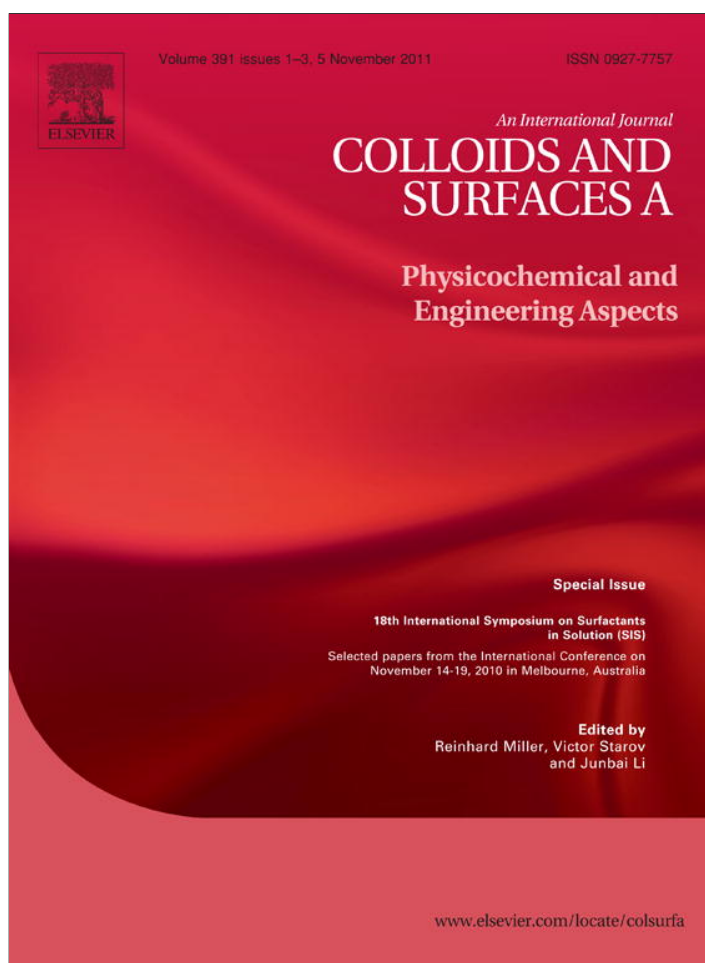


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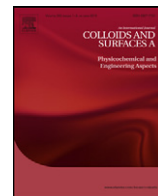
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Global versus local dynamics during destabilization of eco-friendly cosmetic emulsions

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ABSTRACT

Eco-friendly cosmetic emulsions are usually less stable than conventional ones as they involve milder chemicals or less intense (energy consuming) production processes. In order to improve their stability it is important to understand local phenomena occurring within the emulsions during phases separation. Most of the techniques for monitoring local emulsion stability provide information of droplet sizes either from direct visual observations at the boundaries of the emulsion (container wall) or from measurements on withdrawn samples. Therefore, non-intrusive, continuous techniques, capable of sensing the destabilization of emulsion over the entire cross-section of a container, are of particular significance. In this context, measurements of a dual-probe local electrical conductance technique are compared with global volumetric measurements. Eco-friendly cosmetic oil-in-water emulsions are produced with different olive oil fractions, emulsifier (GMS) concentrations and agitation schemes. Local information from electrical signals indicated flocculation phenomena which were completely missed by global volumetric measurements.

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1. Introduction

An emulsion may become unstable due to a number of different physical and chemical processes. Creaming, sedimentation, flocculation, coalescence, phase inversion and Ostwald ripening are examples of physical instability [1,2] whereas oxidation and hydrolysis are common examples of chemical instability [3]. Creaming and sedimentation are both forms of gravitational separation. Flocculation and coalescence are both types of droplet aggregation [4,5].

To form an emulsion that is stable for a reasonable period of time one should produce and disperse small droplets that should not merge. This is achieved by adding substances known as emulsifiers. Emulsifiers are surface-active molecules which absorb at the surface of freshly formed droplets during emulsification and apart from reducing the liquid/liquid interfacial tension (allowing smaller droplets to be produced) they form a protective elastic membrane which prevents droplets coalescence. Of interest to this study are non-ionic surfactants which enhance emulsion stability by generating a number of short-range repulsive forces which hinder the droplets from getting too close together, such as steric, hydration, and thermal fluctuation interactions [6–8].

Emulsions stability is largely dictated by their production process. This may involve a single step or a number of consecutive steps, depending on the nature of the starting materials and the employed methods. The process of converting two immiscible liquids into an emulsion is often termed homogenization [9]. The size of droplets in an emulsion can be reduced by increasing the amount of energy supplied during homogenization as long as there is sufficient emulsifier to cover the surface of the formed droplets [10].

Smaller droplets, as a result of a better emulsifier or a more effective homogenization, lead to a more stable emulsion. This, however, holds only if droplets stay away from each other and do not flocculate (coalescence is less probable in the presence of adequate amount of surfactants). On the contrary, if droplets flocculate then their cluster behaves as a new entity of larger dimension which exhibits more intense creaming or sedimentation than isolated droplets. So sometimes, despite the presence of small droplets, local conditions along the height of the emulsion, e.g. droplet population density, collision of moving droplets, presence of micelles, etc., can enhance flocculation and so deteriorate the stability of the emulsion.

Several techniques have been employed in the past, e.g. optical microscopy, laser scanning confocal microscopy, light scattering, laser diffraction, to investigate the progress of emulsion destabilization. These techniques determine droplets size from either direct visual observations or from measurements performed on withdrawn samples [11–14] and so are limited by the fact that they provide information only from places where there is either visual

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access or a sampling mechanism can be inserted. Additionally, the often required significant dilution of samples before measurement can modify some of the emulsion characteristics (e.g. the major drawback of most microscopic techniques is that the delicate structure of flocs may be disturbed by the procedures used to prepare the samples). Moreover, these methods cannot provide information on local liquid volume fractions and, therefore, on phases separation. In fact, local liquid fractions have been much less exploited than droplet size distributions in assessing emulsion destabilization.

Electrical conductance techniques appear to be a tempting option for measuring non-intrusively the temporal evolution of local liquid volume fractions inside O/W emulsions (opaque or transparent). Such techniques have been used in the past for monitoring other applications such as mixing [15], bubble columns [16], multiphase flows [17,18], solid–liquid filtration [19], and polymerization reactors [20]. 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 [21]. Ring electrodes have been successfully applied to a number of multi phase applications, e.g. [22,23]. Recently, an upgraded version of the technique has been used for monitoring foam drainage [24,25]. It has been reported that in cases of radically 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. Some papers used conductance measurements more as an indicator of global emulsion condition rather than as a tool for determining local volume fractions [26–28]. Recently, in our lab [29–31] we employed ring electrodes placed at different axial locations of a container to continuously register variations of the local phase volume fractions along the height of emulsions in a tomographic fashion. These measurements not only monitored continuously emulsification and destabilization but also offered valuable information on fast local dynamic phenomena [31].

The present work examines the stability of specific eco-friendly cosmetic emulsions. Since antiquity, emulsions have been used in cosmetics. In contrast to pharmaceutical ointments which must penetrate deep into the skin, cosmetic products are meant only for the immediate surface of the skin i.e. the epidermis. However, many commercial cosmetic products contain artificial chemicals that inevitably penetrate the skin. Eco-friendly cosmetics – also known as organic cosmetics – appeared in the early 1900s. The biggest advantage of organic cosmetics is that they are safe for humans and the environment as they do not contain toxic chemicals, they need no animal testing and their results can be as pleasing as those achieved by commercial products. On the other hand, their inevitable disadvantage is that their life time is of the order of a few weeks contrary to synthetic cosmetics which last years.

The structure of the work is as follows. First, the employed materials and the procedures to generate emulsions and then to measure their stability by electrical and volumetric means are described. Next, measurements from both techniques are presented and compared to each other. Finally, a discussion is made to interpret measurements and explain the differences observed between the two techniques.

2. Materials and methods

2.1. Materials

Oil-in-water cosmetic emulsions were prepared using a dilute NaCl aqueous solution, “extra virgin” olive oil and glycerol monos-

Table 1
Olive oil and GMS concentrations with respect to the total mass of the emulsions.

GMS, %w/w	Olive oil, % w/w		
	23	16	6
1	✓	✓	✓
2	✓	✓	✓
4	Very stable	Very stable	Very stable

✓ denotes conditions where emulsion destabilization occurred in reasonable time (less than 5 h).

tearate (GMS) as emulsifier. Aqueous solution was prepared by dissolving NaCl at a concentration of 0.22 g/L into Millipore filtered water. After salt dissolution the electrical conductivity of the aqueous solution was 500 $\mu\text{S}/\text{cm}$, a value common for tap water. The oil phase is extra virgin olive oil (Altis, Elanthy S.A., 2010). This is a natural oil typically used in cosmetics and foods. In addition to being a natural and hypo allergic way to moisturize skin, extra virgin olive oil has the extra advantage of containing strong antioxidants, like vitamins A and E, which help repair and renew skin that has been damaged from overexposure to sun, air pollution and other modern-day environmental hazards [32].

Glycerol monostearate (GMS) (Cognis Chemicals), an esterification product of glycerine and stearic acid, is a white-colored wax-like solid. GMS is an eco-friendly emulsifier widely used in lotions, creams powders, skin cleansing products, make-up bases, sunscreen products, etc. as it is safe for humans and gives skin a soft and smooth appearance [33].

GMS is a non-ionic surfactant with HLB ~ 4 which is soluble in oil and not in water. Using GMS as an emulsifier in oil-in-water emulsions is against Bancroft's rule: “a water soluble surfactant should stabilize oil in water emulsions”. However, there are many important exceptions to this rule [34,35]. The HLB value of olive oil is ~ 8 and according to the HLB concept to achieve optimum stability of an oil-in-water emulsion, an emulsifier with HLB value close or above 8 should be used. However, emulsions can be formed even with lower HLB emulsifiers. So, although GMS does not yield optimum performance, the produced oil-in-water emulsions have appreciable stability depending on emulsification conditions (proportion of oil/water phases, concentration of GMS and intensity of emulsification). The employed oil/water and emulsifier concentrations are displayed in Table 1.

2.2. Emulsification process

Emulsification was implemented by mixing water with olive oil using an impeller (Rushton turbine, $d = 4.6$ cm) rotating at the central axis of a glass vessel with internal diameter of 9.5 cm. The impeller was placed 1.0 cm above the bottom of the vessel and not at the traditional (for mixing applications) 1/3 of the vessel height. Four baffles were placed at 90° intervals around the vessel in order to allow high rotation speeds without vortexing and air suction. Emulsification was performed following two different agitation schemes as shown in Fig. 1. Emulsions were prepared in the above glass vessel as follows. Initially, proper amount of GMS (Table 1) was added to the oil and then the mixture was heated to 70 °C (GMS is solid at ambient temperature). The corresponding amount of aqueous NaCl solution (Table 1) was heated separately to 70 °C. The volume of the aqueous phases was different for different oil-to-water ratios so as to have always a final volume of ~ 250 ml. Emulsification started by adding the hot aqueous phase into the hot oil all at once. At that moment heat supply was turned off and agitation was set at 500 rpm. The impeller was running at 500 rpm, for a total 1.5 min. This period was followed by 40 more minutes of agitation at 300 rpm or 200 rpm (Fig. 1) which was sufficient for the emulsion to cool down to ambient temperature (25 ± 1 °C).

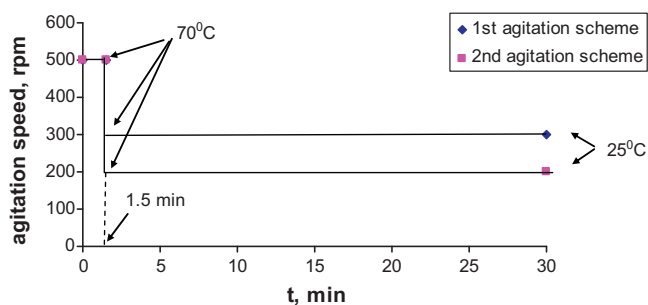


Fig. 1. The two employed agitation schemes for emulsification.

After the end of the emulsification period, the produced emulsion was decanted into a Plexiglas test vessel (Fig. 2) to perform electrical conductance measurements during destabilization. The Plexiglas test vessel had 19.5 cm height and 7 cm internal diameter. The vessel was furnished with 16 stainless steel ring electrodes flush mounted to the inner wall (in order to avoid disturbing the emulsion), placed 1.5 cm apart from each other in the axial direction. Electrodes combined in pairs provide several non-intrusive conductance probes. Only two probes at two different axial positions along the vessel were employed in this work, designated for convenience as *low* and *high* probes (Fig. 2). 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 represent local measurements. The free surface of the emulsion was ~6.5 cm above the bottom of the vessel.

It is reminded here that eco-friendly cosmetic emulsions last only a few weeks contrary to conventional emulsions which last years. This is because they are natural products with short living ingredients and no preservatives. Moreover, to show the difference between global and local measurements it suffices to measure emulsion stability even over a shorter period, e.g., an hour. To achieve this we used lower GMS concentrations and lower agitation speeds than in actual applications where GMS concentration is usually above 4% and agitation speed is above 10,000 rpm or a high pressure homogenizer is used.

2.3. Creaming index from volumetric measurements

Direct optical observations were employed to determine the instantaneous heights of the emulsion and of the aqueous phase

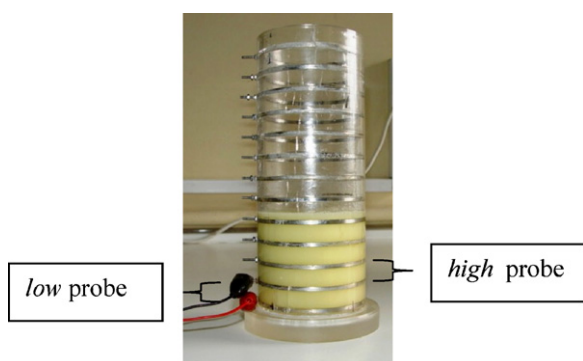


Fig. 2. Emulsion destabilization test vessel furnished with several ring electrodes, flush mounted to the wall. Only the pairs of the first and second electrodes (*low* probe) and the second and third electrodes (*high* probe), counting from the bottom, were employed in this study.

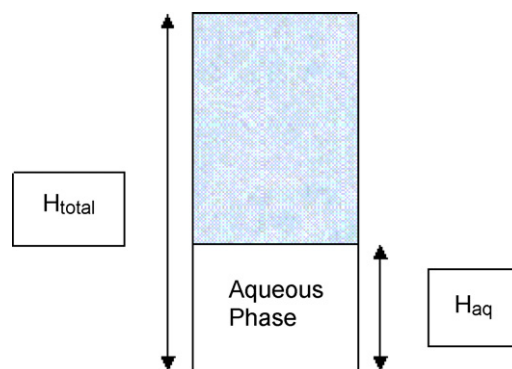


Fig. 3. Schematic representation of creaming index estimation.

inside the Plexiglas vessel and from these values estimate the creaming index according to the formula (Fig. 3):

$$CI = \frac{H_{aq}}{H_{tot}} \times 100 \quad (1)$$

The creaming index represents the instantaneous global (i.e. of the whole liquid volume) volumetric water fraction. It is the most customary measure of emulsion destabilization reflecting phase separation. Nevertheless, there are two disadvantages associated with the creaming index: (1) the interface separating the cream phase (droplet-rich) from the serum phase (droplet-depleted) is never sharp except in the occasion – unlike for real systems – of monodispersed droplet size distributions and (2) it is only possible to obtain information about the location of the interface between the cream phase and serum phase and not about the full vertical concentration profile of droplets.

2.4. Water volumetric fraction from electrical measurements

Electrical conductance data were taken throughout the destabilization process. The technique has been presented in detail elsewhere [24], only a few essential elements are repeated here. An a.c. carrier voltage of $0.250 V_{RMS}$ was applied across each electrode pair at a frequency of 25 kHz. This frequency allows suppressing undesirable electrode polarization and capacitive impedance. The response of each probe was fed to an electronic analyzer-demodulator. The analog 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 PC. The acquired d.c. signals were then converted to apparent conductance K_{app} (the inverse of apparent resistance) of the emulsion using a calibration curve based on precision resistors. Assuming a uniform dispersion of oil in water inside the measuring volume of each probe, the following holds:

$$\left(\frac{K_{dis}^{app}}{K_{aq}^{app}} \right) = \frac{\sigma_{dis}}{\sigma_{aq}} \quad (2)$$

where K_{dis}^{app} and σ_{dis} denote the apparent conductance and conductivity of the dispersion whereas K_{aq}^{app} and σ_{aq} 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 water conductivity. The normalized conductivity measurements were then transformed into water volumetric fractions (f_w) using the equation of Bruggeman (assuming a non-conducting oil phase) which is quite popular for emulsion applications, e.g. [28,29]:

$$\sigma_{dis} = \sigma_{aq}(f_w)^{3/2} \quad (3)$$

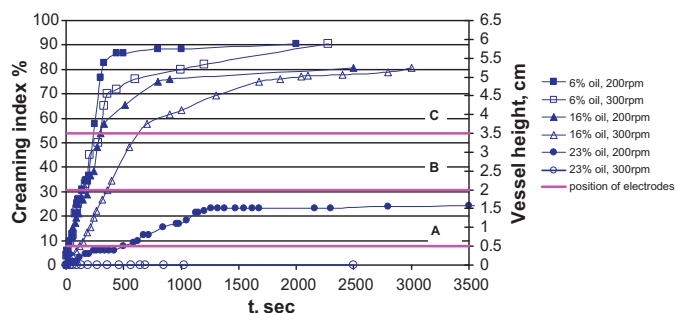


Fig. 4. Creaming index versus time and the corresponding height (0 cm = vessel bottom) of the interface between separating phases for emulsions with 2% GMS and for both agitation schemes. The three horizontal lines designate the height of the three ring electrodes comprising the two measuring probes (AB and BC).

3. Results and discussion

3.1. Creaming index (global dynamics during emulsion destabilization)

In our emulsions the interface separating the cream from the serum phase was not sharp. The cream phase presented a gradual denser opacity from bottom to top whereas the serum phase was always turbid, although less and less with time. Both observations manifest the existence of a broad distribution of droplet sizes in the emulsion. Even so, it was still possible to identify the location of the boundary with the highest contrast between the two phases and this was employed to estimate the creaming index shown in Fig. 4. Results are solely for 2% w/w emulsifier (GMS).

The higher the creaming index, the more destabilized the emulsion. There are two general features in the evolution of creaming index: (1) as the concentration of the oil phase increases, creaming rate decreases and (2) as the energy input (agitation speed) increases, creaming rate decreases. For an emulsion with 23% oil concentration and 300 rpm agitation speed (during emulsification), no sign of creaming was observed for the first 5 h after production. Yet, all other examined cases show some variability with time.

Separation of the two phases was almost complete in less than an hour in the emulsions with 6% and 16% oil, regardless the agitation speed. Interestingly, the final time for phase separation was not so different between the two agitation speeds but intermediate stages of separation were more distinct. The emulsion with 23% oil and 200 rpm agitation speed presented a finite initial creaming rate which, however, after ~1200 s turned to a very slow creaming rate.

Droplets of adequately small size and covered with an elastic surfactant layer lead to very stable emulsions. Stability may also be seen in cases where the viscosity of the continuous phase is high enough to retard the motion of separating droplets, e.g. by dissolving in the continuous phase polysaccharides with low interfacial activity. Another stabilization mechanism encountered in emulsions with a relatively concentrated (>~20% w/w) dispersed phase is the aggregation of droplets into a continuous network of entities (in contact with each other) which prevents droplets from moving freely unless some coalescence or local rearrangement occurs.

In the absence of emulsifier, droplet size decreases as agitation speed increases and as dispersed phase concentration decreases [36]. The stability trend of our emulsions (in the presence of emulsifier) is similar regarding the agitation speed but it is exactly the opposite regarding the concentration of oil. One may argue that in our emulsions the use of higher oil concentration does not deplete the emulsifier since 2% GMS is well above the CMC so droplet sizes may be comparable among different oil concentrations. There are two other parameters, though, that rise drastically with increasing oil concentration: the viscosity of the emulsion and the population

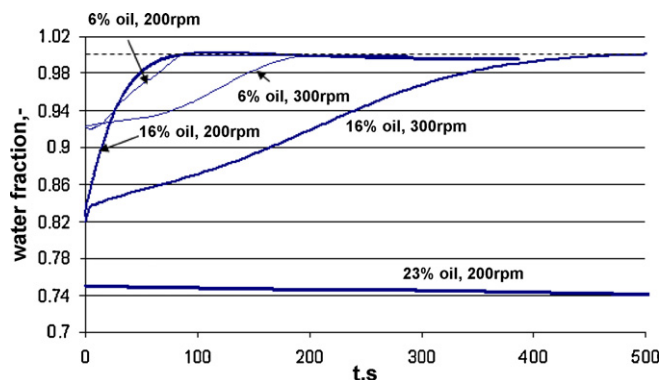


Fig. 5. Water fraction (f_w) as a function of time (t) during destabilization of emulsions at different oil/water concentrations and agitation schemes from the low probe (2% w/w GMS in all runs).

of droplets. Compared to the 6% oil emulsions, the higher viscosity can be blamed for the improved stability of the 16% oil emulsion. However, for the 23% oil emulsions both viscosity and droplets population effects can be significant. This is implied by the abrupt change in the creaming rate of the 23%oil/200 rpm emulsion: the finite initial creaming rate can be ascribed to the increased viscosity but later on (~1200 s) droplets get together and form a network which allows only a very gradual movement of droplets.

3.2. Water fraction by electrical measurements (local dynamics during emulsion destabilization)

Figs. 5 and 6 present electrical measurements of local water volume fraction obtained by the two probes (*low* and *high*) during the destabilization process of oil-in-water emulsions, at different O/W ratios and agitation schemes. Fig. 5 displays data obtained from the *low* probe whereas Fig. 6 data from the *high* probe. The location of the two probes (AB: *low* probe, BC: *high* probe) can be seen in Fig. 4.

Electrical signals from all runs exhibit common features. Time $t=0$ is the moment which corresponds to a well mixed homogeneous emulsion (right after its production) along the test vessel. This means that signals from both probes start from the same initial water volume fraction which for the three examined O/W proportions is 0.92, 0.82, and 0.75, respectively (2% GMS is taken into account). At long times, most electrical curves tend to unity which corresponds to presence of water alone. This is because the two probes are located at the lower half of the emulsion volume so at the end of phase separation electrodes are covered only by water. On the contrary, the curve for 23% oil and 200 rpm is roughly constant in the displayed time frame (500 s) because destabilization is

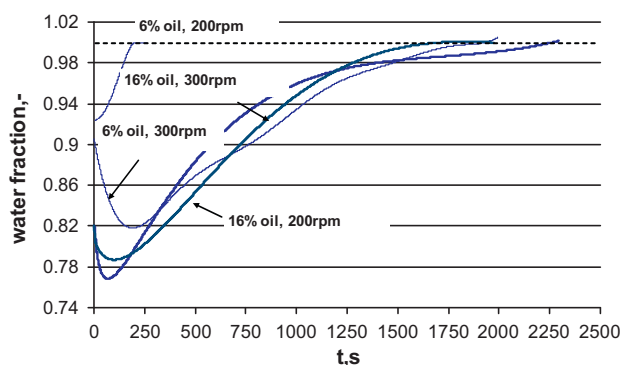


Fig. 6. Water fraction (f_w) as a function of time (t) during destabilization of emulsions at different oil/water concentrations and agitation schemes from the high probe (2% w/w GMS in all runs).

extremely slow, whereas the curve for 23% oil and 300 rpm is completely omitted, because the emulsion is so stable that no variation of the electrical signal is measured even in 5 h.

In all curves of Fig. 5, a fast rise is observed at the beginning which progressively turns into a slower rise at longer times. The initial fast rise corresponds to large oil droplets that separate rapidly from the aqueous phase whereas the subsequent slow rise corresponds to small droplets that take longer to destabilize. The existence of two main slopes in the shape of the water volume fraction curves implies an approximately bi-disperse size distribution of droplets [30].

The electrical curves from the *high* probe in Fig. 6 take more time to reach unity than those from the *low* probe. With the exception of the emulsion with 6% oil and 200 rpm, this is partly attributed to the short inception period at the beginning of destabilization during which water fraction drops. In addition, the initial ascending slopes of the *low* probe are steeper than the corresponding ascending slopes of the *high* probe (Fig. 6). There are two possible explanations for the above. First, for the *low* probe oil droplets departing from the bottom of the container are not replaced by other droplets, whereas, on the contrary, for the *high* probe there are droplets coming from below. Second, as droplets rise to higher locations in the vessel, their concentration increases and this hampers their movement. Such a jamming of droplets might lead to a temporary increase of the local oil fraction. Apparently, the possibility cannot be excluded that complex transient hydrodynamic effects (unable to detect by the techniques employed herein) might also be responsible for the observed behavior.

For the *low* probe the enhanced emulsion stability when increasing the agitation speed and the oil concentration is in line with global observations based on the creaming index (Fig. 4). Smaller droplets and higher viscosity are once more suspected to improve emulsion stability. However, the agreement between global and local dynamics disappears when examining the electrical curves from the *high* probe. In the latter case, three of the four electrical curves are alike despite their different oil concentration and agitation speed. One might think that, just by twist of fate, the effect of the increased viscosity of the 16%/200 rpm run counterbalances the effect of the smaller droplet sizes of the 6%/300 rpm run. But then, the 16%/300 rpm run should have been the most stable of all, combining high viscosity and small droplets. Apparently this is not the case. In the latter run, the initial inception period is shorter and the initial ascending slope is steeper than in the other two runs. Both observations imply that larger droplets are present that move faster than in the other two runs. However, the last stages of destabilization of the 16%/300 rpm are much slower than those of the other two runs in line again with global observations in Fig. 4. This now implies that smaller droplets are present at the end of destabilization of the 16%/300 rpm run.

What appears at first glance paradoxical and inconsistent may have an interesting, yet simple, explanation: flocculation of droplets. Non-ionic emulsifiers, like GMS, can enhance flocculation under certain conditions, e.g. [37,38], which are beyond our scope to repeat here. As explained in the introduction, if small droplets flocculate the flocs behave as new large entities of lower density than the continuous phase and so exhibit a rapid buoyant movement. However, not all droplets flocculate and so the remaining individual droplets govern the last stages of emulsion destabilization. These peculiarities are due to structural local phenomena emerging from the particular conditions prevailing in the emulsion (oil and emulsifier concentration, initial droplet sizes, droplet population, etc.). Such information cannot be captured by global measurements like creaming index.

The employed GMS concentration warrants that there is enough amount of surfactant at liquid/liquid interfaces so in the time frame of measurements coalescence of neighboring droplets is quite

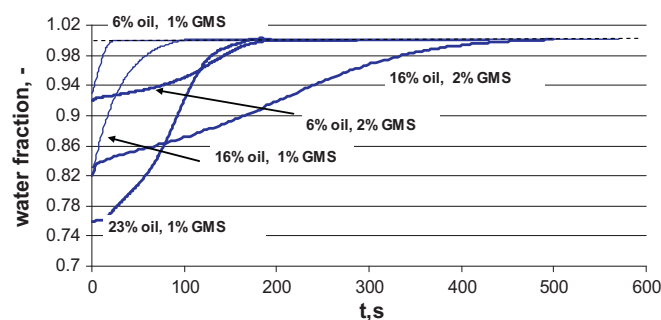


Fig. 7. Water fraction (f_w) as a function of time (t) during destabilization of emulsions produced at 300 rpm with different concentrations of oil (6% and 16% w/w) and emulsifier (1% and 2% w/w). Data obtained from the *low* probe.

improbable and flocculation is more likely to occur. The employed electrical technique – at its present form – cannot ascribe the variation of water fraction to either coalescence or flocculation. Since coalescence is a far more abrupt phenomenon than flocculation, future versions of the technique with data acquisition rates in the order of kHz may allow detailed spectral analysis of signals to discriminate between coalescence and flocculation.

Figs. 7 and 8 compare emulsions made of 1% and 2% w/w/GMS for the three examined oil concentrations and for 300 rpm agitation speed. Fig. 7 presents data from the *low* probe whereas Fig. 8 data from the *high* probe. The electrical curve for 23% oil and 2% GMS is again omitted as it shows no change in the investigated time frame. The arguments made with respect to previous figures hold also here. Water fraction curves start at $t=0$ s from 0.93, 0.83, and 0.76, respectively, corresponding to well mixed conditions at the end of emulsification. Electrical curves move progressively towards unity which corresponds to pure water. A fast rise at the beginning followed by a slower rise is observed, designating again two different main droplet sizes [30]. Overall, by decreasing the emulsifier concentration the emulsions become more unstable. This is reflected in both the shorter time to reach unity and the steeper ascending slopes of the curves. This is rather normal since less emulsifier means larger and less elastic droplets where droplet aggregation phenomena (flocculation and coalescence) are more prone to occur. What is of interest to this work is that for 1% w/w GMS there are no peculiar local phenomena such as those observed for 2% w/w GMS. Apparently, differences between global and local dynamics are not always present and are not easy to predict. On the other hand, efforts aiming to improve the stability of inherently unstable emulsions, such as eco-friendly cosmetic emulsions, should always be concerned with identifying conditions where such discrepancies turn up.

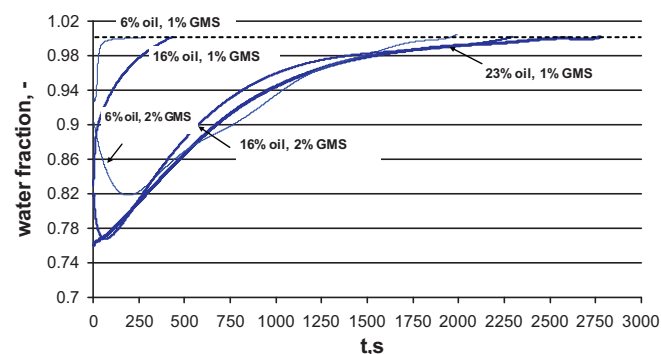


Fig. 8. Water fraction (f_w) as a function of time (t) during destabilization of emulsions produced at 300 rpm with different concentrations of oil (6% and 16% w/w) and emulsifier (1% and 2% w/w). Data obtained from the *high* probe.

4. Conclusions

A non-intrusive electric conductance technique was used to provide information on the local dynamics of destabilization of inherently unstable eco-friendly cosmetic oil-in-water emulsions inside a cylindrical vessel. The examined emulsions were complex systems of practical interest consisting of olive oil, water and glycerol monostearate as emulsifier. Electrical measurements delivered the variation of water volume fractions versus time at two heights (*low* and *high* probe) along the vessel. The *low* probe curves are characterized by two main slopes which are in line with global volumetric measurements of the creaming index. This feature implies an approximately bi-disperse size distribution of droplets. However, at certain concentrations of the oil and the emulsifier the high probe curves present an additional short inception period at the beginning of destabilization during which water fraction drops. This local feature was attributed to flocculation of droplets. Therefore, electrical local measurements proved superior to volumetric global measurements as regards the identification and monitoring of local structural peculiarities in the emulsion. Work is underway to depict the water fraction evolution simultaneously at several heights along the emulsion, including regions where dense cream prevails. This knowledge is considered extremely valuable in efforts aiming to improve emulsions stability.

Acknowledgments

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