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# Treball Final de Grau

**Stabilizing effect of polyglycerides as emulsifiers in cosmetic emulsions.**

**Efecte estabilitzant dels poliglicèrids com a emulgents en emulsions cosmètiques.**

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*True stability results when presumed order and presumed disorder are balanced. A truly stable system expects the unexpected, is prepared to be disrupted, waits to be transformed.*

Tom Robbins

Primer de tot agrair a la Maria Sarret, tutora d'aquest treball, pel seu suport durant el transcurs de la realització del treball, per tot el que m'ha ensenyat i per la seva paciència responent tots els meus dubtes.

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**REPORT**





## **IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)**

The United Nations proposed the Sustainable Development Goal to achieve a better future for the people on the planet. There are 17 goals grouped in the called 5 Ps: People, Planet, Peace, Prosperity, and Partnership. The aim of this section is to identify which of the goals are accomplished in this work.

The objective of this work is to formulate a cosmetic emulsion with 100% natural origin ingredients, more specifically a moisturizing cream intended for people with atopic skin disease. This, apply to the goal 3, "Good health and well-being", concretely the goal 3.9 about reducing the number of deaths and illnesses from hazardous chemicals and air, water and soil pollution and contamination. If more natural origin compounds are used in cosmetic products will not be needed to carry out obtention methods like petroleum distillation to obtain Paraffin Oil, which causes air, land, and water contamination and harms people health.

Also, this situation implies the goals 13 (climate change), 14 (life bellow water) and 15 (life on land) that talk about contamination in the planet.

Investigación y Desarrollo de Cosmeticos S.L. do not have Agenda 2030 by their own.



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## 1. SUMMARY

Emulsions are mixtures of two immiscible phases, a dispersed or internal phase and a dispersing or external phase, stabilized by different mechanisms depending on the emulsifier type. Emulsions are thermodynamically unstable, but their kinetical stability depends essentially on the type of emulsifier used. In this work simple emulsions are prepared, and it is analysed the stabilization effect of three different polyglycerides, non-ionic and natural origin surfactants resulting from the esterification reaction of fatty acids with some molecules of glycerine (in this case four molecules of glycerine). Moreover, three different glycerides are used as support agents (co-emulsifiers) made with the same fatty acid of polyglycerides; this way emulsions have the emulsifier and co-emulsifiers from the same fatty acid. The used compounds are derivatives from oleic, stearic and lauric acids. For each pair of compounds, the emulsion was characterized, and its stability was analysed. The results show that only oleic acid derivatives can be used to obtain emulsions with acceptable stability.

The final goal of this work is to obtain a complete cosmetic formulation using the polyglyceride and glyceride that give the best results in the previous stability study. Since the prepared formulation is a moisturizing cream, the possibility of changing the usual oil (paraffin oil) by natural origin oils was also checked. This way the emulsions would have less allergenic reactions on skin and could be used in atopic skin cases.

**Keywords:** emulsions, emulsifiers, stability, polyglycerides, cosmetic formulation, moisturizing cream.



## 2. RESUM

Una emulsió es una barreja de dues fases immiscibles, una fase dispersa o interna i una fase dispersant o externa, estabilitzades mitjançant diferents mecanismes, segons el tipus d'emulgent present. Una emulsió és inestable termodinàmicament, però la seva estabilitat cinètica depèn essencialment de l'elecció de l'emulgent. En aquest treball es preparen emulsions simples i s'analitza l'efecte estabilitzant de tres poliglicèrids, un tipus de tensioactius no iònics i d'origen natural que provenen de la reacció d'esterificació d'àcids grassos amb més d'una molècules de glicerina (en aquest cas quatre molècules de glicerina). També s'utilitzaran com a agents de suport, els anomenats co-emulgents, tres tipus de glicèrids derivats dels mateixos àcids grassos, de manera que cada emulsió tingui un emulgent i un co-emulgent derivats del mateix àcid gras. Els compostos utilitzats són derivats dels àcids oleic, esteàric i làuric. Per a cada parella s'ha caracteritzat el tipus d'emulsió obtinguda i se n'ha determinat l'estabilitat. Els resultats mostren que només amb els derivats de l'àcid oleic es poden obtenir emulsions amb una estabilitat acceptable.

L'objectiu final del treball és obtenir una formulació cosmètica completa emprant el poliglicèrid i glicèrid que han donat millors resultats d'estabilitat en l'estudi previ. Atès que el preparat és una crema hidratant, s'ha analitzat la possibilitat de substituir l'oli habitual (oli de parafina) per olis d'origen natural, amb menys reaccions al·lèrgiques sobre la pell i que pogués ser utilitzat en el cas de les pells atòpiques.

**Paraules clau:** emulsió, emulgent, estabilitat, poliglicèrids, formulació cosmètica, crema hidratant





### 3. INTRODUCTION

Emulsions are colloidal dispersions formed by mechanical agitation of two immiscible phases and an emulsifier. Classification of emulsions can be based on the structure of the emulsion, the droplet size of the dispersed phase, the concentration of dispersed phase or the nature of the emulsifier.

Referred to structure, if the dispersed phase is oil and the continuous phase is aqueous, we talk about oil in water (O/W) emulsions, whereas if the opposite happens, we talk about water in oil (W/O) emulsions. Emulsions also can be the dispersed phase, which results in multiple emulsions water in oil in water (W/O/W) or oil in water in oil (O/W/O). [1] Finally and less common are same phase emulsions, i.e., water in water emulsions (W/W) formed from two aqueous phases with incompatible polymers as polysaccharides or proteins, or oil in oil (O/O) emulsions, formed from two immiscible organic solvents stabilized by copolymers with residues of differing solubilities in the two components.

Droplet size allows to classify emulsions in macroemulsions (>50 nm), microemulsions (between 10 and 50 nm) and nanoemulsions (<100 nm). Depending on the method of emulsification will be obtained different droplet sizes. [2]

Depending on the volume of dispersed phase emulsion can be classified as diluted, concentrated, and highly concentrated. Diluted emulsions occurs when the volume of dispersed phase is below 20%, concentrated when is between 20 and 74%, and high concentrated when is above 74%. This 74% corresponds to a close-packed of non-deformable and monodispersed spherical droplets. [2]

Regarding the nature of the emulsifier, are known and well-studied three emulsion types: Pickering emulsions with solid particles as emulsifiers, hydrocolloid-stabilized emulsions, and the most common type in cosmetics the surfactant-stabilized emulsions. The latter one is the focus of this work.

### 3.1. EMULSION STABILITY

Stability of emulsions depends on the emulsifier nature, their concentration, and the method of emulsification. Emulsions are thermodynamically unstable, but they can have kinetic stability, which means that they can be stable for some time; this depends on the droplet size of the dispersed phase, the viscosity of the system, and the repulsion between droplets by an electrical double layer or stearic effect from adsorbed polymers. [1]

#### 3.1.1. Instability types

Emulsions can be destabilized by different mechanisms: creaming or sedimentation, Ostwald ripening, flocculation, coagulation, and coalescence. These mechanisms can act alone or together, sequentially, or all at once. [2]

Creaming/Sedimentation: Due to density difference, dispersed droplets may accumulate at the top or the bottom of emulsions, resulting in creaming or sedimentation respectively. It is a reversible destabilization mechanism. [2]

Flocculation: Droplets are agglomerated because of van der Waals forces but keeping a thin film that separates each of the droplet. This mechanism can be reversible or irreversible depending on the intensity of van Der Waals forces between droplets. When the process is irreversible its named coagulation. [2]

Coagulation: When agglomerated droplets starts to break its thin film, coagulation take place and coalescence happens. [2]

Coalescence: The agglomerated droplets break the thin film and starts to form bigger droplets. It is an irreversible destabilization mechanism. [2]

Ostwald ripening: Consist of diffusion of the smallest dispersed droplets to the biggest promoting coalescence. It is an irreversible destabilization mechanism. [2]

The destabilization processes are represented in Figure 3.1.

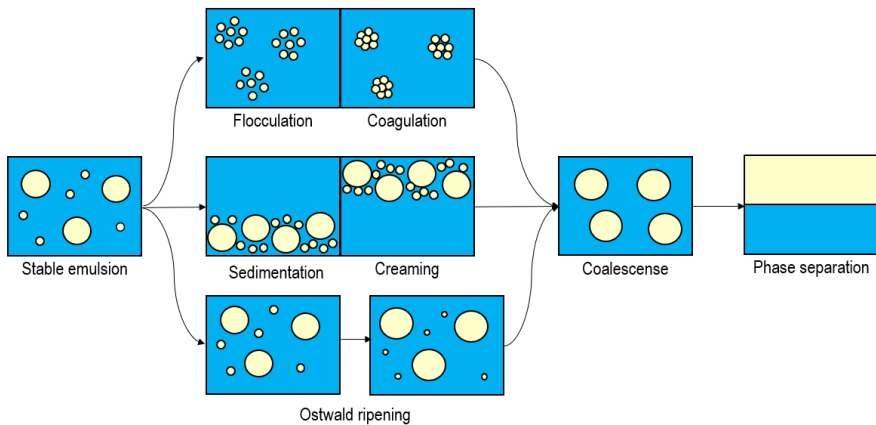


Figure 3.1: Representation of the destabilization processes in O/W emulsion

As has been said, emulsions are thermodynamically unstable but can be kinetically stable. To reach this kinetic stability there are methods such as the increasing of viscosity and the addition of electrolytes. Referring to viscosity, the higher the viscosity is, the more stable the emulsion will be due to immobilization of dispersed phase droplets. About electrolytes effect, depending on if the emulsion is O/W or W/O these will act different. In O/W emulsions electrolytes stabilize by electrostatic repulsions, but in W/O emulsion they stabilize because of dehydration of the surfactant. [3] To understand the behaviour of electrolytes in emulsions is necessary to know about the DLVO theory.

### 3.1.2. DLVO Theory

The DLVO (Derjaguin-Landau-Verwey-Oberveek) theory applies to O/W emulsions but has practical limitations in W/O emulsions, because this theory explains how a specific electrolyte concentration in the continuous phase stabilize emulsions by double-layer repulsions. [1] Since W/O emulsions has oils as continuous phase and electrolytes (salts) do not solubilize in oil, the DLVO theory is not used in that type of emulsions. If electrolytes are used in W/O emulsions, the salt is solubilized in the dispersed phase and double layer repulsions do not occur. [4]

In Figure 3.2 are represented the electrostatic repulsions and van der Waals attraction forces, and its summatory results in a potential energy representation with an energy barrier and a minimum energy point. The highest this barrier is, the most stable the emulsion will be, but only low concentrations of electrolyte increase the height of this barrier. If the concentration of electrolyte is above a certain value, this barrier decreases and disappear. This happens because at

high levels of electrolyte the attraction forces exceed the repulsion forces. So, in conclusion, to stabilize O/W emulsions low concentration of electrolyte can be used to increase the height of the energy barrier.

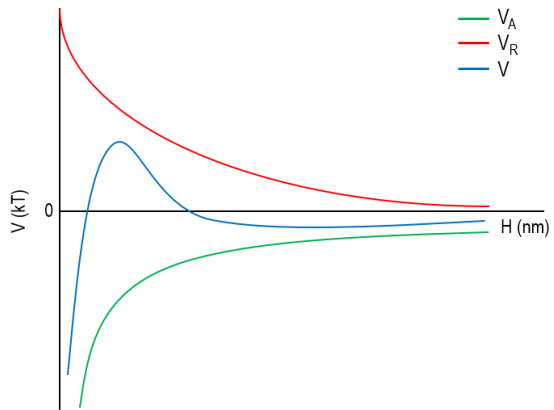


Figure 3.2: Representation of potential energy in front of particle distance.  $V_A$ : Van der Waals attraction forces;  $V_R$ : Electrostatic repulsion forces;  $V$ : Potential energy;  $H$ : distance between particles in nm.

## 3.2. SURFACTANTS

Surfactants are amphiphilic molecules with affinity for aqueous and oily phases due to his double polarity, which consists in a polar part (hydrophilic) and a non-polar part (lipophilic). To act correctly as a surfactant the molecule must have a minimum polarity and at least eight carbon atoms and only if this molecule can modify the interfacial tension, it can be named as a surfactant. [1]

### 3.2.1. Critical Micellar Concentration (CMC)

When a surfactant is dispersed in water, molecules orient the hydrophilic part to outside allowing contact with water and makes the lipophilic part create an internal space with affinity for oils. Under these circumstances, water presents humectant properties due to the decreasing of interfacial tension. If surfactant concentration is high enough, molecules arrange in a way to protect the hydrophobic groups. These are called micelles and the number of formed micelles depends on the surfactant properties such as number of polar groups or spatial distribution

(micelles could be spherical, lamellar, or threadlike). The concentration of surfactant when micelles begin to form is called Critical Micellar Concentration (CMC) and if that concentration is sufficiently high provided emulsions solubilizing activity of oils, which would be trapped at the inside of the micelle. If surfactant is dispersed in oil, the micelles are called reverse micelles because they orient the lipophilic part to outside. [1] [5]

### 3.2.2. Ionic surfactants

Surfactants may be classified by his ionic behaviour in ionic and non-ionic. Ionic surfactants also may be divided by their hydrophilic group, which can be cationic, anionic, and amphoteric.

### 3.2.3. Non-ionic surfactants

Non-ionic surfactants are characterized by their high compatibility with the other three types of ionic surfactant and their wide range of use of pH. In chemical terms, non-ionic surfactants may be classified as esters, amides, ethers, and others. The main type studied in this work are ester surfactants. [1]

## 3.3. NON-IONIC ESTER SURFACTANTS

Non-ionic ester surfactants are formed by Fischer-Speier esterification (in acidic medium) from fatty acids with polyethylene glycol or polyhydric alcohols as shown in Figure 3.3 (esterification reactions). If the reaction is between fatty acid and glycerine the result are glyceryl esters, but if glycerine is previously dehydrated to form polyglycerols the result is polyglyceryl esters, commonly named polyglycerides in cosmetic.

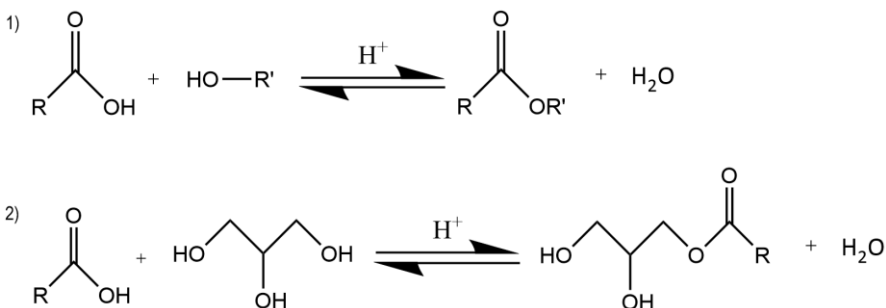


Figure 3.3: Esterification reaction: 1) Reaction of fatty acid with alcohol, 2) Reaction of fatty acid with glycerine.

### 3.3.1. Glyceryl Esters

Glyceryl esters are the product of the esterification of fatty acids with glycerine and they are mainly used as emulsifiers and emollients (skin softeners) in cosmetic, pharmaceutical, and alimentary industry. The number of fatty acid molecules reacting in the esterification reaction determines the glyceride type, i.e., with one molecule will form monoglycerides, with two molecules diglycerides and with three molecules triglycerides. About these three types, monoglycerides are the only studied in this work, three monoglycerides specifically: Glyceryl Oleate, Glyceryl Stearate and Glyceryl Laurate. [6]

#### 3.3.1.1. Glyceryl Oleate

Glyceryl Oleate (GO) is the glyceryl monoester of oleic acid. It is used in cosmetics as emulsifier of W/O emulsions at concentrations up to 5%, occurs as yellowish flakes or as soft semisolid and is soluble in acetone, ethanol, methanol, and mineral oil. GO can form liquid crystalline phases in presence of water. [7]

#### 3.3.1.2. Glyceryl Stearate

Glyceryl Stearate (GS) is the glyceryl monoester of stearic acid and is used in cosmetics as skin conditioner, emulsifier, co-emulsifier, and stabilizer. GS presents in white or cream-colored solid like wax and is soluble in ethanol, acetone, benzene, and mineral oil but insoluble in water. [8]

#### 3.3.1.3. Glyceryl Laurate

Glyceryl Laurate (GL) is the glyceryl monoester of lauric acid. Its use in cosmetics is as an emulsifier agent and skin conditioning; occurs as white solid wax, and is soluble in ethanol, acetone, benzene, and mineral oil but insoluble in water. [6] Of the three glycerides, GL is the less common in cosmetics.

### 3.3.2. Polyglyceryl Esters

Polyglyceryl esters are the result of the esterification of polyglycerine chains and fatty acids, and polyglycerine molecules are formed by polymerization of glycerine molecules and later distillation. According to the number of equivalents of glycerine and fatty acid, and the length of these fatty acids, the polyglyceryl esters can be hydrophilic. In this work are used polyglyceryl

esters of the previous glycerides with four glycerine molecules: polyglyceryl-4-oleate, polyglyceryl-4-stearate, and polyglyceryl-4-laurate (Figure 3.4.). [9]

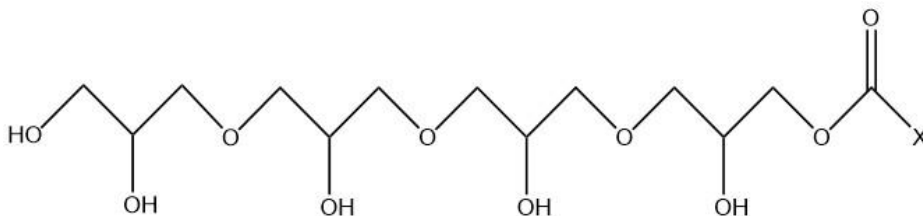


Figure 3.4: Polyglyceryl-4 ester. X: hydrocarbon chain of fatty acids

#### 3.3.2.1. Polyglyceryl-4-Oleate

Polyglyceryl-4-Oleate (PG4O) is the polyglyceryl monoester of oleic acid. It is used in cosmetics as an emulsifier agent and skin conditioning, usually in water-proof formulations such as suntan lotions and corporal paints. [9]

#### 3.3.2.2. Polyglyceryl-4-Stearate

Polyglyceryl-4-Stearate (PG4S) is the polyglyceryl monoester of stearic acid. PG4S is an emulsifier agent but is not commonly used in cosmetics. [9]

#### 3.3.2.3. Polyglyceryl-4-Laurate

Polyglyceryl-4-Laurate (PG4L) is the polyglyceryl monoester of lauric acid. It is used in cosmetics as an emulsifier agent and skin cosmetics, usually in formulations of skin cleansers. [9]

### 3.4. HYDROPHILIC-LIPOPILIC BALANCE (HLB)

The hydrophilic-lipophilic balance (HLB) described by Griffin in 1949 is a quantitative and empirical scale that establishes a number between 1 and 20 according to the hydrophilic or lipophilic activity of the emulsifier, considering hydrophilic an emulsifier with a value of 10 to 20 and lipophilic an emulsifier with a value of 1 to 10. The applications of the surfactants according to its HLB are summarized in Table 3.1.

Table 3.1: Application of surfactant according to their HLB value

HLB range	Use
1 – 3	Antifoaming agents
4 – 6	W/O emulsifying agents
7 – 9	Wetting agents
8 – 18	O/W emulsifying agents
13 – 15	Detergents
10 - 18	Solubilizing agents

Every type of oil requires an emulsifier system with a certain HLB number; this value constitutes the required HLB of the oil phase; if this phase has more than one component its required HLB is calculated by a weighted sum. [10] Once this required HLB is known, the surfactant or combination of surfactants is selected to match this value. However, in addition to the HLB, other considerations must be considered: the optimal concentration of surfactant (above its CMC), its viscosity, the use that the emulsion will have or the preparation method available. In this work, CMC is not considered quantitatively because the concentration of emulsifier added to the emulsion far exceeds the CMC value.

The HLB values of the emulsifiers used in this work are showed in Table 3.2 with their acronyms and chemical names.

Table 3.2: Emulsifiers and co-emulsifiers used in this work and their HLB values.

Chemical name	INCI	Acronym	HLB*
2,3-Dihydroxypropyl octadecanoate	Glyceryl Stearate	GS	3.8
2,3-Dihydroxypropyl dodecanoate	Glyceryl Laurate	GL	5.2
2,3-Dihydroxypropyl octadec-9-enoate	Glyceryl Oleate	GO	3.0
[3-[3-[3-(2,3-dihydroxypropoxy)-2-hydroxypropoxy]-2-hydroxypropoxy]-2-hydroxypropyl] octadecanoate	Polyglyceryl 4-Stearate	PG4S	6.0
[3-[3-[3-(2,3-dihydroxypropoxy)-2-hydroxypropoxy]-2-hydroxypropyl] dodecanoate	Polyglyceryl 4-Laurate	PG4L	11.0



[3-[3-[3-(2,3-dihydroxypropoxy)-2-hydroxypropoxy]-2-hydroxypropoxy]-2-hydroxypropyl] octadec-9-enoate	Polyglyceryl 4-Oleate	PG4O	8.8
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\*: Provider values

### 3.5. INGREDIENTS OF A COSMETIC EMULSION

Cosmetic emulsions have many ingredients classified depending on his utility. In addition to water and emulsifier agents, cosmetic emulsions may have emollients (skin conditioners), thickeners, electrolytes, antioxidants or preservatives, actives, and others (solar filters, colorants, and fragrance).

Emollients are ingredients with hydrating and repairing properties, but they are not humectants. Humectants are hygroscopic substances with the capacity to attract water from air humidity and retain it on skin, but emollients have a different effect on skin. Epidermis has cellules named corneocytes bounded by peptide bonds, but when air humidity is low the proteins of peptide bonds break releasing corneocytes and losing his barrier function. In this case, emollients can repair this barrier. Both humectants and emollients have moisturizing properties but act different in skin.

Thickeners are used in cosmetics as viscosity enhancers and stabilization agents. There are different types of molecules with the capacity to increase viscosity: synthetic polymers, vegetable gums, polyethylene glycol derivatives, some fatty esters, and mineral thickeners. All of them can increase the viscosity and give stability in gel and cream formulations.

Electrolytes, as described in Section 3.1.1 and Section 3.1.2, stabilize emulsions via electrostatic repulsions or dehydration of surfactants.

Antioxidants or preservatives are used in formulations to prevent degradation or rancidity of cosmetic products.

Active ingredients are ingredients with multiple functions. In cosmetics those functions apply to skin and hair care. Some of the active properties are: hydration, anti-ageing, antioxidant, soothing, cleansing, exfoliation, regenerative and brightening, among others.

Other ingredients like colorants, fragrances or solar filters may be used in cosmetics. Colorants and fragrances are used as presentation improvement of products, related to marketing techniques. Solar filters prevent the skin from UVA, UVB, IR and blue light and all the solar filters are synthetic.

In this work the ingredients will be named with the INCI name (International Nomenclature of Cosmetic Ingredients), not by their chemical name.

## **4. OBJECTIVES**

The goal of this study is to analyse the stabilizing effect of three different types of polyglycerides-glycerides in cosmetic emulsions. After that, two cosmetic emulsions are formulated with the combination of the most stable emulsion. Then, the specific objectives are:

- To determine which of the polyglycerides acts properly as emulsifier by studying emulsions stability.
- Once obtained the most stable emulsion, to use this base to prepare a cosmetic formulation, a moisturizer. Two oils of different nature are used to analyse their influence on the characteristics of the emulsion.

## 5. EXPERIMENTAL SECTION

The experimental part is divided in two parts. The first part is about the study of polyglycerides as emulsifiers and in the second part two cosmetic emulsions are formulated with the most stable result of the previous study.

### 5.1. MATERIALS AND REAGENTS

The basic formulation of all the emulsions with polyglycerides was the same. The oily phase contains the emulsifier and co-emulsifier with Paraffin Oil and the aqueous phase contains Deionized Water and Glycerine. The co-emulsifiers were: Glyceryl Stearate, Glyceryl Laurate, Glyceryl Oleate. The emulsifiers were: Polyglyceryl-4-Sterate, Polyglyceryl-4-Laurate and Polyglyceryl-4-Oleate. All emulsions were made in 400mL beakers, and the ingredients weighted with aluminium spatulas (solids) and plastic pipettes (liquid or fluid ingredients).

For the formulation of the two different emulsions the emulsifier and co-emulsifier were PG40 and GO, the actives were Natural Alpha Bisabolol, Urea, D-Panthenol, Aloe Vera Gel and Olive Oil and the conservative was Sensiva PA 40 (a mix of phenylpropanol, propanediol and caprylyl glycol). Also, the formulation had Glycerine as humectant, Sodium Chloride 99.9% pure as stabilizer electrolyte, Xantham Gum, Apifil (Polyethylen glycolated beeswax) and Stearic Acid as a consistency agent and a fragrance. The differences between the two formulations were the oils. One formulation had Paraffin Oil and the other had Vita Silky Fluid (a mix of tetradecane, dodecane and diethyl succinate) and Bergabest MCT (Caprylic/Capric Triglyceride). The provider names are in Appendix 1.

### 5.2. PREPARATION OF EMULSIONS

All the emulsions followed the same procedure. At first, were weighed the ingredients of the two phases separately on two different beakers and then heated to 75°C in a hot water bath. Then, the aqueous phase was added to the oily phase under mechanical stirring (with Sylverson L5M-A) for three minutes approximately incrementing the speed to 3500-4000 rpm. The emulsion

was cooled to 30°C under stirring (with Overhead Stirrer Hei-TORQUE 200) and finally homogenized with Sylverson L5M-A for one minute at 3500 rpm. The conditions of each sample are indicated in Tables 5.1 to 5.5.

Another previous step was needed on the emulsification process of the two developed formulations. Before warming the two phases, the aqueous phase was homogenized with Sylverson L5M-A because of the Xanthan Gum.

Table 5.1: Concentration of each ingredient in emulsions with Oleate family emulsifiers

Experiment	% (w/w) GO	% (w/w) PG4O	% (w/w) OIL	% (w/w) H2O	% (w/w) GLYCERINE
1	-	10.0	30.0	55.0	5.0
2	2.60	2.40	20.0	70.0	5.0
3	2.60	2.40	15.0	75.0	5.0

Table 5.2: Concentration of each ingredient in emulsions with Stearate family emulsifiers

Experiment	%(w/w) GS	% (w/w) PG4S	% (w/w) OIL	% (w/w) H2O	% (w/w) GLYCERINE
1	-	10.0	30.0	55.0	5.0
2	5.0	5.00	30.0	55.0	5.0
3	-	5.00	20.0	70.0	5.0
4	5.0	9.00	11.0	70.0	5.0

Table 5.3: Concentration of each ingredient in emulsions with Laurate family emulsifiers

Experiment	% (w/w) GL	% (w/w) PG4L	% (w/w) OIL	% (w/w) H2O	% (w/w) GLYCERINE
1	-	10.0	30.0	55.00	5.0
2	0.900	4.10	30.0	60.00	5.0
3	0.900	4.10	10.0	80.00	5.0
4	1.80	8.20	5.00	80.00	5.0
5	1.80	8.20	5.00	79.25*	5.0

\*: The remaining 0.75% was Sepinov EMT (stabilizing agent)

Table 5.4: Concentration of each ingredient in cosmetic emulsions with Paraffin Oil

Experiment	%(w/w) GO	% (w/w) PG40	% (w/w) OIL	% (w/w) H2O	% (w/w) NaCl	% (w/w) XANTHAN GUM	% (w/w) OTHER INGREDIENTS*
1	2.60	2.40	15.00	72.45	-	-	7.550
2	3.25	3.00	15.00	71.20	-	-	7.550
3	3.25	3.00	14.25	71.20	0.75	-	7.550
4	3.25	3.00	14.50	61.35	0.50	0.50	16.90

\*: Other ingredients include actives, preservatives, glycerine, and fragrance.

Table 5.5: Concentration of each ingredient in cosmetic emulsions with natural origin oils

Experiment	%(w/w) GO	% (w/w) PG40	% (w/w) OILS* <sup>1</sup>	% (w/w) H2O	% (w/w) NaCl	% (w/w) XANTHAN GUM	% (w/w) OTHER INGREDIENTS* <sup>2</sup>
1	2.60	2.40	15.0	72.85	-	-	7.150
2	3.70	4.00	14.0	71.40	-	-	6.900
3	4.25	4.60	13.0	70.85	-	-	7.300
4	1.00	6.00	10.5	71.20	0.75	-	10.55
5	2.00	4.00	10.5	73.20	0.75	1.0	8.550

\*<sup>1</sup>: Include Vita Silky Fluid, Bergabest MCT and Olive Oil (provider names). \*<sup>2</sup>: Other ingredients include actives, preservatives, glycerine, and fragrance.

### 5.3. INSTRUMENTS AND CHARACTERIZATION METHODS

Once made the emulsions, their characterization was done with four instruments: Rheometer R/S-CPS plus to study their rheometry, Centrifuge Hettich EBA 200 and LUMiSizer to study stability with time and temperature as controlled parameters and Microscope OPTIKA B-500 to qualitatively observe droplet size.

### 5.3.1. Rheometer R/S-CPS plus

The rheologic behaviour of the emulsions was studied with the Rheometer R/S-CPS plus (Figure 5.1). This instrument is a rotational rheometer type, which means it controls the shear stress and permits to made measures of viscosity, thixotropy or relaxation time among others. In this work only viscosity over time is measured at constant rate.

Before measurements, rheometer was calibrated as described in SOP (Standard Operating Procedure). Once calibrated, 8mg of the cream were putted on the plate and pressed with a metal cone to start the study. This consist in two parts: the first part serves to condition the sample and the second part is the main study of viscosity. The first part is at constant shear rate value of 5 1/s for 60 seconds and the second part measure the viscosity increasing shear rate from 5 to 100 1/s and taking 10 measures every three seconds. All the measure were taken at room temperature (24-25°C).



Figure 5.1: Rheometer R/S-CPS plus

### 5.3.2. Centrifuge Hettich EBA 200

The centrifuge shows how stable were emulsions over time. This is not a numeric result but provides information about stability that is useful to analyse better the stability with LUMiSizer. At first, one test at 5000 rpm for 10 minutes was realized. If the result of the test was a complete separation, this was immediately stopped, but if the emulsion did not separate, is realized another test at 5000 rpm for 89 minutes. The second test gives better information about the stability of the emulsion.

### 5.3.3. LUMiSizer

The equipment consists in the dispersion analyser LUMiSizer (Figure 5.2) and a computer with SEPVView software. First, the sample cells were filled with the emulsions to analyse and putted into the centrifugate system. Then, were configurated the temperature, centrifugation velocity, profiles, and time. In this case the parameters were 45°C, 4000rpm, 300 profiles and 80 minutes respectively. Those parameters simulate three months of stability at 25°C without centrifugation.



Figure 5.2: Dispersion Analyzer LUMiSizer

### 5.3.4. Microscope OPTIKA B-500

Finally, the droplet size was observed with the microscope. The goal was to compare the emulsions and explain the differences observed between them. The lens had 40x magnification, 0.65 numerical aperture, 160mm tube length and 0.17mm thickness of cover glass.

### 5.3.5. Techniques to verify emulsion types

To verify if the emulsion obtained is W/O or O/W, two techniques were used.

In the first one, a bit portion of cream is stirred in water. In case the cream solubilizes in water, the emulsion was O/W but if a big droplet was formed the emulsion was W/O.

In the second technique, a single droplet of water-soluble colorant (in this case methylene blue) is added to a bit portion of the emulsion. If the colour of the emulsion was intense, the emulsion was O/W but if the colour does not change significantly, the emulsion was W/O.



## 6. RESULTS AND DISCUSSION OF EMULSIONS WITH POLYGLYCERIDES AS EMULSIFIERS

The study of emulsion stability using emulsifiers of different glyceride families was started with qualitative centrifugation tests. Table 6.1 shows the result of the tests.

Emulsions with oleate family emulsifiers showed great stability at centrifugation test. In all the three experiments was formed a W/O emulsion because of the HLB value of emulsifiers. Experiment 1 was emulsified only with PG4O, which HLB value is 8.8 (Table 3.2) and knowing that required HLB of Light Paraffin Oil is 4 it was expected a separation of the emulsion. [11] With experiments 2 and 3 the emulsion has PG4O and GO in a proportion that results in a HLB value of 5.8. The difference between experiment 2 and 3 is the concentration of Paraffin Oil. Experiment 3 has less Paraffin Oil, therefore, the resulting emulsion is more concentrated of dispersed phase and the viscosity is higher respect to experiment 2. Thus, experiment 3 is more stable than experiment 2 because of the increasing viscosity.

About emulsions with stearate family emulsifiers, the results were not what was expected. Experiment 1 emulsion with PG4S did not emulsify, the phases were clearly separated. In experiment 2 is added GS but keeping Paraffin Oil concentration, and emulsion also separates. In experiment 3 Paraffin Oil concentration is significantly decreased and GS is removed to verify if PG4S can emulsify by their own, but it goes wrong again. The final experiment has PG4S and GS in a proportion that made the HLB value be 4.6 and is reduced again the Paraffin Oil concentration. During the preparation of experiment 4, when emulsion was agitated a foam-like cream was formed, but at centrifuge test it separates. At this point, no more experiments with PG4S and GS were done and only the last experiment was characterized.

With laurate emulsifiers all the tests were wrong, so to stabilize the last experiment polymeric compounds used to stabilize O/W emulsions were added. The compounds are Hydroxyethyl Acrylate and Sodium Acryloyldimethyl Taurate Copolymer, and his commercial name is SEPINOV EMT 10. With the addition of this polymeric compounds, the viscosity of the emulsions increases

significantly, making emulsion more stable but not totally. Figure 6.1 shows the appearance of the emulsions obtained with the three families of emulsifiers.



Figure 6.1: Resulted emulsions. A: Experiment 4 stearate emulsion; B: Experiment 5 laurate emulsion; C: Experiment 3 oleate emulsion

Table 6.1: Centrifugation tests of emulsions with Oleate, Stearate and Laurate family emulsifiers

Experiment	Centrifuge test at 5000 rpm during 10 min	Centrifuge test at 5000 rpm during 99 min
<b>Oleate family emulsions</b>		
1	Not noticeable separation at the surface.	Separation at the surface.
2	Do not separate	Small separation at the surface
3*	Do not separate	Not noticeable separation at the surface.
<b>Stearate family emulsions</b>		
1	Test not realized*	Test not realized*
2	Test not realized*	Test not realized*
3	Small separation at the bottom	Complete separation of the phases
4*	Small separation at the bottom	Complete separation of the phases. Top phase looks like foam

### Laurate family emulsions

1	Complete separation of the phases	Test not realized*
2	Complete separation of the phases	Test not realized*
3	Complete separation of the phases	Test not realized*
4	Complete separation of the phases	Test not realized*
5*	Small separation at the surface	It appears more separated phase, but do not occur complete separation

\*Experiments characterized

As indicated in Table 6.1, the last experiment of each family was characterized with Rheometer R/S-CPS plus and LUMiSizer to make a quantitative evaluation of the emulsion stability.

### 6.1. RHEOMETRIC MEASUREMENTS

Rheology is the science that studies how materials or fluids deform and flow respectively. There is another term related with rheology, the rheometry. Rheometry studies both equipment and measurements allowing to obtain rheological information. Therefore, rheometry is complementary to rheology. In this work rheometric studies were performed to determine the viscosity of the emulsions, directly related with stability. The results of rheometric measurements give a Viscosity (cP) - Shear rate (1/s) graphic and a table with these and other related values. Figure 6.2 shows the graphic obtained with oleate emulsion (experiment 3 in Table 6.1); the other graphics are in Appendix 2.

It can be seen how viscosity decreases when shear rate values increase and how at certain shear rate value the viscosity stabilizes, so can be concluded that emulsions behave like non-Newtonian compounds. In that case, the lower the shear rate, the longer it will take to attain the viscosity. [12]

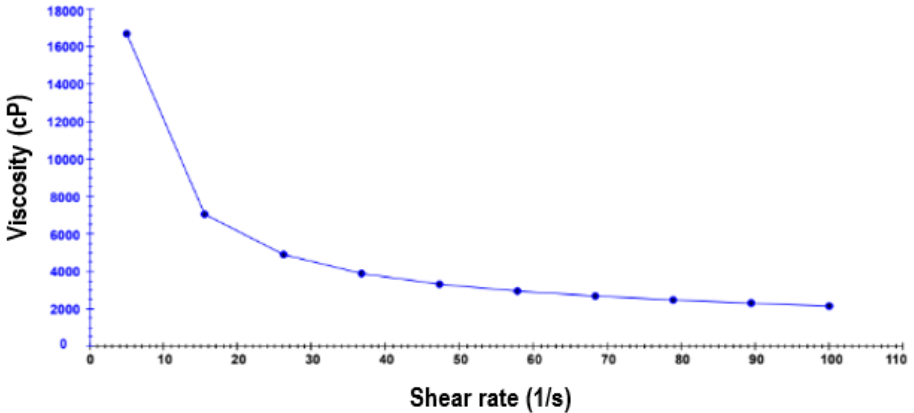


Figure 6.2: Rheometric study graphic of Experiment 3 oleate emulsion

Since ten measurements of viscosity are always taken, the company establishes the fourth value as the viscosity of the emulsion. So, the values of viscosity of the three studied emulsion are 3899 cP (Experiment 3 oleate emulsion, Figure 6.2), 1562 cP (Experiment 4 stearate emulsion, Appendix 2.1), and 7462 cP (Experiment 5 laurate emulsion, Appendix 2.2). Although laurate emulsion has the higher viscosity, this does not mean that it is necessarily the most stable emulsion. The LUMiSizer analysis will establish the real stability of the emulsions.

## 6.2. STABILITY STUDY: LUMISIZER OBSERVATIONS

LUMiSizer is a dispersion analyser with photocentrifugation system at controlled temperature. The equipment uses STEP (Space and Time resolved Extinction Profiles) technology, based on the percent of light transmitted through the emulsion. The light goes through the cell in parallel and is detected by 2087 detectors of CCD-line to subsequently be converted into extinction profiles. [13] These profiles start being red and finish in green to differentiate the ending and beginning of the emulsions state and determine if it occurs any instability type. [14] The recorded profiles are represented in a graphic that relates transmission of light in % with position in mm.

Experiment 3 emulsion with PG4O and GO graphic (Figure 6.3) shows an almost perfect stability in three months, only two extinction profiles at the beginning look different because of a small migration of oil droplets to the surface.

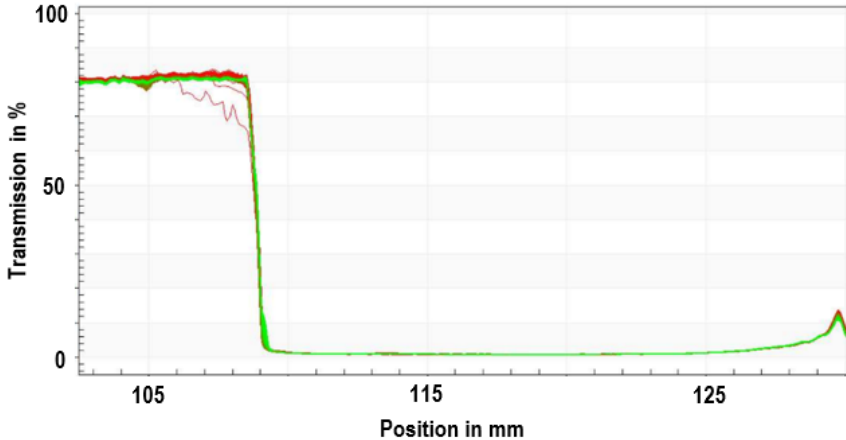


Figure 6.3: LUMiSizer stability analysis graphic of experiment 3 emulsion with PG4O and GO

Experiment 4 emulsion with PG4S and GS graphic shows a clearly unstable emulsion. As shown in Figure 6.4, the graphic is divided in three regions. In region A the transmission is between 90% and 70% because of phase separation. As the emulsion is W/O, water droplets migrate to the bottom of the cell causing phase separation and allowing light to go through the emulsion. In region B there are still many droplets of water due to the high concentration of dispersed phase and the light cannot pass through the emulsion. Finally, in region C a foam formed by agitation made easier the vaporization of water at 40°C, preventing light from passing as it should and decreasing transmission.

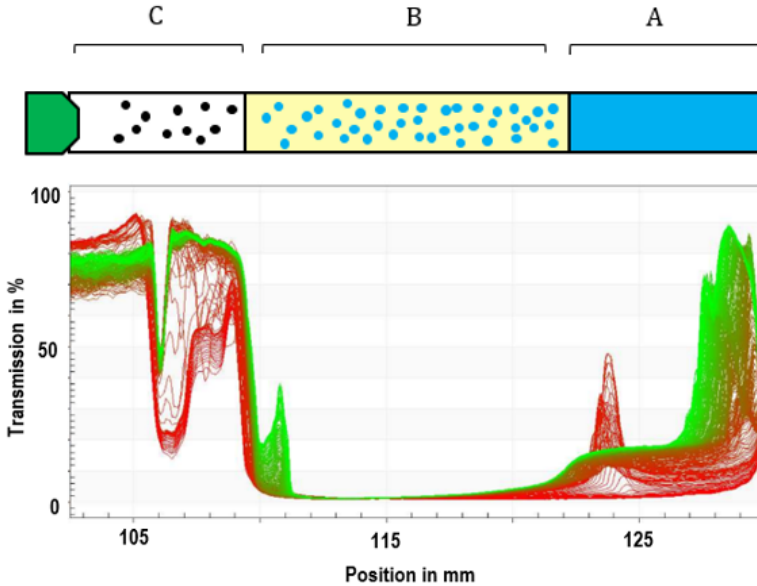


Figure 6.4: LUMiSizer stability analysis graphic of experiment 4 emulsion with PG4S and GS. Blue droplets: dispersed water; Black droplets: volatilized water

In the representation of Experiment 5 with PG4L and GL (Figure 6.5) is observed an increase of transmission at the surface. Considering that the emulsion is O/W, in this case this is due to the creaming of dispersed oil droplets.

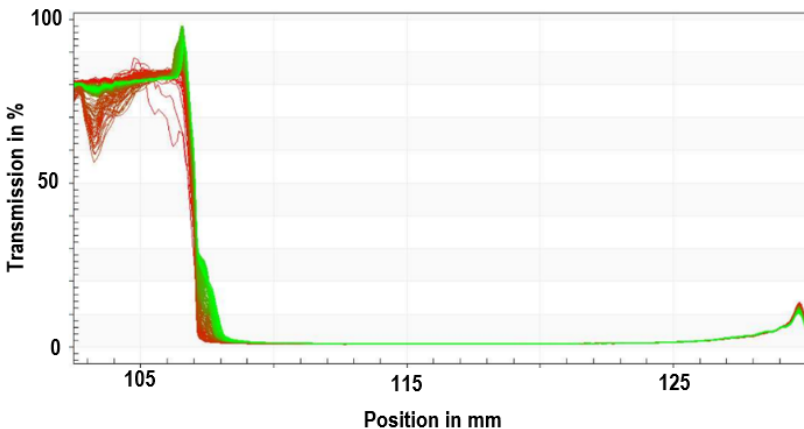


Figure 6.5: LUMiSizer stability analysis graphic of experiment 5 emulsion with PG4L and GL

### 6.3. MICROSCOPE OBSERVATIONS

The microscope images of the three emulsions are showed in Figure 6.6. Comparing the three of them, it can be observed that emulsion with PG4O and GO is more polydisperse and the droplet size is smaller than the other emulsions, verifying it is the most stable emulsion. It cannot be appreciated instability types in images, but during the observation under microscope a movement of droplets on emulsions was observed. In case of PG4O and GO emulsion droplet move slowly and did not formed floccules, but in PG4S and GS emulsion the droplets agglomerates creating new floccules causing creaming and coalescence. The emulsion with PG4L and GL had the droplets immobilized by the effect of the thickener SEPINOV EMT, but these droplets are way bigger in comparison with the PG4O and GO emulsion.

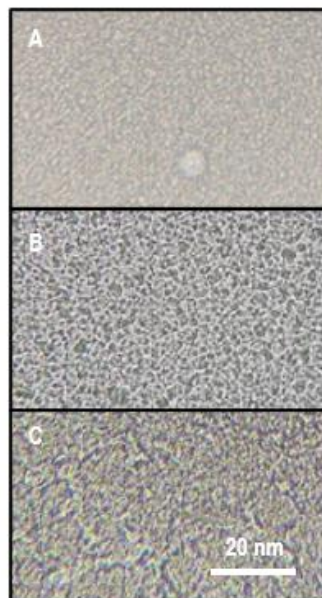


Figure 6.6: Images taken with microscope OPTIKA B-500. A: Oleate emulsion; B: Laurate emulsion; C: Stearate emulsion.

After the characterization and study of the three emulsions were concluded that emulsion with oleate emulsifiers gives better results and the most stable emulsion. Using the same proportion of PG4O and GO that in experiment 3 of Table 5.1 (p. 19), two cosmetic emulsions were formulated.

## 7. RESULTS AND DISCUSSION OF COSMETIC EMULSIONS

The first complete emulsions were those summarized in Table 5.4 (p. 19): oleate emulsifiers, Paraffin Oil and different actives, fragrances, and preservatives. Four emulsions of different composition were prepared.

As in the previous study, centrifugation tests (Table 7.1) were done on the cosmetic emulsions to observe their behaviour. If the emulsion was unstable and separate other stabilization agents were added.

Since the emulsions with Paraffin Oil come from Experiment 3 PG4O and GO emulsion good behaviour was supposed, but due to the addition of actives and the rest of ingredients the emulsions show little instabilities at centrifugation tests. To stabilize the emulsions, 0.75% of Sodium Chloride was added to promote electrostatic repulsions, and it seems to work since the separation at the surface is smaller. It is important to note that DLVO theory does not explain the stability increase in the case of this W/O emulsion but is known that electrolytes such as Sodium Chloride can stabilize W/O emulsion by dehydration of the surfactant. [3] In the final experiment 0.50% of Xanthan Gum was added to increase the viscosity and the concentration of Sodium Chloride was decreased to 0.50% to prevent the separation of the emulsion. Experiment 4 was the better result and the last experiment done of a cosmetic emulsion with Paraffin Oil and was characterized the same way than the previous study.

The next step was to change the paraffin oil for oils of natural origin to try to obtain a more natural emulsion. The composition of the checked emulsions was summarized in Table 5.5 (p.19). Emulsions with natural origin oils were more complicated to stabilize. The first three experiments were done with the same components of Experiment 3 PG4O and GO emulsion but increasing the concentration of emulsifier and co-emulsifier. The three experiments gone wrong, probably due to the polarity of the oils. Searching information about the required HLB of oils it was concluded that the proportion of emulsifier and co-emulsifier could be wrong. [15] The formulation



had three different oils to consider: Vita Silky Fluid, Bergabest MCT and Olive Oil. Vita Silky Fluid is the mix of three components: two hydrocarbon oils (tetradecane and dodecane) and an ester (diethyl succinate) in less proportion. The provider does not give the required HLB of the ingredient but considering that it is almost a hydrocarbon, Vita Silky Fluid will be a non-polar oil with a required HLB similar to that of Paraffin Oil. Bergabest MCT is caprylic/capric triglyceride, the triglyceride of coconut extract oil, and has a required HLB value of 5 on W/O emulsions given by provider. Olive Oil has four fatty acids in his composition: oleic acid, palmitic acid, linoleic acid, and linolenic acid. This makes difficult to calculate its required HLB and the provider does not give the value. Knowing the fatty acids required HLB values, it can be estimated a required HLB value for Olive Oil: taking into account the concentration of each oil in the formulation, an approximated value of required HLB value of 3-4 was considered.

On experiment 4 GO concentration was increased and PG4O concentration was decreased making the HLB value of the mixture of 3.8. Also, 0.75% of Sodium Chloride and 2% of Apifil (beeswax that increases viscosity) were added, but the emulsion separated at the end of the centrifuge test. Since the beeswax modifies the required HLB of oils and it is difficult to obtain the required HLB value, in experiment 5 0.50% Glyceryl Stearate and 0.50% Stearic Acid were used and approximately calculated a new HLB value of 4,85 of the emulsifier system. Moreover, the same concentration of Sodium Chloride and 1% of Xanthan Gum was added. The result of the centrifuge test is considerably better than the other results. Experiment 5 is taken as the final experiment and characterized.

Table 7.1: Centrifugation tests of cosmetic emulsions

Experiment	Centrifuge test at 5000 rpm during 10 min	Centrifuge test at 5000 rpm during 99 min
<b>Emulsions with Paraffin Oil</b>		
1	Do not separate	Small separation at the surface
2	Do not separate	Small separation at the surface
3	Do not separate	Smaller separation at the surface than experiment 2

4	Do not separate	Smaller separation at the surface than experiment 3 but bigger than experiment 3 of Table 6.1
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### Emulsions with natural origin oils

1	Separation at the surface	Complete separation of phases
2	Separation at the surface	Complete separation of phases
3	Separation at the surface	Complete separation of phases
4	Small separation at the surface	Separation at the surface
5	Not noticeable separation at the surface	Smaller separation than experiment 4 but still notorious.

## 7.1. RHEOMETRIC MEASUREMENTS

Experiment 4 emulsion with Paraffin Oil had a viscosity of 1525 cP and Experiment 5 emulsion with natural origin oils had a viscosity of 2030 cP. The graphics are shown in Appendix 2.3 and 2.4. Although these values are similar or even with natural oils the viscosity is slightly higher, this does not ensure the stability of the emulsions. Viscosity only helps the emulsion to increase the stability, but if the emulsification system does not work the emulsion will not be stable.

## 7.2. STABILITY STUDY: LUMISIZER OBSERVATIONS

Figure 7.1 shows the stability representation graphic of Experiment 4 emulsion with Paraffin Oil. At the beginning of the study (red profiles) the emulsion remains stable, but at the end (green profiles) two peaks appear at the top of the cell (110 nm). These peaks represent a separation of oil phase because of water droplets migration to the bottom of the cell.

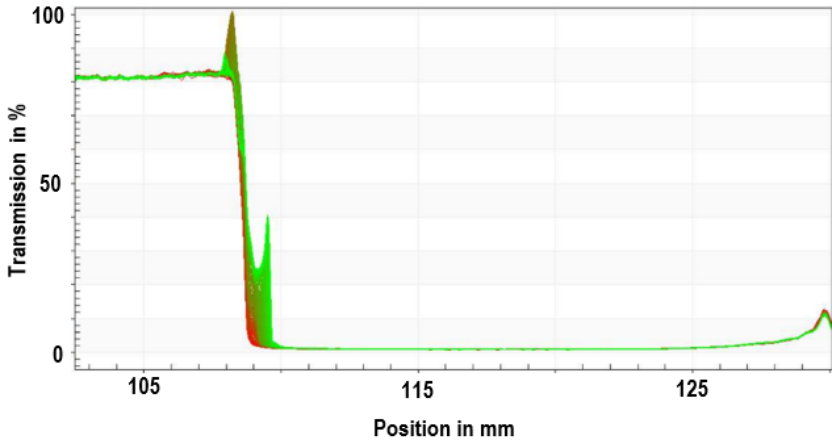


Figure 7.1: LUMiSizer stability analysis graphic of Experiment 4 emulsion with Paraffin Oil.

Figure 7.2 shows the stability representation graphic of Experiment 5 emulsion with natural origin oils. In this case, the emulsion started to separate at the beginning and the volume of separated oil increases over time. The result is a significant separation of oil phase at the surface, which means the emulsion was not stable at three months.

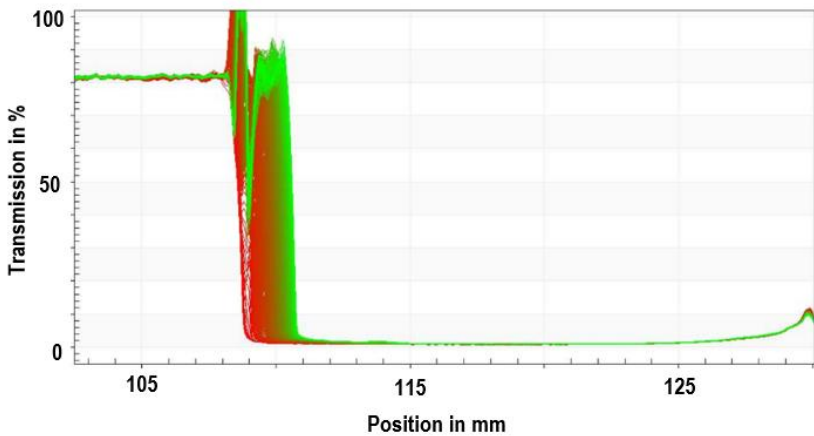


Figure 7.2: LUMiSizer stability analysis graphic of Experiment 5 emulsion with natural origin oils.

### 7.3. MICROSCOPE OBSERVATIONS

The microscope images (Figure 7.3) confirmed the results of the LUMiSizer, the most stable emulsion is the one with Paraffin Oil. Emulsion A is similar to the emulsion of Experiment 3 with PG40 and GO but Emulsion B has more floccules, and the dispersed droplets are bigger than the Emulsion A.

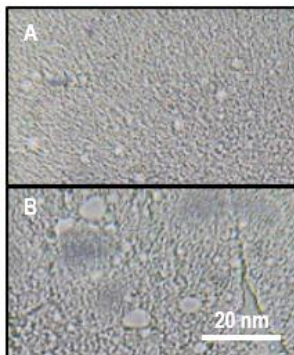


Figure 7.3: Images taken with microscope OPTIKA B-500. A: Emulsion with Paraffin Oil; B: Emulsion with natural origin oils.

## 8. CONCLUSIONS

Regarding the first objective of the study, the results with the three pairs of glycerides allow us to conclude:

- PG4O was the emulsifier with the better results with GO as co-emulsifier. Using the appropriate concentrations of both compounds it is possible to obtain a basic W/O stable emulsion.
- PG4L did not work well as emulsifier with the co-emulsifier GL. Their HLB value are 11 and 5.3 respectively so the only option is a O/W emulsion type since was difficult to obtain an HLB value under 6 with the mix of the emulsifiers. With high concentration of emulsifier, it was not possible to stabilize the emulsion and a thickener and stabilizing agent were needed. Then, PG4L is not a proper main emulsifier but can be considered as co-emulsifier in O/W emulsions with another emulsifier agent.
- PG4S with GS did not work properly either, probably because its low HLB. While doing this study it was found that another provider had PG4S with a higher HLB value, but it was too late to characterize and do the emulsions.

With the pair PG4O and GO complete cosmetic formulations were prepared using oils of different origin:

- In the cosmetic emulsion with Paraffin Oil the emulsion remains stable, but not as stable as the previous emulsions without all the active ingredients.
- If Paraffin Oil is changed by other oils with different required HLB value, the proportion of emulsifier and co-emulsifier change. In this work was not possible to stabilize the emulsion with the selected oils with PG4O and GO, because the required HLB of all the used oils was not bibliographically disponible and neither given by providers.

Although the results have not been entirely positive, with additional work it could be improved: the new oils required HLB may be determined experimentally and then, the correct proportion of emulsifier and co-emulsifier could be determined.

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## 10. ACRONYMS

CMC: Critical Micellar Concentration

cP: centi Poise (0.001 Pa·s)

DLVO: Derjaguin-Landau-Verwey-Oberveek

GL: Glyceryl Laurate

GO: Glyceryl Oleate

GS: Glyceryl Stearate

HLB: Hydrophilic-Lipophilic Balance

IR: InfraRed

O/W: Oil in Water

PG4L: Polyglyceryl 4-Laurate

PG4O: Polyglyceryl 4-Oleate

PG4S: Polyglyceryl 4-Stearate

UVA: UltraViolet A

UVB: UltraViolet B

W/O: Water in Oil



# APPENDICES



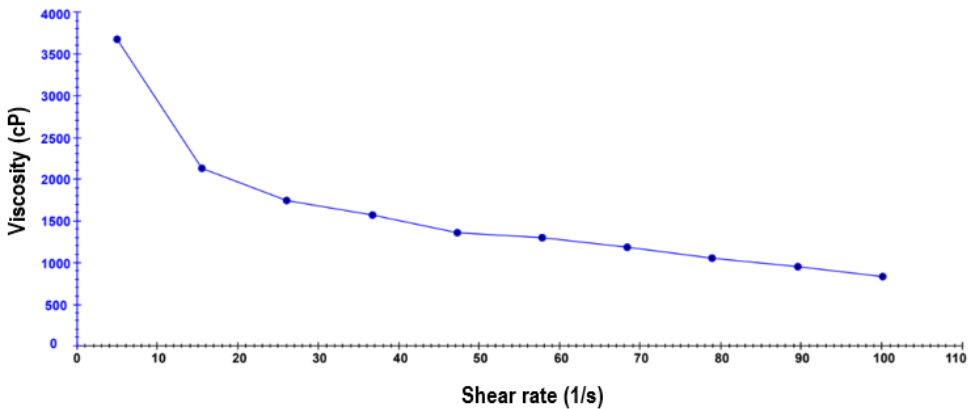
## APPENDIX 1: INGREDIENTS PROVIDERS

Ingredient	Cosmetic use	Provider
Paraffin oil	Emollient	Sucesores de Jose Escuder S.L.
Glycerine	Humectant	Caila & Pares
Glyceryl Stearate	Emulsifier, co-emulsifier and consistency agent	Quimidroga
Glyceryl Laurate	Co-emulsifier and preservative	Colonial Chemical Inc.
Glyceryl Oleate	Emulsifier and co-emulsifier	Evonik
Polyglyceryl 4-Stearate	Emulsifier	SABO S.p.A
Polyglyceryl 4-Laurate	Emulsifier	SABO S.p.A
Polyglyceryl 4-Oleate	Emulsifier	Iwase Cosfa Europe
Titrated extract of Asiatic Pennywort	Active	Gattefosse
Natural Alpha Bisabolol	Active	Sucesores de Jose Escuder S.L.
D-Panthenol	Active	Disproquima S.A.
Aloe Vera Gel	Active	Provital S.A
Olive Oil	Emollient and active	Gustav Hess
Sensiva PA 40	Preservative	DKSH
Sodium Chloride 99.9% pure	Stabilizing electrolyte	Sucesores de Jose Escuder S.L.
Vita Silky Fluid	Emollient	Quimivita
Urea	Active	Sucesores de Jose Escuder S.L.
Bergabest MCT	Emollient	Sucesores de Jose Escuder S.L.
Stearic Acid	Consistency agent	Quimidroga
Apifil	Emulsifier and consistency agent	Gattefosse

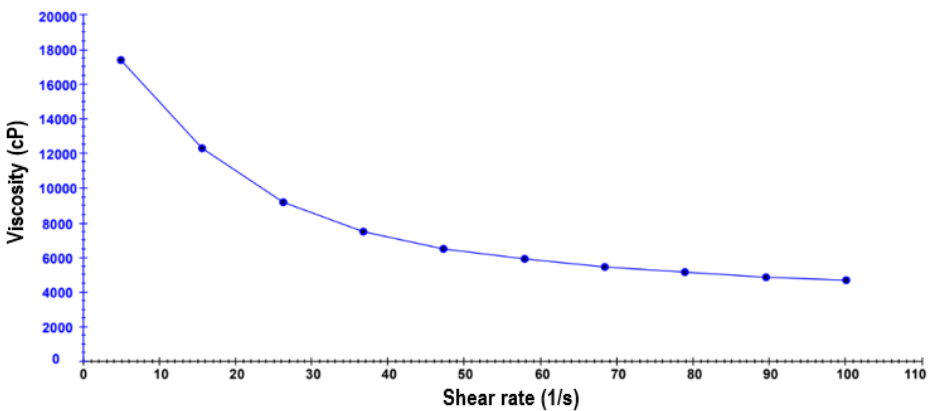


## APPENDIX 2: RHEOMETRIC GRAPHIC RESULTS

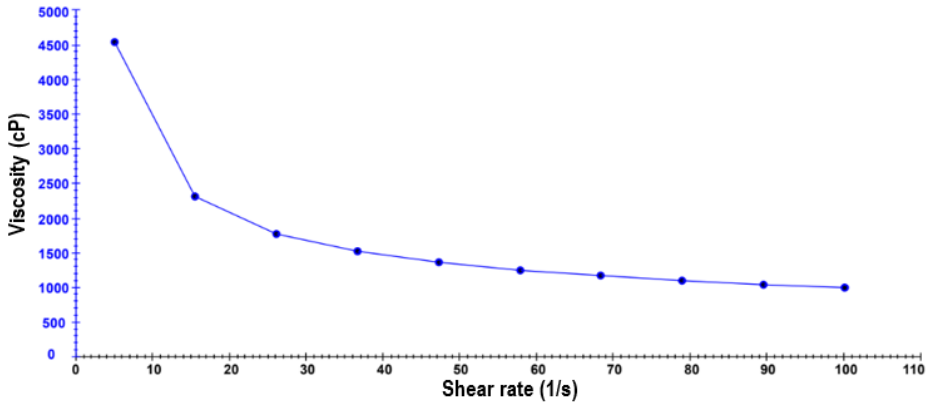
### APPENDIX 2.1: EXPERIMENT 4 STEARATE EMULSION



### APPENDIX 2.2: EXPERIMENT 5 LAURATE EMULSION



### APPENDIX 2.3: EMULSION WITH PARAFFIN OIL



### APPENDIX 2.4: EMULSION WITH NATURAL ORIGIN OILS

