Emulsions preparation based on ternary phase diagrams: comparative study using two oils (Miglyol and Sweet Almond) with two distinct surfactants (Tween 80 and Saponin)

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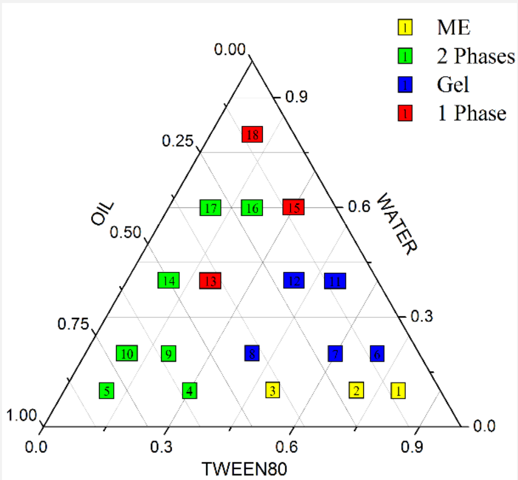

An emulsion is a colloidal dispersion composed by a mixture of two immiscible liquids, being one the dispersed phase, as droplets, and the other one the continuous phase. In this work, a comparative study comprising the surfactants Tween 80 (synthetic surfactant) and Saponin (natural surfactant) and the oils Miglyol 812 and Sweet Almond was performed. The development of emulsions based on ternary phase diagrams showed that different phases can be formed giving rise to different formulations: microemulsions, gels, and mixtures with 1, 2 and 3 phases. The application of the HPH technique produced stable nanoemulsions with narrow distributions. Considering Tween 80, and comparing the two oils, Miglyol 812 gave rise to emulsions with lower particle size (0.023µm), comparatively to Sweet Almond Oil (1.009µm). This difference can be related with the oil viscosity, which is lower for Miglyol 812. Comparing the two surfactants, natural Saponin was very effective in the o/w composition range.

Introduction

Emulsions are systems formed by mixing components presenting three distinct characteristics; hydrophilic, lipophilic and amphiphilic. In other words, water, oil and surfactant (or a combination of surfactants), forming, for certain levels of compositions, a macroscopically homogeneous system that presents important technological features. In fact, because of its versatile character, the technological application of emulsions is vast, including food, pharmaceutic and cosmetics industries. Among the different types of emulsions, micro and nanoemulsions present the most appealing properties due to their higher stability and possibility to serve as potential carriers for functionalities delivery.

Nowadays, an important topic in the field of emulsions is the introduction of natural products to act as surfactant. This is partly motivated by consumer demands for more sustainable, natural and environmentally friendly formulations, which is also connected to the current environment concerns and legislation. Thus, industry and researchers are searching for products with friendly-natural label, more specifically to surfactants, which have a high economic importance and face problems due to the large utilization of synthetic forms [1]. This is particularly valid in certain areas, e.g. the food industry, which accounts for around 67% of the global market volume [2].

Recent studies are being focused on the use of a highly surface-active group named Saponins [3], whose properties (biological and physicochemical) led to a number of industrial applications [4]. The abundance of Saponins in nature result in a wide range of natural matrices for their commercial production, being Quillaja Bark one of them [5]. In this context, the objective of this work is to perform a preliminary study concerning the preparation of emulsions, building the ternary phase diagrams either using a traditional or natural surfactant, to help in the decision of the best formulations.

Methods

The studied surfactants were Tween 80 and Saponin from Quillaja Bark. Two oils with different chemical composition and viscosity (Sweet almond oil (SAO) and Miglyol 812) were selected as the lipophilic constituent. To build the entire diagram, different samples covering the appropriate range of compositions were prepared using a Vortex system. The prepared samples were analyzed macroscopically to identify the type of emulsion formed. Thereafter, the more suitable compositions were prepared by using a high-pressure homogenizer (HPH) and the droplet size determined by laser diffraction (LD) technique.

Results

Figure 1 shows the ternary diagrams in terms of mass fraction for the systems: a) Water + Tween 80 + Miglyol 812, b) Water + Tween 80 + Sweet Almond Oil and c) Water + Saponin + Sweet Almond Oil. The different samples were classified in: 1 Phase, 2 Phases, 3 Phases, Gel or microemulsion (ME), giving a first general analysis of the mixture state according to composition. Potentially, the 1 phase and the gels are the most interesting forms to explore from a technological point of view.

Tween 80, a commercial surfactant formed emulsions in the entire range of compositions. The ME zone for these systems comprise the use of high amounts of surfactant, which is not commercially desirable as the compositions with low level of surfactant are the most attractive ones. For all the three studied systems, an area corresponding to gel formation was observed for water compositions between 0.15 and 0.5 and surfactant mass fraction higher than 0.5.

The Saponin-based system, using SAO also gives rise to the formation of emulsions, but only when composition comprised more water than oil (probable o/w emulsions). However, some compositions, namely the ones with high oil content (probable w/o emulsions), were difficult to prepare (in some cases impossible) and no emulsion was formed.

Comparing both surfactants, the Tween 80 has a strong ability to form emulsions in the entire range of composition, while the Saponin not. However, considering the top of the ternary diagram (high amount of water), the Saponin was able to form emulsions with only one phase.

The droplet size of the sample 18, for the three tested systems, was determined by LD technique. The average particle size in number are shown in Table 1.

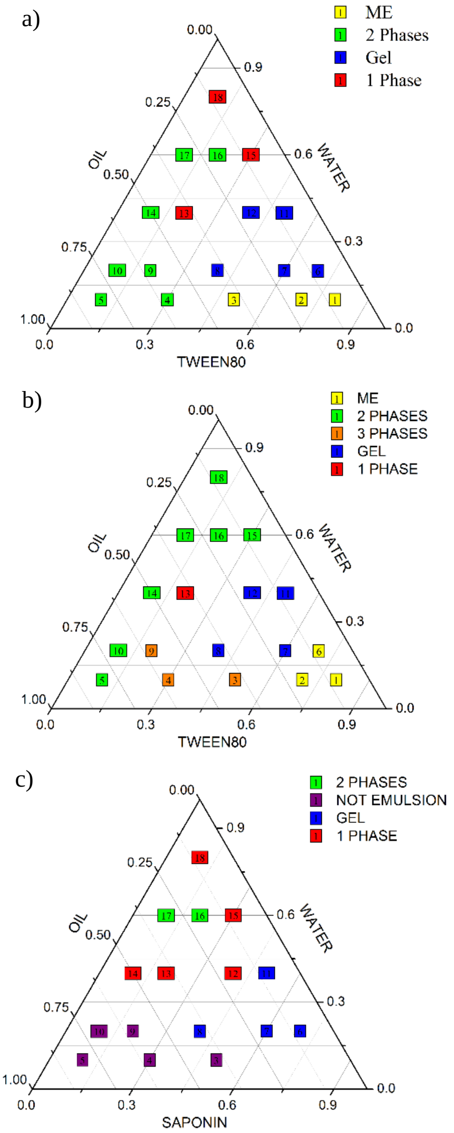

Figure 1. Ternary diagrams for the systems a) Water/Tween 80/Miglyol 812 b) Water/Tween 80/Sweet Almond Oil and c) Water/Saponin/Sweet Almond Oil.

Table 1. Average particle size, in number, for the three tested systems.

System	Average Particle Size in number
Tween 80/Miglyol 812	0.0230 μm
Tween 80/SAO	1.0085 μm
Saponin/SAO	0.5682 μm

The smallest droplet size corresponded to the system comprising Tween 80 and Miglyol 812. Comparing the two oils, for the same surfactant (Tween 80), it is possible to note that the one based on SAO presented the larger particle size, which was associated to the higher viscosity of this oil (Miglyol 812 has a viscosity of 27 mPa.s and Sweet Almond Oil a viscosity of 43 mPa.s; room temperature). Additionally, and comparing the same oil (Sweet almond oil) for the two surfactants, the Saponin presented the ability to decrease the droplet size almost in half, showing a better performance for o/w emulsions.

For the nanoemulsion production, using the HPH system, the composition of sample 18 was chosen, and the effect of the number of cycles (3, 6, 9, 12 and 15 cycles) on particle size was analyzed. Table 2 shows the results achieved for the system using Saponin as emulsifier.

Table 2. Droplet size by HPH for Saponin/SAO system.

Number of cycles	Droplet Size (μm)	Number of cycles	Droplet Size (μm)
0	0.5682	9	0.0254
3	0.0551	12	0.0250
6	0.0321	15	0.0224

As expected, the average droplet size decreased as the number of cycles increased turning the emulsion to the nanoscale, which might increase the stability as reported in some works [6]. The influence of the number of cycles was higher at the beginning (application of the fist cycles), comparatively with the latter. After six cycles the size tends to stabilize, reaching a plateau.

Conclusion

The ternary diagrams using the commercial surfactant (Tween 80), and two oils (Miglyol 812 and Sweet Almond Oil), pointed out for the existence of different typology of samples (ME, gel 1, 2 and 3 phases). The alternative natural surfactant, Saponin, was not effective for some compositions, but in the range of o/w emulsions gives rise to emulsions with lower particle size, comparatively with the ones prepared with Tween 80.

The HPH technique showed to be effective, reducing both droplet size and sample heterogeneity. The results showed that as the number of cycles increase the droplet size decrease until reaches a point where a stable final droplet size is achieved.

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