

Phase Inversion Emulsification

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Phase inversion refers to a phenomenon that occurs when agitated oil in water emulsion, reverts to a water in oil and vice versa. Emulsification via phase inversion is widely used in fabrication of cosmetic products, pharmaceutical products (e.g., vesicles for drug delivery), foodstuff and detergents. Emulsification process is strongly affected by preparation method; very different droplet size distribution could be achieved, which is strictly linked to the product stability. Phase inversion process leads to the formation of finely dispersed droplets in a continuous phase. In this work an experimental investigation of phase inversion emulsification to produce stable samples has been performed. The emulsion morphology has been characterized in detail by direct observation via optical and confocal microscopy.

1. Introduction

Emulsions are fluids systems composed of at least two immiscible phases. An emulsion can be considered (meta)stable if its kinetic evolution toward the thermodynamic equilibrium, i.e. complete phase separation, is slow enough (Leal-Calderon et al., 2007). These systems present a dispersed phase, usually in form of droplets, surrounded by a continuous matrix. In some conditions the dispersed phase can be the one present in smaller quantity in the system. One phase is usually organic and is called "oil phase". The inorganic one is called "aqueous phase". There is a variety of phenomena acting to influence the system morphology and eventually lead to the phase separation: coalescence (two droplets merge into one) (Caserta et al., 2004), collision (Caserta et al., 2007), creaming and sedimentation (density driven separation), flow induced droplet re-arranging (Caserta et al., 2005), diffusion (De Luca et al., 2008) involving at least of the low molecular weight fraction in each of the phases (Jonas et al., 2010) of one phase into the other through the continuous phase (Ostwald ripening). Phase separation can be flow induced (Caserta et al., 2008) in order to minimize the viscous dissipation (Caserta and Guido, 2012), or, even in static conditions, due to sedimentation or creaming. By equating viscous and gravitational forces acting on a droplet immersed in the continuous phase we can obtain the Stokes' law, that expresses the gravitational separation velocity. From Stokes' law is clear that in order to slow down the drop sedimentation it is possible:

- i) Reduce the density difference between the two phases
- ii) Reduce the droplet radius (coupling with a narrow droplet size distribution)
- ii) Increase continuous phase viscosity

It is known for example that oil in water (o/w) emulsion are unstable due to the creaming that becomes significant when droplet radius is greater than 0.5 μm .

The main mechanism responsible for the increase of droplet size is coalescence, that can be inhibited by using surfactants (Di Scipio et al., 2011; Pommella et al., 2012), amphiphilic molecules which migrate from the bulk to the interface where they act to lower the interfacial tension and to elicit Marangoni stresses. The Marangoni effect slows down the drainage of the continuous phase film between two opposing

droplets, which is an essential step leading to coalescence. In general, it is very important to understand the relation of flow dynamics vs emulsion morphology structure (Caserta et al., 2006).

Phase inversion, i.e. the phenomenon by which the dispersed phase becomes the continuous phase and vice-versa, can be considered a useful route to produce emulsion made of very fine droplets.

A phenomenon always accompanying phase inversion is the spontaneous change in the surfactant arrangements at the oil-water interface. Phase inversion can be brought about by changing the temperature of the system, by changing the volume fraction of the phases, by adding salts or by imposing particular flows; e.g. extensional flow (Akay et al., 2000). This process is defined by some authors as a catastrophic event (Fernandez et al., 2004), because it appears to be a sudden and dramatic change in morphology caused by a gradual change in experimental conditions. Galindo-Alvarez and co-workers (Galindo-Alvarez et al., 2011) showed the influence of oil viscosity and process conditions on catastrophic phase inversion. Jahanzad et al. (Jahanzad et al., 2009) showed the formation of multiple emulsion accompanying catastrophic phase inversion. Sajjadi et al. (Sajjadi et al., 2004) pointed out the catastrophic phase inversion of abnormal emulsions in the vicinity of phase inversion point, and nanoemulsion formation by catastrophic phase inversion (Sajjadi et al., 2006). Shinoda & Arai were the first (Shinoda & Harai, 1964) to point out the effect of temperature on phase inversion. They founded that, by increasing temperature, non-ionic surfactants become more hydrophilic, so they change their chemical configuration and physical arrangement promoting phase inversion.

Emulsification via phase inversion is widely used in fabrication of cosmetic products, pharmaceutical products (e.g., vesicles for drug delivery), foodstuff and detergents.

Emulsification process is strongly affected by preparation methods that can lead to very different droplet size distribution, which is strictly related to the final product stability. Processes that involve phase inversion can lead to the formation of finely dispersed droplets in a continuous phase, while the typical emulsion preparation process, which consists in dissolving the surfactant in the continuous phase and adding the dispersed phase under appropriate agitation can typically result in the formation of unstable macroemulsions. Achieving phase inversion by changing temperature is the so-called "phase inversion temperature" (PIT) method (Shinoda & Arai, 1964), where miscibility of the two phases plays a key role. Another way is to increase gradually the amount of the minor phase up to the "emulsion inversion point", EIP (Fernandez et al., 2004) (also known as "phase inversion concentration", PIC).

This work has been focused on emulsification of mixtures composed by water, oil and two non-ionic surfactants, with the objective to define protocols able to produce o/w emulsions stable over an extended time frame i.e., systems that show no significant phase separation after several months.

Temperature, flow (such as stirring rate) and surfactant concentration play a key role in the control of the system morphology. The methodology we followed is based on the "emulsion inversion point" method. In this way it has been possible to produce long term stable emulsions with great energy saving, due to: i) low energy mixing requirement, ii) room temperature process of emulsification. Static images of the emulsion acquired by optical microscopy and confocal light scanning microscopy have been reported, in order to evaluate the emulsification evolution based on system morphology. In addition, static light scattering (Horiba) was used to assess emulsion stability. This methodology can be a valid tool for industrial process development, that is one of the key issues of chemical engineering (Asprion et al., 2011).

2. Materials and Methods

The emulsification was carried out at room temperature. Mineral oil and surfactants (polyoxyethylene sorbitan fatty acid esters, Tween, Sigma Aldrich and sorbitan fatty acid esters, Span, Sigma Aldrich) were poured together in a beaker. The surfactant concentration was optimized in order to obtain long term stability. Water was then added drop by drop until a concentration of 76-80% wt was reached. The vessel was agitated with a magnetic stirrer at 250 rpm, that is the minimum speed required to ensure emulsion stability (low energy mixing). Static images of the emulsion acquired by optical microscopy have been analysed in order to evaluate the system stability, based on fluid morphology. In addition, static light scattering (Horiba) has been used to assess emulsion stability.

3. Results and Discussion

By this process methodology, long term stable emulsions characterized by very small average diameter, i.e. 0.17 μm , and narrow droplets size distribution has been obtained. The droplet, given their reduced

size, have been observed to show random brownian motion. In Figure 1 we report an optical microscopy image of the final emulsion, and the droplet size distribution.

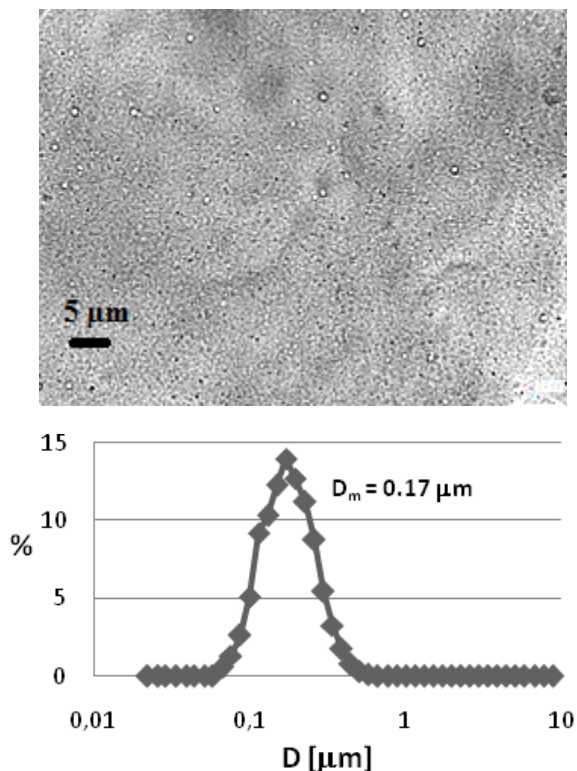


Figure 1: Optical image of the finished emulsion and correspondent droplet size distribution, water weight fraction is 76%.

By adding a fluorescent dye into the aqueous phase (Pommella et al., 2012), confocal light scanning microscopy was used to follow emulsion morphology evolution as a function of water concentration. In Figure 2 images acquired at different water concentration are reported, the fluid was placed on the microscope slit directly from the stirred vessel; about 10-30 second elapsed between the sampling and image acquisition. Since the process starts by adding water drops into the oil plus surfactants mix, an initial w/o emulsion was obtained. Despite the gradual alimentation of water, a sudden change in morphology, often named "catastrophic" event, was observed around the 20 %wt of water concentration, thus showing a bicontinuous morphology structure. After further water feeding, the bicontinuous structure disappeared quite fast, leading to the formation of an o/w emulsion. Therefore, around to the 20%wt of water concentration, the dispersed and continuous phase invert. Finally, water was fed, up to the final water concentration of 76%wt. In Figure 3 a magnification of the confocal image at 76 %wt of water is reported, it is possible to observe the complexity of the morphology that point out the presence of droplets in droplets in the bigger emulsion droplets. Probably, the intermediate bicontinuous structure favours the trapping of one phase into the other, leading to the formation of droplets in droplets inclusion.

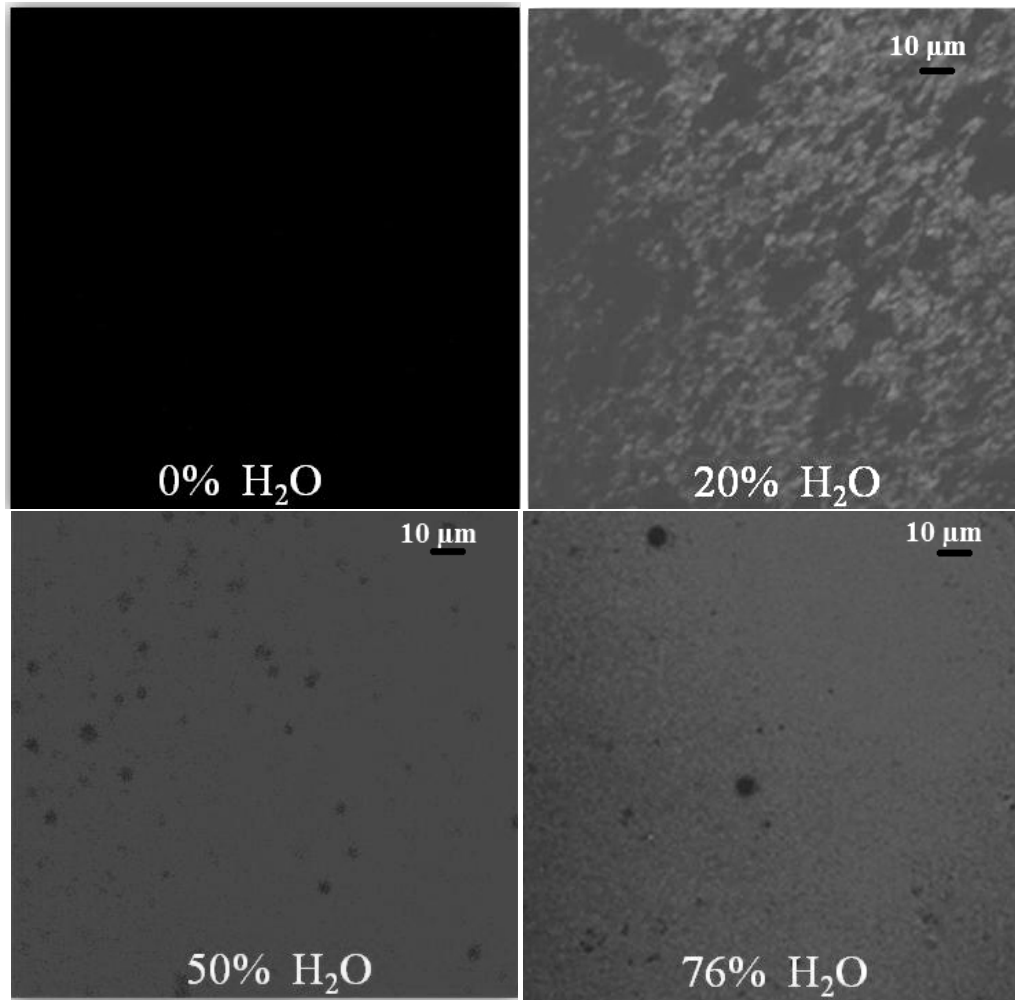


Figure 2: Confocal image at different water concentration, percentages are in weight.

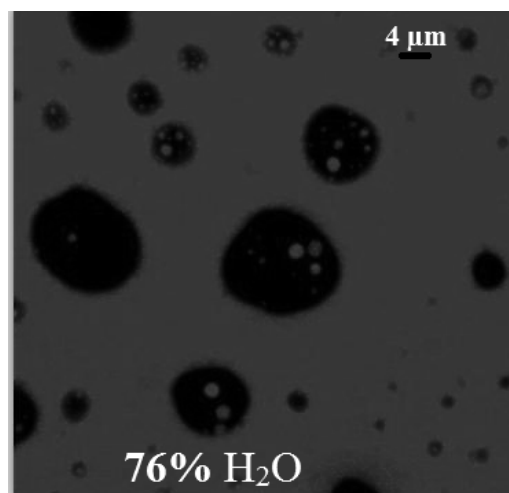


Figure 3: Confocal image, water weight fraction is 76%. It is possible to observe the presence of multiple emulsions.

4. Conclusions

In this work we reported an experimental investigation of phase inversion emulsification to produce stable samples. The emulsion morphology has been characterized in detail by direct observation in confocal microscopy. Long term stable emulsions have been obtained with great energy saving. Higher emulsions stability is associated with both small droplet size and low polydispersity of the droplet size distribution. Confocal microscopy can be exploited to follow the time evolution of the phase inversion process. Confocal imaging clearly shows the formation of bicontinuous structure during the emulsification process, that signs the two phases point of inversion. Furthermore, this bicontinuous phase, can eventually trap one of the two phase into the other, thus creating a complex morphology that presents inclusion of droplets in droplets.

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