
IFSCC 2025 full paper (IFSCC2025-633)

"Impact of the simultaneous presence of surfactants and particles on the quality of a cosmetic emulsion: interaction mechanisms"

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1. Introduction

Emulsions have many applications in various sectors, including the cosmetics industry.^[1] These systems are thermodynamically unstable and consist of a mixture of two immiscible liquids, to which an emulsifier is added to ensure the emulsion's kinetic stability.^[2] Various types of emulsifier can be used, such as surfactants, polymers, or colloidal particles.^[2] Surfactants are widely used to stabilize so-called classic emulsions. The mechanism for stabilizing oil droplets when using surfactants is defined by reversible adsorption at liquid-liquid interfaces, inducing a drop in interfacial tension.^{[1][3]} The use of surfactants offers numerous advantages, such as the achievement of small emulsion droplets and a good sensory experience.^{[4][5]} However, some surfactants have negative effect on human health and environment.^{[6][7]} This is why replacing surfactants with colloidal particles to form a so-called Pickering emulsion could be a suitable alternative. Indeed, the use of natural particles such as clays^{[8][9]} or chitosan^{[10][11]} to stabilize emulsions could lead to the development of more environmentally-friendly cosmetics.

Pickering emulsions are widely studied in various fields, and the stabilization mechanisms of this type of emulsion are now well understood.^[12]

However, many cosmetic products can contain surfactants and particles at the same time, as is the case for sunscreen products which may contain inorganic particles such as titanium dioxide (TiO_2), for example. The laboratories carry out research aimed at developing stable, fully emulsified systems: conventional emulsions, stabilized by surfactants, Pickering emulsions, which use colloidal particles to stabilize liquid-liquid interfaces, and mixed emulsions, containing both surfactants and particles.^{[4][13]} In the latter case, two main mechanisms are described in the literature: competitive and synergistic mechanisms.^{[14][15]}

In a synergistic mechanism, the surfactants will adsorb to the surface of the colloidal particles, resulting in a modification of the particles' surface properties.^{[14][15]} Stabilization of liquid-liquid interfaces will therefore be ensured by the surfactant-particle complex. On the other hand, in the case of competition between surfactants and particles, the latter are simultaneously present at liquid-liquid interfaces.^{[14][15]} The predominance of one of these mechanisms can be influenced by various parameters such as: the nature of the emulsifiers^[16], the concentration of surfactants in the medium^{[17][18]} or the order in which the emulsifiers are introduced^[19]. However, the existence of a predominant mechanism and its impact on the stability of a system are still being questioned. Therefore, many questions about the stabilization mechanisms of these mixed systems, their stability and their physicochemical and sensory properties are raised by the simultaneous presence of these two types of emulsifiers in a cosmetic emulsion.

To answer these questions, three systems were developed: a conventional surfactant-stabilized emulsion (CE-St10), a Pickering emulsion (PE- TiO_2 10) and, finally, an emulsion containing both surfactants and particles (ME-St5 TiO_2 5). A study of the physicochemical properties of each of the systems developed was carried out to determine the impact of the simultaneous presence of two emulsifiers within the same system.

2. Materials and Methods

2.1. Materials

The raw materials used to produce the emulsions are all cosmetic grades. The surfactant system used corresponds to a combination of a polyoxyethylene (2) stearyl ether (Steareth-2; CAS No. 9005-00-9, HLB = 4.9) and a polyoxyethylene (21) stearyl ether (Steareth - 21; CAS No. 9005-00-9, HLB = 15.5) at a ratio of 6:4. The resulting HLB of this surfactant mixture is around 9. The particles selected are titanium dioxide (CAS no: 13463-67-7) coated with silica (CAS no: 7631-86-9) and cetyl phosphate (CAS no: 3539-43-3). The oil phase of the emulsion corresponds to caprylic/capric triglyceride (CAS no: 73398-61-5). The preservative used is a commercial mixture of different compounds: benzyl alcohol (CAS no: 100-51-6, 77-86 %m), salicylic acid (CAS no: 69-72-7, 8-15 %m), glycerin (CAS no: 56-81-5, 3-6 %m), and sorbic acid (CAS no: 110-44-1, 1-4%m). The emulsions were formulated using ultrapure water with a resistivity of 18 MΩ.

2.2. Emulsions formulation

Conventional emulsion formulation (CE-St10): the oil phase and surfactant mixture were heated to 80 °C with mechanical stirring at 500 rpm. After heating the aqueous phase to 80 °C, the oil phase and surfactant mixture were introduced into the aqueous phase using a rotor stator disperser(UltraTurrax T25 Digital, IKA, 25 mm generator shaft S25N-25F) for 30 s at 11,000 rpm. Emulsification was continued using the UltraTurrax for 1.30 min. The emulsion obtained was then placed under stirring at 400 rpm (Turbotest, VMI Raynerie) until 30 °C was reached, after which the preservative was added. Finally, the emulsion was homogenized for 15 min at 400 rpm (Turbotest, VMI Raynerie).

Pickering emulsion formulation (PE-TiO₂10): Titanium dioxide particles were pre-dispersed under mechanical agitation in the aqueous phase for 5 min at 500 rpm. The particles were dis-

persed using an ultrasonic dismembrator (Fisher Scientific FB-705 with a standard 1/2" diameter probe (4220)), at 80% amplitude until 25 kJ of energy was returned to the system, in an ice bath. The resulting particle dispersion is then heated to 80 °C with mechanical stirring at 500 rpm. The oil phase was then added using a rotor stator disperser (UltraTurrax T25 Digital, IKA, 25 mm generator shaft S25N-25F) for 30 s at 11,000 rpm. The emulsification process was carried out with the UltraTurrax for 1.30 min at 11,000 rpm. Once the emulsion was obtained, it was stirred (Turbotest, VMI Raynerie) until 30 °C was reached, then the preservative was added. Finally, the system was homogenized for 15 min at 400 rpm (Turbotest, VMI Raynerie).

Mixed emulsion formulation (ME-St5TiO₂5): The titanium dioxide particles were dispersed under the same conditions as for the Pickering emulsion formulation (PE-TiO₂10), and the resulting dispersion was then heated to 80°C with mechanical agitation at 500 rpm. The oil phase, surfactant system and dispersion were then heated to 80 °C with mechanical agitation at 500 rpm. The oil phase-surfactant mixture was introduced into the particle dispersion with a rotor stator disperser (UltraTurrax T25 Digital, IKA, 25 mm generator shaft S25N-25F) for 30 s at 11,000 rpm before continuing emulsification for 1.30 min under the same conditions. The resulting emulsion was mechanically stirred to 30 °C at 400 rpm (Turbotest, VMI Raynerie) before introducing the preservative, then homogenized for 15 min at 400 rpm (Turbotest, VMI Raynerie). For all three system, Table 1 shows the composition of the formulas.

Table 1: Summary table of the compositions of each of the three formulated systems

Sample	TiO ₂ (%m)	Surfactant (%m)	Water phase (%m)	Oil phase (%m)	Preserva- tive (%m)
CE-St10	-	10	69	20	1
PE-TiO₂10	10	-	69	20	1
ME-St5TiO₂5	5	5	69	20	1

The three systems were stored at room temperature and at 50 °C for a stability study. The physicochemical properties of each emulsion were determined two days after formulation.

2.3. Microscopy

Observations of emulsion microstructure were made using an optical microscope (Nikon - Eclipse Ni-U) equipped with a digital camera. Nikon software was used for image acquisition and processing. Three samples were taken from each system: at the surface, in the middle and at the bottom of the emulsion, and observed at x200 and x400 magnifications.

2.4. Droplet size and droplet size distribution

The size distribution of emulsion droplets was measured by static light scattering (SLS) using a laser diffraction particle size analyzer (SALD 7500 Nano, Shimadzu) at 405 nm. Data acquisition and processing were carried out using WingSALD II-7500 software, according to Mie's theory. The emulsions were dispersed in distilled water to achieve an absorbance value of between 0.180 and 0.200. Each measurement was carried out in triplicate and the size distribution calculation was based on volume. Mean and modal diameter values were recorded for each system.

2.5. Rheological measurement

The rheological properties of the three emulsions were evaluated using a controlled stress rheometer (TA instrument Discovery HR2). TRIOS software was used for data acquisition and processing. The viscoelastic properties of each system were determined using a 40 mm aluminum cone/plane geometry, with an angle of 1.992° and a gap of 50 microns. Each measurement was carried out at a temperature of 25 °C, allowing 120 s equilibration time for the sample under the geometry. A solvent trap was also used to inhibit sample evaporation.

Oscillatory measurements were carried out on each emulsion in triplicate, enabling the linear viscoelastic domain of each sample to be determined. These measurements were carried out at a frequency of 1 Hz over a deformation range from 0.01 to 100%. The values of the storage (G') and loss (G'') modulus as well as $\tan\delta$ were collected and compared between each system.

3. Results

3.1. Macroscopic observations

Sample CE-St10 is homogeneous and shows no signs of destabilization. Application of this system generates a significant amount of foam, inducing a whitening effect, explained by the presence of a large quantity of surfactants^[13]. The PE-TiO₂10 emulsion also shows no signs of destabilization. However, the emulsion's appearance is different from that of a conventional emulsion. It leaves a crunchy finish on the skin and a white film, caused by the presence of TiO₂, which is also a white pigment^[13]. Finally, the ME-St5TiO₂5 mixed emulsion has an intermediate appearance to the two systems mentioned above. It leaves a greasy film, as is the case with the classic emulsion, and a white film, as is the case with the Pickering emulsion. Investigations into the microstructure and rheological properties of these three systems should provide some answers to the intermediate behavior observed in the case of the mixed emulsion.

3.2. Microstructure of the three systems

Microscopic observations for each system are shown in figure 1. Sample CE-St10 shows small emulsion droplets dispersed homogeneously in the medium. No flocculation is observed. For the PE-TiO₂10 emulsion, several observations were made. Firstly, the emulsion droplets form a dense, interconnected network, potentially pointing out the formation of a three-dimensional network within this system. Particle aggregates are also observed. Finally, in the case of the ME-St5TiO₂5 mixed emulsion, an intermediate microstructure between the CE-St10 and PE-TiO₂10 samples is obtained. In this case, the emulsion droplets present a less dense network,

although particle aggregates are still observed. An initial assessment of the variation in emulsion droplet sizes for each system indicates that the mixed emulsion has intermediate droplet sizes, between those of conventional and Pickering emulsions.

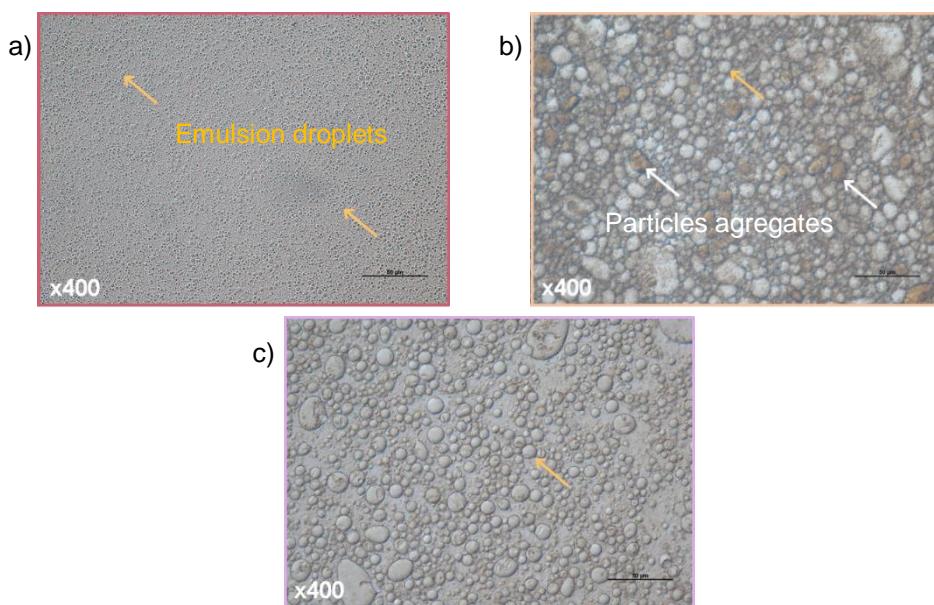


Figure 1: Microscopy of formulated systems, a) CE-St10, x400, b) PE-TiO₂10, x400, c) ME-St5TiO₂5, x400. Orange arrows represent emulsion droplets, and white arrows correspond to particle aggregates.

3.3. Comparison of droplet size distribution

Primary microscopy observations were confirmed by droplet size measurements in SLS, as shown in figure 2. Indeed, sample CE-St10 shows two populations ranging from 0.291 to 13 microns with a modal diameter of 2.106 μm and an average droplet size of 1.440 μm with a standard deviation of 0.283 μm (Figure 2a). The resulting emulsion is therefore fine, which confirmed the above microscopic observations. The PE-TiO₂10 sample has two distinct populations (Figure 2b): a first population between 0.200 and around 3 μm (P1) and a second between 3 and 70 μm (P2). The population range is much wider than in the case of the classic emulsion, which corroborates the microscopic observations showing a dense network of droplets of larger sizes than in the CE-St10 sample.

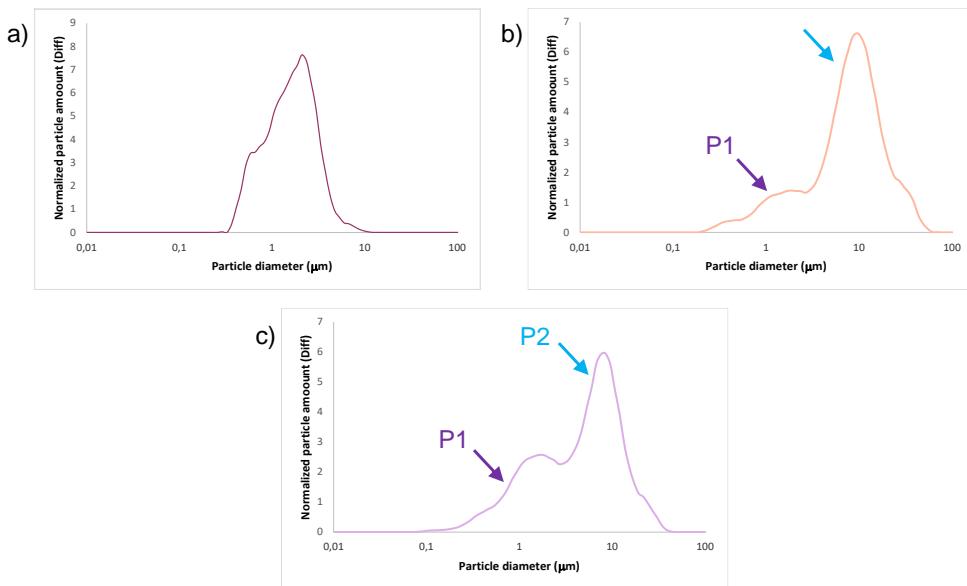


Figure 2: Droplets size distribution by volume of a) CE-St10, b) PE-TiO₂10, c) ME-St5TiO₂5

Indeed, the average diameter of emulsion droplets here is $6.483 \pm 0.441 \mu\text{m}$ and the modal diameter is $8.521 \mu\text{m}$. For the ME-St5TiO₂5 system (figure 2c), two populations are also observed, as for the Pickering emulsion, ranging up to $3 \mu\text{m}$ (P1) for the former and up to $43 \mu\text{m}$ (P2) for the latter. The total range is therefore reduced in comparison with the Pickering emulsion, highlighting the involvement of surfactants in the stabilization of this system. In addition, the first population represents a larger volume than for PE-TiO₂10, reflecting a greater representation of small droplets and supporting the hypothesis put forward previously. As with the microscopic observations, analysis of the droplet size distribution of the ME-St5TiO₂5 system seems to highlight an intermediate character between the classic emulsion and the Pickering emulsion.

3.4. Study of rheological properties

The rheological properties of the classic CE-St10 emulsion show solid viscoelastic behavior with a tangent delta value of 0.39. Results for the ME-St5TiO₂5 system also show solid viscoelastic behavior (tangent $\delta = 0.40$). The PE-TiO₂10 emulsion also exhibits solid viscoelastic behavior, but with higher storage modulus and loss values than in the other two

cases, as well as a lower tangent delta value ($\tan \delta = 0.06$). In addition, an increase in G'' is observed upstream of the intersection point ($G'=G''$), reflecting weak gel behavior, linked to the presence of a three-dimensional network within the system.^[9] These measurements confirm the contribution of surfactants to the stabilization of the ME-St5TiO₂5 system.

4. Conclusion

In this study, three types of systems were analyzed: a conventional emulsion stabilized by surfactants, a Pickering emulsion stabilized by colloidal particles, and a mixed emulsion containing surfactants and particles simultaneously. In-depth physicochemical characterization of these systems revealed the respective contributions of the two types of emulsifier in the mixed system. In the joint presence of surfactants and particles, an intermediate size distribution is observed between those obtained for PE and CE, suggesting that the particles play an active role in stabilizing the emulsion. On the other hand, the rheological behavior of this mixed emulsion is comparable to that of the classic emulsion, indicating a major contribution by surfactants to maintaining the viscoelastic stability of the system. These results underline the significant influence of emulsifier type on the physicochemical properties of emulsions. They also highlight the importance of taking several key parameters into account when formulating cosmetic products that simultaneously incorporate two types of emulsifier. From a more fundamental point of view, there is a real need for a better understanding of how particle-surfactant interaction mechanisms influence the properties of systems, whether through synergy or competition. These questions constitute the short-term prospects for this research work.

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