformity and homogeneity of the produced emulsion, non-intrusive continuous measurement of phase volume fractions and droplet size distribution along the height of the emulsion during emulsification is important.

Several methods have been employed in the past, e.g., light scattering, laser diffraction, optical microscopy, to investigate the progress of emulsification which determine droplets size from either direct visual observations, or from measurements performed on withdrawn samples [1–6]. These methods are limited by the fact that they provide information of droplet sizes only from places where there is either visual access or a sampling mechanism can be inserted. Sampling can alter the emulsion characteristics by exerting forces different than those existing in the emulsifier. Additionally, the often required significant dilution of samples before measurement can modify some of the emulsion characteristics (e.g., destroy flocks or aggregates). Moreover, these methods cannot provide information on phase volume fraction distributions. Electrical techniques appear to be a tempting option for measuring non-intrusively the temporal evolution of local volume fractions inside emulsions (opaque or transparent). Such techniques have been used in the past for monitoring other applications such as mixing [7], bubble columns [8], multiphase flows [9,10], solid-liquid filtration [11], and polymerization reactors [12]. In those studies different electrode geometries and possibilities to arrange/configure electrodes have been employed. Measurements taken with small size electrodes, even if not intrusive, yield information chiefly from the region close to electrodes since there the electric field strength is very high compared to the rest of the measuring volume. This information may not be representative of the entire cross-section of the vessel. On the other hand, intrusive type of electrodes e.g., grid or screen, spanning the whole cross-section of a vessel may severely interfere with fluid motion and so influence phase separation.

A pair of ring electrodes running the internal circumference of a vessel and separated by a certain distance in the axial direction constitutes a probe which, apart from being non-intrusive, is particularly sensitive to phase distribution patterns in the cylindrical segment between the ring electrodes [13]. Ring electrodes have been successfully applied to a number of multi-phase applications e.g., [14–16]. Recently, an upgraded version of the technique has been used for monitoring foam drainage [17,18]. It has been reported that in cases of radially homogeneous dispersions the
separation distance between electrodes can be significantly reduced in favor of more localized (axially) measurements.

To our knowledge there has been no systematic use of electrical measurements for studying the phases’ distribution in emulsions. In other words, to measure the evolution of local volume fractions during emulsification. Some papers used conductance measurements more as an indicator of global emulsion condition rather than as a tool for determining local volume fractions [19–21]. In the present work, we examine the application of a non-intrusive, on-line, electrical conductance technique for monitoring the evolution and spatial distribution of local phase volume fraction inside opaque oil-in-water (O/W) emulsions. Multiple ring electrodes located at different axial locations of the container register variations along the height of the emulsion in a tomographic fashion [22].

Emulsification of hexane-in-water mixtures is performed in a stirred vessel using pentaethylene glycol monodecyl ether (C_{10}E_{5}) as emulsifier. C_{10}E_{5} is a non-ionic surfactant belonging to the n-alkyl polyethylene glycol ethers (C_{E_j}) group of surfactants. These surfactants are broadly used as emulsifiers in applications such as tertiary oil recovery, medicine, cosmetics, nanoscience and analytical chemistry [23–25]. In addition, their interfacial physicochemical and rheological properties have been studied extensively. For this reason, hexane/water/C_{10}E_{5} emulsions are chosen for emulsification studies in the FASTER facility of the International Space Station, a project where the present authors are actively involved [26].

Apart from the above, this system exhibits a particularly intriguing behavior regarding phase development (droplet formation) during emulsification if the surfactant is initially dissolved only in one phase since C_{10}E_{5} is highly soluble to both hexane and water.

In the following sections, the emulsion preparation procedure is presented first, followed by a description of the experimental setup and measuring techniques. Measurements on essential physicochemical and rheological properties of hexane/water/C_{10}E_{5} interfaces are given next. Finally, a section comes with electrical data obtained during emulsification along with an effort to explain the observed trends on the basis of energy input (mixing) and interfacial properties.

2. Materials and methods

2.1. Materials

Oil-in-water emulsions were prepared using a NaCl aqueous solution, n-hexane and C_{10}E_{5} C_{10}H_{21} (OCH_{2}CH_{2})_{5}OH as emulsifier. The aqueous solution was prepared by dissolving NaCl at a concentration of 50 mg/L into Millipore filtered water in order to provide a small but finite electrical conductivity necessary for electrical measurements. After salt dissolution the electrical conductivity of the aqueous solution was 125 μS/cm. Hexane was spectroscopy grade (purity ≥ 98.5%, Uvasol, Merck). Three different oil-to-water volume ratios: 40/60, 20/80, 5/95 were used for making emulsions. The emulsifier, C_{10}E_{5} (Nikko Chemicals Ltd.), was initially dissolved in water but once in contact with hexane during emulsification it started dissolving into hexane and partitioned between the two phases. The partition coefficient of C_{10}E_{5} between water and hexane is K_{p} = 13.9 [27]. To achieve the same final C_{10}E_{5} concentration after partitioning are displayed in Table 1 for all concentration of C_{10}E_{5} initially dissolved in water and the final concentration of C_{10}E_{5} after partitioning (C_{f}) at the different hexane concentrations (C_{i}) used for emulsion preparation.


2.2. Measurement of interfacial properties

For the determination of interfacial properties two tensiometers have been used, one based on the Drop Shape analysis (Profile Analysis Tensiometer, PAT) [28], and the other on the Capillary Pressure measurement (Capillary Pressure Tensiometer, CPT) [29].

The first tensiometer (PAT, SINTERFACE Technologies, Berlin) has been used for measuring the dynamic and equilibrium interfacial tension as well as for the dilatational viscoelasticity at low frequencies of interfacial deformation. The other tensiometer (CPT) has been used for measuring dilatational viscoelasticity at high frequencies of interfacial deformation. The combined use of these two tensiometers allowed the rheological characterisation of interfaces over a broad frequency range from 0.005 Hz to 20 Hz.

In both apparatuses, rheological measurements were performed according to the oscillating drop method where a low amplitude sinusoidal oscillation of the drop surface area is applied at a given frequency and the response of interfacial tension is determined by means of a suitable data reduction procedure specific for each tensiometer.

2.3. Emulsification test section

Emulsification was conducted inside a cylindrical Plexiglas vessel having 19.5 cm height and 7 cm internal diameter. The vessel was furnished with sixteen stainless steel ring electrodes flush mounted to the inner wall, 1.5 cm apart from each other. Electrodes combined in pairs provide several non-intrusive conductance probes. Electrical signals from multiple probes combined with a multiplexer and a suitable inverse reconstruction algorithm for data reduction constitute a tomographic imaging system [30]. As this was an attempt to employ tomographic measurements to emulsification, tests were initially conducted with signals taken from all possible views of the sensing electrodes. Due to the intense mixing during emulsification virtually no angular or radial variations of volume fractions were found but only variations in the axial direction. To ease the computational effort and increase data acquisition rate, only three probes at different axial locations along the vessel were eventually employed, designated for convenience as high, middle and low (Fig. 1). These probes consisted of adjacent electrodes which offered certain advantages: the 1.5 cm separation distance between rings was large enough to average droplet size undulations yet small enough to prevent the local character of measurements. All probes were located at the lower half of the emulsion, 1, 4, and 7 cm, respectively, from the bottom of the vessel (distances calculated from the center of probes). The free surface of the emulsion was 16 cm above the bottom of the vessel.

Emulsification was implemented by intense mixing of water and oil using an impeller (Rushton turbine, having a diameter, d = 4.6 cm) placed at the central axis of the vessel. The impeller was placed 1.7 cm above the bottom of the vessel and not at the traditional (for mixing applications) 1/3 of the vessel height. This was done in order to be able to employ high rotation speeds without vortexing and air suction. Hexane was fed gradually into the ves-
At 22 final mixture volume. Experiments were conducted in triplicates (v/v). This period was followed by 10 min at 750 rpm which again amount of hexane to make the most hexane rich mixture: 40/60 was 8 min. This was also the time for introducing the required in the vessel. The total time the impeller was running at 290 rpm

Hexane was fed at the same flow rate in all experi-
sions in order to maintain similar hydrodynamic conditions upon

ments in the region above the impeller blades. The immersed

emulsion. The immersed silicon tube was kept still during mixing

by attaching it to a polymeric rigid rod (diameter 6 mm) of equal

length. High shearing rates and intense mixing which are neces-

sary for producing fine oil droplets characterized the hydrodynamic

conditions in the region above the impeller blades. The immersed

assembly of silicone tube/polymeric rod served as a baffle suppress-
ing vortexing.

2.4. Emulsification procedure and microscopy measurements

Initially, the vessel was filled with the appropriate volume of

aqueous surfactant solution (different for different hexane/water

ratios) so that together with the final added hexane would sum

up to a total volume of 616 ml. Emulsification started by feeding

the oil at a steady flow rate of 0.5 ml/s under continuous agitation

at 290 rpm. Hexane was fed at the same flow rate in all experi-

ments in order to maintain similar hydrodynamic conditions upon

hexane entrance into water. The 290 rpm was the highest possible

speed without creating vortexing in the initial aqueous solution

in the vessel. The total time the impeller was running at 290 rpm

was 8 min. This was also the time for introducing the required

amount of hexane to make the most hexane rich mixture: 40/60

(v/v). This period was followed by 10 min at 750 rpm which again

was the highest possible speed without air suction in the 616 ml

final mixture volume. Experiments were conducted in triplicates

at 22 ± 1 °C. Reproducibility was satisfactory along the whole elec-
trical curves obtained during emulsification (see below) with an

average variance of 0.1 among runs.

After the end of emulsification, a 0.5 ml sample was carefully

withdrawn from the vessel using a 5 mm i.d. tube (wide enough to

prevent droplets jamming) and was added to a 20% (w/v) Tween

80 solution to prevent droplets coalescence. The addition of Tween

80 is not expected to affect single droplets sizes. The sample was

then put under a microscope where several photos were taken until

reaching a population of droplets above 300 to ensure statistical

significance in the determination of droplets size. A custom-made

software [31] was employed to obtain droplet size distributions and

from them calculate the average droplet size and standard
deviation.

2.5. Electrical conductance measurements

Electrical conductance data were taken throughout the emulsifi-
cation process, simultaneously from all three probes. The technique
has been presented in detail elsewhere [17], only a few essential

elements are repeated here. An alternating current (a.c.) carrier

voltage of 0.250 V GMS was applied across each electrode pair at a

frequency of 25 kHz. This frequency allows suppressing undesir-
able electrode polarization and capacitive impedance. The response

of each probe was fed to an electronic analyzer-demodulator. The

analog direct current (d.c.) output signal of the analyzer from the
different probes was acquired at a rate of 1 Hz with the aid of a
data acquisition card (ADAM 4018, Advantec) interfaced to a per-
sonal computer. The acquired d.c. signals were then converted to

apparent conductance and conductivity of the dispersion whereas

Kapp and σaq denote the apparent conductance and conductivity of

the aqueous phase. The normalization of conductance measurements with respect to the conductance of the aqueous phase eliminates errors owing to variations of liquid conductivity. The normalized conduc-
tivity measurements were then transformed into water fraction (f_w)

measurements using the equation of Bruggeman which is quite

popular for emulsion applications, e.g. [21]:

\[
\sigma_{\text{dis}} = \sigma_{\text{aq}} (f_w)^{3/2}
\]

Because of the simplifying assumptions made to develop

Bruggeman’s model it is supposed to be accurate only for dilute
dispersions (i.e., less than 15%, v/v, dispersed phase). However,
measurements on emulsions have shown that it is accurate even

for concentrated emulsions in which the volume fraction of the

dispersed phases is 0.5 or greater [32].

2.6. Breakage model for droplet diameter prediction

Hinze [33] reported that breakage of an isolated droplet is dic-
tated mainly by the ratio of external and internal stresses acting on

such a droplet. There are two main external forces: (1) turbulent

pressure fluctuations and (2) viscous stress due to velocity gradi-

ents in the surrounding continuous phase. The restoring forces are

mainly due to (1) interfacial tension and (2) internal viscous stress. For the present case of intense turbulent mixing and oil viscosity of

the same order with that of water the actual balance is between

pressure fluctuations and interfacial tension. Hinze ignored the

restoring effect of interfacial elasticity and viscosity which are

properties related to the dynamic interfacial tension (see subse-
quent section). According to Hinze a drop would brake if the ratio

of the deforming internal stress across its diameter due to pres-
sure fluctuations and the restoring stress due to interfacial tension

exceeds a critical value. Based on this notion, it was proposed that

the diameter of the maximum stable drop (d_{max}: diameter above

which breakage occurs) in the emulsion in a stirred tank can be

given as:

\[
d_{\text{max}} = C D_{\text{amp}} \text{We}^{-0.6}
\]
where $D_{\text{imp}}$ is the impeller diameter and $C$ is a constant between 0.126 and 0.15 and $We$ is the Weber number which is given as:

$$We = \frac{\rho N^2 D_{\text{imp}}^3}{\gamma}$$

where $\rho$ is the density of the continuous phase, $N$ is the stirrer speed and $\gamma$ is the oil–water interfacial tension.

It must be noted that such a simple model for isolated droplets cannot account for the effect of different oil/water volume fractions in producing droplets of different size. Usually, the effect of oil volume fraction on maximum droplet size is accounted for through a turbulent intensity damping factor [34].

2.7. Computational fluid dynamics (CFD) flow field

The frequency of collisions between droplets and the frequency of their breakage depend on the turbulence intensity inside the vessel which in this way affects the droplets size. In applications, droplets size is customary correlated with the average energy dissipation rate $\epsilon$ in the vessel. However, the actual spatial distribution of $\epsilon$ in the vessel is so non-uniform that makes the above type of correlations (like Eq. (3) derived for an average $\epsilon$ in the vessel) meaningless. In order to get a better idea of what happens in the emulsification vessel, CFD simulations of the flow field were performed. The emulsification vessel was designed in full detail in 3 dimensions. Although the vessel is cylindrical and it could be simulated invoking the 60° symmetry (only the one sixth, because of the number of the impeller blades), the presence of the immersed oil feed tube destroys the symmetry. The apparatus’s active volume was designed in a CAD program (ANSYS© Workbench 10.0) and it was cut into pieces in order to form a 3 dimensional grid. The grid consisted of hexahedral and tetrahedral elements, but near the walls consisted of multiple layers of flat parallelepipeds (a well known technique for simulating wall effects). In total, about 400,000 grid elements were used which resulted in about 125,000 computational nodes. The surface grid and its detail in the region of oil entrance are shown in Fig. 2a and b, respectively. The initial and boundary conditions were set and the commercial CFD code ANSYS© CFX 10.0 was used to run the simulations. The applied computational technique was the single phase model with Multiple Frames of Reference (MFR) as regards the moving parts of the impeller and a standard $k$–$\epsilon$ model for turbulence. The properties (density and viscosity) of the simulated single phase were computed employing the properties of the components of the mixture. The single phase assumption precludes the prediction of oil fraction non-uniformities but gives an idea of the local hydrodynamic conditions in the stirred vessel.

3. Results and discussion

3.1. Computational fluid dynamics flow field

It is very useful to start by presenting results from CFD simulations. Several simulations were performed for the three oil volume fractions used in the experiments and impeller speeds between 290 and 750 rpm. The only effect of varying the oil volume fraction was a change of physical properties (viscosity and density) of the liquid leading to qualitatively similar results. The same was true for the case of changing the impeller speed but the quantitative difference between results was more noticeable. The velocity contour at a horizontal plane 5 cm above the impeller is shown in Fig. 3a for 750 rpm. The velocity contour for the same rotation speed at a vertical plane cutting the oil feed tube is shown in Fig. 3b confirming the radial flow pattern created by this type of turbine. Inspection of all simulations shows that the velocity magnitude scales with the rotation speed.

The distribution of turbulent energy dissipation rate $\epsilon$ in the vessel for 290 and 750 rpm is shown in Fig. 4. The strong non-uniformity of $\epsilon$ is apparent, with high values around the impeller and around the oil-feed tube and very small values below the impeller. The breakage occurs almost exclusively at the high $\epsilon$ region close to the impeller. This confirms that the oil entrance is located at the right point ensuring an effective breakage of the introduced oil droplets. The value of $\epsilon$ is about ten times larger for 750 rpm than for 290 rpm. According to theories of breakage $d_{\text{ave}} \propto \epsilon^{-0.4}$ [33,35] and employing Stokes low (approximately valid for small droplets) the buoyancy velocity of oil droplets is proportional to $(d_{\text{ave}})^2$ and correspondingly to $\epsilon^{-0.8}$. From $k$–$\epsilon$ theories the turbulent dispersivity is proportional to $(\text{turbulent kinetic energy})^2/\epsilon$ [36,37]. The oil mass fraction non-uniformity depends on the ratio of buoyancy velocity to turbulent dispersivity. Combining the above, this ratio is proportional to $\epsilon^{0.2}/(\text{turbulent kinetic energy})^2$. Using data from the performed simulations it is estimated that this ratio is five times smaller for 750 rpm than for 290 rpm indicating that any observable non-uniformity at 290 rpm disappears at 750 rpm.

3.2. Interfacial properties versus partitioning of surfactant

The interfacial properties of the surfactant adsorbed layer at the water/oil interface are expected to be associated with the
characteristics of the corresponding emulsion. It is well known that low values of interfacial tension favour the emulsification of liquid–liquid systems, because, in this case, the energies required to break interfaces and consequently to form small, stable droplets are lower. Nevertheless, this process depends strongly on the dynamic aspect of interfacial tension. In fact, a faster surfactant adsorption into continuously formed fresh interfaces better contrasts the increase of interfacial tension due to the imposed interface expansion. On the other hand, the formation of an adsorbed layer on small droplets hinders drop coalescence when they are colliding [38, 39].

Concerning the liquid–liquid system investigated herein, Fig. 5 presents the equilibrium interfacial tension at the water/hexane interface as a function of C₁₀E₅ concentration. Old published data [40] are obtained in the absence of salt whereas present measurements (obtained by PAT and CPT) were conducted using salt concentrations equal to those used in the emulsification experiments. As can be seen, the presence of salt at the applied concentrations virtually does not affect the values of interfacial tension at equilibrium which are in agreement with those reported in ref. [40] Furthermore, the equilibrium interfacial tension tends, as expected, to decrease as surfactant concentration increases, attaining in all cases considerably low values which promotes emulsification. Although these values are important, because they characterize the interfaces at adsorption and partition equilibrium and so are related to the emulsification ability of the system, it is the dynamic interfacial tension at a timescale relevant to the rapid
phenomena occurring during emulsification which plays a major role in droplet breakage and coalescence.

The dynamic interfacial tension data reported in Fig. 6 refer to two different C10E5 concentrations (10\(^{-4}\) M and 5 \times 10\(^{-4}\) M) in the aqueous phase measured for two different cases of C10E5 distributions among the two bulk phases. In one case, a fresh interface is formed between two pre-equilibrated phases which means that surfactant has been dissolved in both water and hexane and partition between phases was given enough time to equilibrate. In the other case, surfactant has been initially dissolved only in water while hexane was completely surfactant-free. In both cases, for experimental convenience measurements were made with relatively large hexane droplets (d \sim 2.7 mm) forming in water. For the case of pre-equilibrated phases, measurements show an adsorption characteristic time shorter than 1 s. For the case of initially surfactant-free hexane, the interfacial tension drops fast in the first second but then approaches gradually the same equilibrium value.

The observed slow equilibration time in the latter case is essentially dictated by the sluggish diffusion process of surfactant from the interface to the hexane drop interior and refers to a static state (no agitation) of the two liquid phases. However, under intense stirring conditions as well as for higher surfactant concentration in water and for smaller dimensions of hexane droplets this time is expected much shorter [41]. Indeed, the present experiments employ excessively higher initial concentration of surfactant in water and smaller hexane droplets (see Tables 2 and 3) so it can be assumed that interfacial tension can reach the equilibrium value at a time scale closer to that of the case of pre-equilibrated phases, i.e., in the order of a second. This is confirmed by the observed effective emulsification (see below).

Apart from dynamic interfacial tension, the emulsification process is expected to be affected by rheological interfacial properties

In this study, as droplets expand upon exiting from the capillary, they break into smaller droplets (due to the shearing action of the impeller), collide to other droplets or slide against each other (due to the complex flow field inside the emulsification vessel). Traditionally, emulsification is dictated by the first two phenomena: droplet breakage and coalescence. For the present high surfactant concentrations, which in most cases are well above the CMC, and the speculated fast adsorption dynamics, we believe that breakage is more important than coalescence since the latter can be effectively prevented by stable adsorption layers.

Both breakage and coalescence are related to the stability of adsorption layers which, as already found in other experimental works [43], is not only governed by forces operating normal to the interface, but also by rheological characteristics of the adsorbed layer [44, 45], which determine the capability of dampening external disturbances. These characteristics can be quantitatively accounted for by surface dilational viscoelasticity, \( E \), which describes the response of an interface to expansion and contraction perturbations. This is a complex quantity, \( E = E_R + iE_I \), whose real part is the dilational elasticity, while the imaginary part is related to the dilational viscosity \( \eta \) of the interfacial layer, \( \eta = 2\pi \eta \).

As can be seen in Fig. 7 the imaginary part of the dilational viscoelasticity (\( E_I \)) is very small for all measured deformation frequencies (\( f \)) in the range 0.005 Hz to 20 Hz by coupling measurements from the drop shape and capillary pressure tensiometers. The high frequency limitation is due to intrinsic experimental difficulties typical for liquid–liquid systems.

As can be seen in Table 3 the imaginary part of the dilational viscoelasticity (\( E_I \)) is very small for all measured deformation frequencies (\( f \)).
quencies and can be considered having a negligible contribution to the process. This holds also for all other examined concentrations (results not shown). The values of interfacial dilatational elasticity ($E_E$) are typical for this type of surfactant at the water/hexane interface according to previous works [40,46] and much smaller than those obtained for larger molecules such as food proteins [47].

Fig. 8 presents the effect of C$_{10}$E$_5$ concentration on the modulus of the dilatational viscoelasticity ($|E|$) as a function of area perturbation frequency. As can be observed $|E|$ is weekly dependent on C$_{10}$E$_5$ concentration for the examined deformation frequencies and surfactant concentrations. This is in agreement with previous results with the same system but in the absence of salt and at lower C$_{10}$E$_5$ concentration and with results for water/hexane interfaces but with different polyoxyethyleneated glycols as surfactants and in the absence of salt [40,46]. According to Fig. 8 the modulus of interfacial dilatational viscoelasticity ($|E|$) is expected to increase rapidly at higher frequencies and tend to a maximum (high frequency) limit. Even if our measurements do not allow us to determine this maximum limit and the frequency at which it is reached, this behavior can be approximately predicted by extrapolation of best fit curves calculated using theoretical models appropriate for these surfactant systems [48]. Thus, at least qualitatively, we can assume that emulsion stability is improved increasing the high frequency elasticity occurring increasing the C$_{10}$E$_5$ concentrations.

More critical is finding a correlation between these data and the behavior of droplets during emulsification. Apparently, it is difficult to assess whether the examined dilatational frequencies correspond to strain rates in the same range of values with those encountered during the employed intense stirring. We believe that the frequency range examined in our interfacial rheology measurements represents the lower region of strain rates encountered during emulsification. In addition, the concentration of surfactant in the aqueous and oily phase change continuously as a function of time due to ongoing partitioning. However, even if not fully representative of the whole emulsification process, these rheological data provide a characterization of the dynamics of the investigated liquid–liquid interface which is, generally, related to droplet breakage/coalescence processes [49].

3.3. Predicted versus measured (optically) droplet diameters

Based on the dispersion model of Hinze (1955), the predicted maximum stable droplet diameter for the employed experimental conditions is presented in Table 2. As already mentioned, the dispersion model does not include any dependence on the oil/water volume fraction.

Contrary to the above, the optically determined average droplet diameter at the end of the emulsification period practically coincide among the different surfactant concentrations (fluctuations within experimental error) and shows just a small decrease as a function hexane concentration which however is not statistically significant (standard deviation is large) (Table 3).

What is perhaps more important is that the measured values are much lower than those predicted by the dispersion model at 750 rpm. This is due to the fact that Eq. (3) was derived using the assumption that the turbulent dissipation rate is uniformly distributed throughout the vessel. CFD results showed that the distribution of $\varepsilon$ is actually highly non-uniform with a primary peak in the impeller region. Combining this with the fact that breakage rate is a highly non-linear function of $\varepsilon$, yields that breakage occurs only in the impeller region. This implies that the $\varepsilon$ value at the impeller region must be used for the analysis of Hinze. The present CFD calculations showed that $\varepsilon$ in impeller region is 6–7 times larger than the average $\varepsilon$ values. This combined with the scaling $d_{\text{max}} \propto \varepsilon^{-0.4}$ leads to max predictions 2–2.2 times smaller than those in Table 2. The new modified predictions taking into account $\varepsilon$ non-uniformity can be considered compatible with the optical measurement having into mind that the former refers to maximum sizes whereas the latter to average sizes.

3.4. Monitoring of emulsification using ECT

In the plots which follow although the periods that the impeller was running at low and high speed were the same in all experiments, the time to complete hexane addition was different among experiments due to the different hexane-to-water volume ratios. Symbol ‘E’ in the figures denotes the end of hexane addition.

Fig. 9 presents measurements of water fraction obtained by the three probes during the emulsification of a 40/60 (v/v) (final proportion) hexane–in–water emulsion at different C$_{10}$E$_5$ concentrations. It is reminded that measurements by all probes are from the lower half of the final emulsion volume. In Fig. 9a, where the lowest C$_{10}$E$_5$ concentration is used, at low impeller speed (290 rpm) only a small amount of hexane (~2% of the total volume) gets dispersed in the water phase. The rest separates and floats at the top of the emulsion. This agrees with macroscopic visual observations. Under these conditions emulsification is ineffective because initially large droplets form (due to both limited surfactant concentration and limited energy provided by the impeller for droplet breakage) which cannot be maintained in suspension by the low turbulent dispersivity.

Increasing the impeller speed to 750 rpm is enough to change entirely the picture: all the oil gets instantly dispersed in the water. This is the result of increased energy provided by the impeller for droplet breakage combined with the increased convective velocities and turbulent dispersivity.

Interestingly, for both 290 and 750 rpm the measured part (lower half) of the emulsion is homogeneous (comparable signals from all three probes). For 290 rpm this is because of poor oil dispersion whereas for 750 rpm it is the result of efficient mixing (in line with CFD suggestions and optically measured droplet diameter).

Increasing the C$_{10}$E$_5$ concentration to $2 \times 10^{-4}$ M (Fig. 9b) changes the situation. Considerable amount of hexane gets dispersed in the aqueous phase even at low impeller speeds. This indicates that droplets are smaller than in the previous case. This is
Subparts (a) through (d) present emulsions with different emulsifier concentrations. The hexane-in-water emulsion at a 40/60 (v/v) (final proportion) oil/water volume ratio. The transition from an impeller velocity of 290 rpm to 750 rpm.

In (a) \( C = 1 \times 10^{-4} \) M, (b) \( C = 2 \times 10^{-4} \) M, (c) \( C = 5 \times 10^{-4} \) M and (d) \( C = 1 \times 10^{-3} \) M where \( C \) is the concentration of surfactant after partitioning between the two phases. E in the figures denotes the end of hexane addition. The dotted line denotes the transition from an impeller velocity of 290 rpm to 750 rpm.

Fig. 9. Water fraction \( f_w \) as a function of time \( t \) during emulsification of a hexane–in-water emulsion at a 40/60 (v/v) (final proportion) oil/water volume ratio. Subparts (a) through (d) present emulsions with different emulsifier concentrations. It is interesting to note that although hexane is added at a constant rate throughout the whole period of low impeller speed, the decrease in water fraction is not constant throughout this period. In particular, during the first \( \sim 300 \) s the water fraction decreases approximately linearly as hexane is gradually added to the vessel. However, the decrease in water fraction does not correspond to the added amount of hexane since extrapolating the linear part of these curves till the end of the low speed period does not lead to 0.6 water fraction. In other words, during the first \( \sim 300 \) s only part of the hexane gets dispersed in the water and significant phase separation occurs. After this point, the water fraction changes at a gradually decreasing rate and ultimately reaches a roughly constant value (plateau) around 0.77 at \( \sim 400 \) s. Thus, it seems that after \( \sim 300 \) s the freshly added hexane fails more and more to disperse in the water and accumulates at the upper half of the emulsion. A possible explanation for this could be the progressive depletion of water solution from emulsifier as it steadily dissolves into hexane which would result in larger hexane droplets at later times. A role by coalescence at these later times is also more likely since large droplets are also more prone to coalescence due to less interfacial coverage by surfactant. An increase of impeller speed to 750 rpm, suffices to disperse the separated amount of hexane evenly across all volume as in Fig. 9a. Again, the coincidence of the three signals manifests the homogeneity of the emulsion.

Fig. 9c is qualitatively similar to Fig. 9b. Only now that the initial decrease in water fraction corresponds exactly to the amount of the added hexane—extrapolating the linear part of these curves leads to 0.6 water fraction. After this point, the water fraction gradually levels-off towards a plateau value around 0.7 at \( \sim 400 \) s. The progressive depletion of water from emulsifier resulting in larger hexane droplets at later times as well as the increased role of coalescence at these later times are again invoked as mechanisms dictating the observed phase distribution. Increasing the impeller speed to 750 rpm disperses the hexane evenly across all volume as in Fig. 9a and b.

Increasing further the \( C_{10}E_5 \) concentration to \( 1 \times 10^{-3} \) M leads to efficient dispersion of all added hexane already at the lower speed period (Fig. 9d). The large increase in initial surfactant concentration and its effect on interfacial tension and interfacial elasticity result in smaller and harder to coalesce droplets. Apparently, such small droplets can be evenly suspended in the aqueous phase even at the low impeller speed as shown by the linear drop of the water fraction \( f_w \) from 1 to almost 0.6. Increasing the impeller speed to 750 rpm has only a marginal effect. The efficient dispersion of droplets is also supported by the fact that the three signals coincide all along the emulsification period.

Fig. 10 displays the evolution of water fraction during emulsification as measured by the three probes for a 20/80 (v/v) (final proportion) hexane/water mixture. Each plot refers to a different final (after partitioning) \( C_{10}E_5 \) concentration. At low impeller speed, the higher surfactant concentration yields the higher dispersed amount of hexane in water. Like in Fig. 9 this is due to smaller droplets as surfactant concentration increases. However, the slopes of the curves before E are smaller than in Fig. 9. This demonstrates the effect of the higher initial surfactant concentration in the 40/60 (v/v) hexane/water mixtures which lead to smaller droplets than in the 20/80 (v/v) hexane/water mixtures.

An interesting inversion of the signals’ initial reducing trend was observed right after the completion of hexane addition (point E) designating a partial separation of the two phases. Although it was observed only after point E, partial phases separation should have been present even during hexane addition but the increasing hexane volume in the mixture has masked it in the electric signals.
Fig. 10. Water fraction \( f_w \) as a function of time \( t \) during emulsification of a hexane-in-water emulsion at a 20/80 (v/v) (final proportion) oil/water volume ratio. Subparts (a) through (d) present emulsions with different emulsifier concentrations. In (a) \( C_f = 1 \times 10^{-4} \text{ M} \), (b) \( C_f = 2 \times 10^{-4} \text{ M} \), (c) \( C_f = 5 \times 10^{-4} \text{ M} \) and (d) \( C_f = 1 \times 10^{-3} \text{ M} \) where \( C_f \) is the concentration of surfactant after partitioning between the two phases. \( E \) in the figures denotes the end of hexane addition. The dotted line denotes the transition from an impeller velocity of 290 rpm to 750 rpm.

This was also macroscopically observed: some hexane separated and floated at the top of the emulsion already from the beginning of hexane addition into water.

After the end of hexane addition, running the impeller for more than 200 s at low speed did not result in dispersing more hexane in the emulsion. This was because the low rotation speed could not agitate effectively and re-suspend the hexane that has gathered at the top of the emulsion. This was also confirmed by macroscopic observations.

It is interesting that at \( 5 \times 10^{-4} \text{ M C}_{10} \text{E}_{5} \) concentration (Fig. 10c) the degree of inversion and partial hexane separation were higher than at the other concentrations. This can be attributed to the particular size of droplets and degree of coalescence at this specific surfactant concentration. Droplets are initially small enough and so are effectively agitated at 290 rpm but as surfactant gets progressively depleted (because of dissolution to hexane) droplets become larger and easier to float (with or without coalescence). There is a short period (~40 s) of roughly constant water fraction after point \( E \) during which coalescence may occur leading to larger droplets that subsequently float to the free surface. As the concentration of the emulsifier increases further (Fig. 10d) droplets are much smaller and better protected against coalescence despite the depletion of surfactant so after point \( E \) droplets that are already suspended remain suspended.

Again, as it holds in the case of 40/60 hexane/water experiments (Fig. 9) increasing the speed to 750 rpm results in dispersing all hexane in the emulsion (Fig. 10a–d). In addition, when the impeller is running at 750 rpm signals from different probes are very much alike indicating a homogeneous situation. This is not always true for the low impeller speed.

Fig. 11 presents the evolution of water fraction during the emulsification of a 5/95 (v/v) (final proportion) oil-in-water emulsion at different surfactant concentrations. The plots show that at the end of the low impeller speed period the hexane dispersed in the emulsion varies between 1% (Fig. 11a) and 3% (Fig. 11d). The rest of the hexane amount, i.e., up to 5%, separates and floats at the top of the emulsion during the low impeller speed period. The slopes of curves before point \( E \) are much smaller than in Figs. 9 and 10 indicating the presence of much larger droplets as a result of the lower initial surfactant concentration in the 5/95 (v/v) mixtures. However, a new feature appears in Fig. 11. After the completion of hexane addition (point \( E \)), there is a short period of phase separation (inversion of signal trend) probably due to coalescence but soon the water fraction starts to decay again. This implies that the low speed agitation can break some of the very large droplets of hexane and disperse them into water. At first glance, it is strange that coalescence may be more pronounced at the 5/95 (v/v) mixtures where the oil volume fraction is lower than the other employed mixtures since it is well known that the rate of collisions is proportional to the volume fraction of the dispersed phase. This may be explained by the complexity of the particular physical system. The higher concentration of surfactant dissolved in the water phase for higher oil volume fractions (in order to fulfill the required equilibrium concentration) may lead to temporal accumulation of surfactant on the droplet surface and correspondingly to a reduction of coalescence efficiency which counterbalances the increase of collision rate.

Increasing the impeller speed to 750 rpm results in dispersing all floating hexane into the emulsion, as also occurred with the 40/60 (v/v) and 20/80 (v/v) mixtures. Interestingly, this does not happen instantly but gradually. One might intuitively expect the re-suspension of floating hexane to be faster as surfactant concentration increases since this corresponds to lower interfacial tension and so easier droplet breakage. However, electrical signals showed the opposite trend. Interfacial elasticity increases slightly with surfactant concentration making droplets a bit harder to break but...
Fig. 11. Water fraction ($f_w$) as a function of time ($t$) during emulsification of a hexane in water emulsion at a 5/95 (v/v) final proportion oil/water volume ratio. Subparts (a) through (d) present emulsions with different emulsifier concentrations. In (a) $C_f = 1 \times 10^{-4}$ M, (b) $C_f = 2 \times 10^{-4}$ M, (c) $C_f = 5 \times 10^{-4}$ M and (d) $C_f = 1 \times 10^{-3}$ M where $C_f$ is the concentration of surfactant after partitioning between the two phases. E denotes the end of hexane addition. The dotted line denotes the transition from a impeller velocity of 290 rpm to 750 rpm.

this is not quantitatively enough to explain the observed trend. The possibility cannot be excluded that breakage occurs above the measured range of shear strain and in such high rates interfacial rheology differences may be more pronounced. More work is needed to elucidate this issue.

4. Conclusions

The developed multi-probe electrical conductivity technique was capable of registering non-intrusively the variation of water fraction during emulsification of an hexane-in-water mixture with C$_{10}$E$_5$ as emulsifier. The technique provided accurate measurements of local water fractions at different heights inside the mixing vessel and so allowed assessing the homogeneity of the mixture during emulsification. Electrical signals obtained at high impeller speed indicated a homogeneous dispersion of the two phases under all examined conditions. This is in line with the CFD computations. However, at low impeller speed the emulsion was not always homogeneous. In general, the higher the surfactant concentration and the hexane-to-water ratio the easier it was to disperse hexane in water at low impeller speeds. It is believed that this was a combined effect of interfacial properties (strongly affected by partitioning of C$_{10}$E$_5$ between water and hexane) and turbulent dispersivity. The examined physical system presents very complicated kinetics of emulsification leading to peculiar spatial phase distributions and droplet sizes which vary with emulsification conditions. This makes it a very challenging test field where accurate, fast, non-intrusive, on-line measurements are required. We believe that our technique is a valuable tool as it combines all the above.

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