Universidade de Lisboa

Faculdade de Farmácia

Formulation of sustainable concentrated rinse-off products

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Mestrado Integrado em Ciências Farmacêuticas

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Formulation studies of sustainable concentrated rinse-off products

Ana Sofia Valente Rocha

Monografia de Mestrado Integrado em Ciências Farmacêuticas apresentada à Universidade de Lisboa através da Faculdade de Farmácia

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Resumo

Contexto: Nos últimos trinta anos, os produtos de higiene concentrados, têm sido alvo de especial atenção, como alternativa mais ecológica aos produtos de higiene tradicionais. Tal deve-se às inúmeras vantagens que a versão concentrada apresenta, já que a redução da quantidade de água do produto permite uma redução do conteúdo nominal, o que leva ao menor uso de material de acondicionamento primário, bem como à possibilidade de transporte de mais unidades de produto numa só viagem, e portanto menos viagens e uma redução da carga transportada com menores consumos de combustível e consequentemente a uma diminuição da pegada ambiental. Contudo, a investigação e desenvolvimento de produtos de higiene sustentáveis é um trabalho extenso que requer conhecimentos sobre a totalidade do ciclo de vida do produto e em especial uma profunda compreensão da teoria dos comportamentos de tensioativos e de como formular para se atingirem os atributos desejados do produto.

O objetivo deste estudo foi adquirir conhecimentos sobre a microestrutura de misturas simples de tensioativos a várias concentrações, visando manter as características de desempenho e de eficácia a que os consumidores estão habituados, sobretudo em termos de baixo potencial irritativo e na boa formação de espuma.

Materiais e Métodos: Quatro tensioativos diferentes foram utilizados sendo dois tensioativos aniónicos, um tensioativo anfotérico e outro não-iónico replicando as misturas mais básicas presentes no mercado. Prepararam-se 60 formulações com concentrações e rácios diferentes de tensioativos. Posteriormente, procedeu-se a avaliação das suas características macroscópicas e da sua microestrutura, através da observação ao microscópio ótico com luz polarizada. Os valores de viscosidade e pH foram também determinados.

Resultados: A aparência macroscópica dos sistemas de tensioativos variou de uma solução aquosa transparente até um gel de alta viscosidade opaco. Nas concentrações mais baixas de tensioativo total (10-20%) obtiveram-se soluções isotrópicas, de fluxo Newtoniano e baixa viscosidade. Com um aumento da concentração total de tensioativo verificou-se um aumento da viscosidade e um comportamento pseudoplástico do gel com aparecimento de propriedades birrefringência e anisotropia ao microscópio ótico de luz polarizada, o que indica a presença de cristais líquidos nas misturas.

Conclusão: Foi alcançado o objetivo de formular produtos de higiene com uma concentração significativamente reduzida em comparação com as opções tradicionais. Obtiveram-se soluções de cristais-líquidos de tensioativos. Não obstante, tratam-se de resultados preliminares que necessitam de mais estudos para alcançar os resultados desejados.

Palavras-chave: Tensioativos, produtos de enxaguamento, microestrutura

Abstract

Purpose: Concentrated rinse-off products have, for the past three decades, been receiving more attention as a means of providing a more ecological alternative to traditional wash-off products, because of their advantages when it comes to sustainability. Reducing the amount of water transported allows the reduction of the products volume, leading to more product unities being distributed in one trip and therefore less trips, and weight, leading to lower fuel consumptions and thus a decrease on the carbon footprint, as well as reduction of packaging material.

However, research and development of sustainable rinse-off products is a strenuous job that requires knowledge of the entire life cycle of the product and in particular a understanding of surfactant science, and how to manipulate formulations to attain the desired product attributes.

The purpose of this study was to acquire knowledge about the microstructure and rheological behaviour of simple surfactant mixture at various concentrations, their microstructures and rheology, while aiming to maintain the performance characteristics desired by consumers, in terms of product use, mildness and foaming.

Materials and Methods: Four different surfactants were used, two anionic surfactants as primary surfactants and one amphoteric and another non-ionic surfactant, used as secondary surfactants, replicating basic surfactant blends on the market. Thus, 60 formulations were prepared with different surfactant combinations at different ratios. Subsequently, the formulations were observed under an optical microscope with polarized light, their macroscopic characteristics were identified, and their viscosity and pH were obtained.

Results: The physical appearance of these systems varied from transparent aqueous solution to an opaque gel with high viscosity. At low concentrations of total surfactant (10-20%), isotropic solutions, presenting a low viscosity Newtonian flow were present. As total surfactant concentration was increased an increase in viscosity was observed and the gels became shear-thinning, presenting birefringence when observed under microscope polarised light, which indicated the presence of liquid crystals in the blends.

Conclusion: The goal to obtain concentrated surfactant systems was achieved, and surfactant liquid crystals were obtained.

This study provides possible explanations regarding the results obtained and point out factors that should be tackled to overcome the formulation problems.

Keywords: surfactants, sustainable, concentrated, liquid-crystals, cosmetic, rinse-off product.

Abbreviations

SC – *Stratum corneum*

CMC - Critical Micellar Concentration

APG - Alkyl Poly Glucosides

SLES – Sodium Laureth Sulfate

CAPB – Cocamidopropyl Betaine

DLS – Disodium Lauryl Sulfosuccinate

LG – Lauryl Glucoside

SLS – Sodium Lauryl Sulfate

TEWL – Transepidermal Water Loss

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1 INTRODUTION

1.1 The Struture of the Skin

Skin is the number one target for most cosmetics and personal care products. And while cosmetics are not intended to change the structure of the skin, they can be used to cleanse, protect, moisturize, peel, or cover this organ (1).

The skin is the largest organ of the human body, presenting around 1.5-2 m^2 (2). It is an integumentary organ, responsible for the protection against injury, pathogens and dehydration, sensory feeling, metabolic pathways, such as the synthesis of vitamin D and the regulation of body temperature. It is composed by three main layers, the epidermis, the dermis and the hypodermis, from the outer to the inner layer, respectively, as portrayed in Figure 1(2–5).

The epidermis forms the outer layer of the skin and it consists of stratified squamous epithelial tissue, composed by four or five layers of keratinocytes namely, from the inside out, the *stratum basale* is a single layer of keratinocytes at their initial stages of differentiation, being characterized by its intense mitotic activity; the stratum spinosum, where differentiation begins; the stratum granulosum consist of layers of keratinocytes undergoing their final stages of differentiation and keratinization; and the stratum corneum**,** composed by an outermost layer of corneocytes(6).

The *stratum corneum* (SC) is a protective layer that consists of 15-20 layers of fattened keratinocytes that have undergone nucleus degradation, loss of DNA and formation of a cornified envelope. These nonnucleated keratinized dead cells shed and are replaced by new ones. These new cells at the base of the epidermis divide rapidly and push the older cells closer to the surface. This turnover of the *stratum corneum* takes on average 14 days in an adult (7).

A fifth epidermal layer, the *stratum lucidum*, can be found in the palms and soles, consisting of a thin, translucent layer of extremely flattened eosinophilic cells. The nuclei and organelles of the eosinophilic cells have been lost and the cytoplasm consists of a densely packed keratin filament (2).

Underneath the epidermis comes the dermis a layer of connective tissue which is mainly composed by three types of microfibers. Collagen that provides strength to the skin, elastin that provide its stretching ability, and reticular fibres, forming a complex fibrous matrix infiltrated with blood vessels that provide nutrition for both dermis and epidermis, nerves, lymphatic cells, and an interfibrillar gel of glycosaminoglycan. The highly organized network of these fibres is what bestows the skin its mechanical properties (2).

Below the dermis lies the subcutaneous tissue. The subcutaneous tissue is a loose connective tissue. It is the contact layer between the skin and the underlying tissues such as muscles and bone. This adipose layer acts as a shock absorber, protecting the skin from mechanical impacts and as a heat insulator (2,8).

1.1.1 Sweat glands, sebaceous glands, and hair

Hair follicles stem in the dermis and enfold at the epidermis. Sweat glands released a dilute salt solution into the surface of skin. The evaporation of this solution makes skin cool and this is important for temperature regulation of both body and skin. Sweat glands are present all over the body (Figure 1).

The sebaceous glands adjacent to hair follicles produce a lipid-rich substance called sebum (Figure1). Sebum is a semifluid oily substance, that consists mainly of fat, keratin, and cellular material, and has the function to protect and lubricate the surface of the skin. It is released into the hair follicles and from there onto the skin surface (2). The presence of sebum at the surface of the skin favours the growth of facultative anaerobes, like *Cutibactirium* (*Propionibacterium) acnes* that hydrolyses the triglycerides present in sebum, releasing free fatty acids which reduce the skin pH and inhibits the proliferation of pathogenic microorganisms such as *Staphylococcus aureus* and *Streptococcus pyogenes* (9).

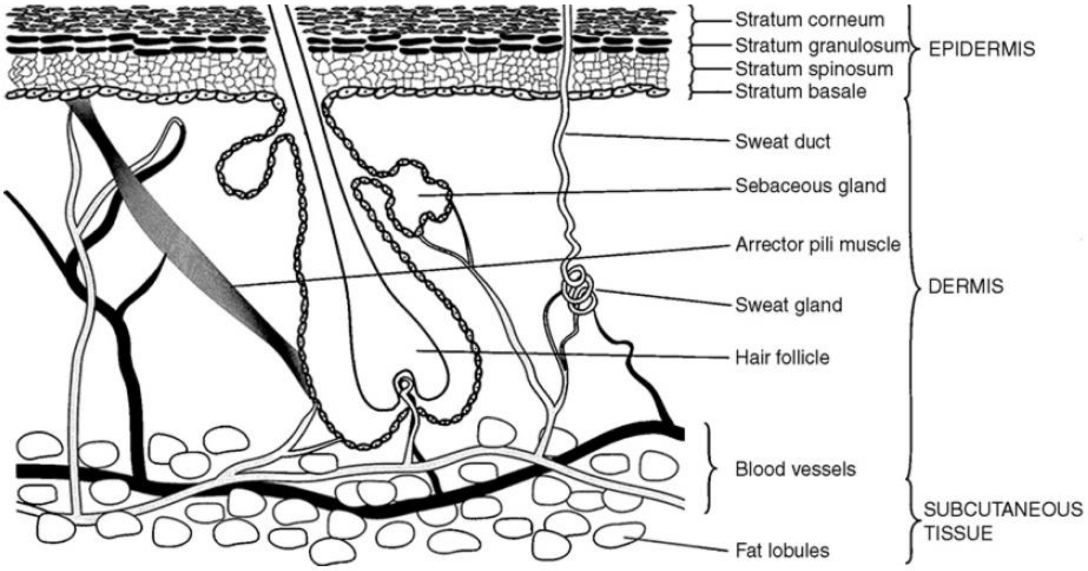


Figure 1. Representation of a cross-section of the human skin struture, showing different cell layers and appendages*. Adapted from: Transdermal and Topical Drug Delivery: from Theory to Clinical Practice by Adrian Williams*

1.2 Rinse-off products

Personal hygiene is the first line of defence against pathogens, and a ritual that has become deeply integrated in practically every modern society. Cleansers are the most commonly used skin-care product, and their impact cannot be overemphasized (10). A rinse-off product is according to Regulation (CE) nº 1223/2009 of the European Parliament a cosmetic product (11,12). And therefore, part of a competitive, fast-growing multibillion-dollar industry that keeps growing every year, the cosmetic industry (13).

Over the last century, liquid rinse-off products have become the favourite cleansing products of consumers, because of their ease of use and the softness sensation they provide to the skin (11). The main function of a rinse-off product is to remove dirt and sebum, as well as bacteria and odours caused by them from the surface of the skin or hair. The absence of odour is essential in personal hygiene. These odours arise from the interaction of bacteria from the microbiome of the skin and the secretions of the apocrine gland (sebum). One of the roles of cleaning products is to kill or inhibit the odour and the bacteria responsible for the odour (9).

Excess sebum and the entrapment of dirt particles onto the sebum layer can cloth skin pores and cause skin problems (9).

Since sebum is mainly an oily substance it cannot be removed by water alone. Oils and waxes are insoluble in water. This water insolubility is caused by hydrophobic interaction. The intermolecular forces between the oil molecules are weaker than the intermolecular bonds between water molecules, which causes the oil molecules to be repelled minimizing the water-oil interfacial area. The direct contact of water with oil causes an entropy decrease in the system, this tendency is counteracted by forcing the oil phase to separate from the water and reduce the contact area between these two phases to the strictly necessary. Because sebum is an oil it cannot be removed by water alone and the presence of amphiphilic molecules like surfactants is indispensable for its removal (9).

Even though the rinse-off products market is very extensive, formulation wise differences between the products of a given form are not especially dramatic, and the same ingredients are present. Logically, these ingredients can be formulated in a variety of ways to bring about different benefits, while also leading to differing levels of aesthetic acceptance (14).

1.3 Surfactants

1.3.1 General Aspects

Surfactants are, as the name indicates, surface active agents, and an indispensable component of most rinse-off products (15).

To be considered a surfactant the chemical compound should possess both a polar and non-polar group, exhibit surface activity and self-assemble into aggregates when above certain concentrations (16).

These amphiphilic molecules are composed by a long lyophobic tail, normally a hydrocarbon chain, but in some surfactants, it can be a (silicone) polydimthyldiloxane or a fluorocarbon that establishes strong interactions between themselves that drive the formation of self-assembled aggregate structures like micelles and liquid crystals, and by a small round lyophilic head group that conveys water solubility and the ability to adsorb (15).

The hydrocarbon chain can vary in length, being composed with between 8 and 18 carbon atoms. Fewer than 8 carbons atoms in the hydrocarbon chain results in the surfactant having low surface activity, whilst more than 22 results in the surfactant being too insoluble in water (8,17).

The selection of surfactants in the pre-formulation step is a complex task, with many factors to be considered. Essential to this process, and perhaps the most obvious of these factors is the function which is to be fulfilled by the surfactant in that given cosmetic product, either it being for their cleansing power, removing sebum and dirt particles from the skin or hair, but also for the functions as solubilizing agents, emulsifiers, antifogging agents, defoaming agents and deinking agents (18,19).

The main functions of surfactants in a rinse-off product are to lower the interfacial tension between the soil and the substrate, to emulsify oils and to disperse solid matter, allowing for a feeling of cleanliness in the skin and hair (8).

The relative sizes and shapes of the hydrophobic and hydrophilic parts of the surfactant molecule determine many of its properties, as will be discussed later (20).

1.3.2 Surfactant Classification

Surfactants are classified in four main groups according to the nature of their hydrophilic moiety: anionic, cationic, non-ionic and amphoteric (8).

The ionic surfactants are molecules that dissociate into ions when dissolved in water establishing an ionic bond with the water molecule. This group has two subcategories in accordance with the charge of the moiety of the hydrophilic group. The anionic surfactants are molecules that when incorporated in an aqueous solution their hydrophilic moiety presents a negative charge except if the pH acid. The cationic surfactants on the other hand, possess a positively charged hydrophilic head when incorporated in an aqueous solution (8).

Amphoteric surfactants are surfactants that can exhibit positive, negative or both negative and positive charges depending on the pH of the solution they are inserted in. These surfactants are cations in acidic solutions, anions in alkaline solutions and zwitterions at the intermediate pH, around the isoelectric point, exhibiting the lowest solubility (21).

Non-ionic surfactants are surfactants that present a head group with a neutral charge and that do not dissociate in water, and thus achieve water solubility through hydrogen bonds with the water molecule (21).

1.3.2.1 Anionic Surfactants

Anionic surfactants are the most used class of surfactants and are present as the primary surfactant in almost all rinse-off products formulations due to their excellent detergency properties. In addition to their ability to emulsify oily soils, they can lift these soils from the surface there were embedded in, due to their negatively charged head group being repelled from most surfaces, the opposite action can be observed in the case of cationic surfactants, where the positively charged moity is adsorbed onto surfaces (22).

The anionic polar group can be a carboxylates, sulfonates (sulfosuccinates) or sulfate (alkyl sulfates, alkyl ethoxylates sulfates), used commonly in cosmetic products due to their high cleansing and foaming ability (8,18). Most anionic surfactants possess high critical micellar concentrations which tend to be responsible for the great detergency properties of anionic surfactants, but also for their irritancy potential (23).

Anionic surfactants alone rarely provide the formulator with all the properties consumers expect in a good rinse off products, common deficiencies being low viscosity, unsuitable texture and stability, excessive detergency, and excessive irritancy (mildness). Hence, it is common good practice to add other surfactant classes, known as a secondary surfactant, mainly non-ionic and amphoteric surfactant to overcome these deficiencies (8).

1.3.2.2 Cationic Surfactants

The cationic surfactants carry a positive charge that makes them absorb onto negatively charged surfaces such as the skin, hair and cell membranes of bacteria, making them as potential conditioning and lubricant agents. Their major interest in cosmetic industry resides in hair care, where they are extensively used in hair conditioners and antistatic agents (8).

1.3.2.3 Amphoteric Surfactants

Depending on the pH of the solution these surfactants are solubilized in, the hydrophilic polar head of the amphoteric surfactants can present itself as a cation in acidic solutions, an anion in alkaline solutions or a zwitterion at an intermediate pH range (8).

They can be acyl ethylenediamines and derivates, N-alkyl amino acids or imino diacids. And are generally used as secondary surfactant, having proven to help formulations with foam stabilisation, modifying detergency, viscosity modification, foam structure improvement, their thickening capacity, mildness (skin irritation reduction capacity) on alkyl sulfates and alkyl ethoxy sulfates and improvement of the conditioning effects of the product (24)

Therefore, they are often used in facial cleansers as secondary surfactants to help boost foam, improve conditioning, and reduce irritation (25).

1.3.2.4 Non-ionic Surfactants

Non-ionic surfactants do not possess charge, and solubilization in water is achieved through hydrogens bonds the bulky hydrophilic moity established with the water molecule (8).

There are three types of non-ionic surfactants. The ethoxylates, that have an ethylene oxide chain as their polar head, the esters, that have the problem of being poorly soluble and the ones derived from carbohydrates, which can be completely made from renewable resources, such as alkyl poly glucosides (APG) (26,27).

They usually deliver a weak to moderate foam and are mainly appreciated for their good skin and eye compatibility as well as for their anti-irritant potential when combined with anionic surfactants in the right concentration ratio. Their main drawback is that they do not lather well, being for that matter normally used as a secondary surfactant and mixed with anionic surfactants. (8).

1.3.3 Adsorption

In order to understand the role of surfactants, one must understand the chemical and physical interactions that make water an oil immiscible. Substances like sugar and salts dissolve in water because the interaction between water and the ions or molecules of these substances is favoured over the interactions between the salt ions and sugar molecules between themselves. Conversely, substances like dirt are insoluble in water because the silica molecules attract one another with greater strength than the molecules of water do. Substances like oils and fats are insoluble in water because the intermolecular forces between the oil molecules with water are weaker than the intermolecular bonds between water molecules with each other, which causes the water to repel oil and minimize the water-oil interfacial area to the minimal necessary, a phenomenon called hydrophobic interaction . This interaction at the oil-water interface leads to a decrease in entropy of the system, that is counterbalanced by forcing the oil phase to separate from the water phase and thereby reduce the area of contact between the oil and water. The molecular structure of surfactants conveys them the ability of counteracting this phenomenon (9,28,29). Surfactants in this case have the function of lowering surface and interfacial tensions and solubilizing oils and waxes, as well as enhancing wetting and permitting the dispersion of dirt particles in water (8,30).

Molecules in the bulk of liquids are attracted on all directions uniformly by their neighbouring molecules, presenting a zero-net force. However, the same does not apply for the molecules present at the gas-liquid interface which are subjected to an imbalance of forces, being attracted only by the subsurface liquid molecules but having almost no interaction with the widely spread gas molecules on the liquid-gas boundary, non-zero net force. This imbalance of intermolecular forces leads to, the molecules at the liquid surface presenting a greater free potential energy than the molecules in the bulk of the liquid, this excess free energy per unit area is known as surface tension (γ) (9,21,30).

A similar interaction occurs at the interface between two immiscible liquids and the free energy per unit area is known as interfacial tension (21).

Surfactant molecules present in an aqueous media, tend to migrate to the surface air/water or to the interface (liquid/liquid, solid/water, solid/solid), self-orienting themselves in a matter that minimises the contact between the hydrophobic moiety and water, while satisfying the polar head attraction to the water molecules. (8,9). The driving force for surface adsorption derives from hydrophobic interaction Coulombic forces between the hydrocarbon chain between themselves, and interaction between the polar moiety and water through polar, ionic, Lewis acid/Lewis base, and London dispersion. This adsorption causes the surfactant concentration at the surface to be much higher than the surfactant concentration in the bulk of the solution (31).

1.3.4 Aggregation

When surfactants are added to an aqueous media at low concentrations, they exist as monomers (32). The surfactant molecules lie on the water/air surface, through the mechanism explained above and the hydrophobic tail of the surfactant molecule either lies flat on the surface (few surfactant molecules at the interface) or assumes a more upright position (sufficient number of surfactant molecules at the interface) while the hydrophilic head orientates itself towards the polar phase, as portrayed in Figure 2 (9,30).

The surfactant molecules pack together at the interfaces, maximising the reduction of surface tension and forming a monolayer. How close the molecules pack together depends on electrical repulsions, in the case of ionic surfactants, and steric hindrance of hydrophiles, in the case of non-ionic surfactants (30). Through this mechanisms surfactant at low concentration will adsorb at the surface or interface and significantly reduce the amount of work required to expand those interfaces. The denser the surfactant packing at the interface, the larger the reduction in surface tension (30,33).

As the surfactant concentration continues to increase, it saturates the surface of the air/water surface or oil/water interface. Therefore, the greater the concentration, the greater the packing and the lower the interfacial tension (9).

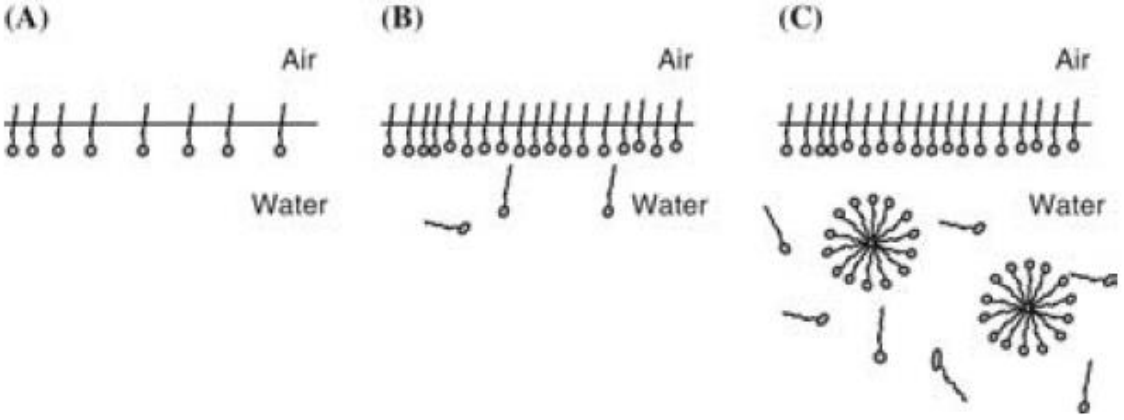


Figure 2. Surfactant behaviour in solution with concentration increase. (A) At low surfactant concentration, the amphiphilic molecules have the tendency to adsorb at the interface, where the solubility of both the hydrophilic and hydrophobic groups, is satisfied; (B) As the Air/Water interface becomes saturated the surfactant molecules become present in the solution as monomers; (C) As surfactant concentration is increases above the CMC, micelles appear through hydrophobic interaction. Adapted from: Handbook of Cosmetic Science and Technology, by André O. Barel, Marc Paye and Howard I. Maibach.

1.3.5 Micellization of Surfactants

As surfactant concentration increases, the available area at the interfaces diminish and become saturated, and surfactant monomers start accumulating at the bulk of the solution. However, the accumulation of surfactant molecules as monomers is not favoured as the free energy of the solution increases and the solution becomes itself also saturated (21,34).

The hydrophobic effect and chemical potential drives surfactant molecules to self-assemble into dynamic aggregates with significant molecular mobility that exist in equilibrium with the surfactant monomers (21,35). Micelle formation occurs in a very narrow window of concentrations known as the critical micelle concentration (CMC). This region is very small to define and therefore for the purpose of practicality, it is represented as a single value, the CMC. Each surfactant has its own individual CMC, that indicates the point at which monolayer adsorption is saturated and the surface-active properties are at an optimum (36,37). Non-ionic surfactants have low CMC since the steric hindrance between their polar moieties is not very strong force. And so, at low concentrations of non-ionic surfactants the presence of hydrophobic effect itself is sufficient to drive molecules to assemble into micelles. Contrarily, ionic surfactants have strong ionic repulsions between their hydrophobic groups and thus require a greater concentration of surfactants to pack into a micelle, meaning they have a higher CMC (38).

Above the CMC, the concentration of monomers remains constant, and the excess surfactant molecules arrange themselves into micelles. This reverberates in the fact that there are no significant changes in surfactant properties of the solution since monomers are the cause for surface activity. Hence an increase in surfactant concentration does not significantly impact the monomers in the solution but greatly changes the structure of the micelles (9,21,36).

The formation of self-assembled surfactant structures can be detected by the presence of changes in increased turbidity, or decrease in electrical conductivity in the case of ionic surfactants and stability in surface tension, interfacial tension, solubilisation, auto diffusion and osmotic pressure (39).

Micelles are configurationally stabilized by assembling their hydrophobic tails at the core and directing their hydrophilic groups to the outside facing the aqueous phase minimizing the contact between the hydrophobic groups and water. This configuration grants them the ability to solubilize in their core lipidic molecules such as sebum. A phenomenon that constitutes the basis of the mechanism of detergency and soil removal (9,40).

When a micelle is assembled two opposing forces are present, the tight cohesion of the core due to hydrophobic interaction and the repulsion between the polar moieties with one another, either by repulsive forces between similar charges (ionic surfactants) or by solubilization with water. Imposing in this matter the curvature the micelle takes (41).

Decreased repulsion between hydrophobic head groups or increased steric hindrance between the hydrophobic core molecules causes a decrease in the curvature of the micelle struture. The decrease in curvature of the micelle forces them to transition into different shapes, from round micelles, into elliptical spheroids, to rods to worms to hexagonal phase (packed rods) to lamellar phase to inverse rods and inverse spheroids.

Surfactants pack according to intermolecular interactions, and consequently the decrease in curvature forces the micelles to transition in shape from spheres to elliptical spheroids to rods to worms to packed rods (hexagonal phase) to infinite two-dimensional layers (lamellar phase) to inverse rods and inverse spheroids (42–44).

The shape and the size of the aggregate can be determined by the surfactant packing parameter. Spherical micelles are formed where the value of surfactant packing parameter is less than 1/3 (single chain surfactants with large head groups such as anionic surfactant).

Rod-like micelles are formed when the surfactant packing parameter is between 1/3 and ½ .As the packing factor is increases, the rood like micelles grow into wormlike micelles (42). Lamellar phase is present when surfactant parameter is between ½ and 1.

Any change in solution properties which causes a reduction in the effective size of hydrophilic head groups will change the aggregate size and shape. The addition of electrolyte reduces the effective hydrophilic area of ionic surfactants because the increased counterions reduce the repulsion between ionic polar head groups. Addition of co-surfactant with a smaller head group size also contributes to mixed micelle formation of cylindrical shape. Increasing the temperature reduces the ethoxylated non-ionic head groups. Furthermore, changing the pH changes the degree of protonation of amphoteric surfactants and affects the head size (45).

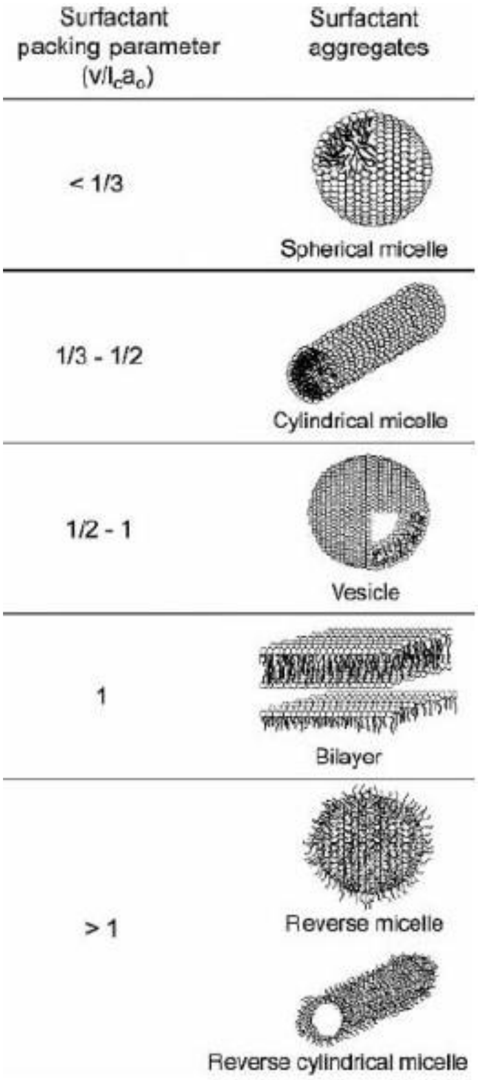


Figure 3. Surfactant structures as a function of surfactant packing parameter. Adapted from: Chemistry and Technology of Surfactants by Hatice Gecol edited by Richard J. Farn

1.3.6 Crystalline Phase

Micellar shape plays a dominant role in controlling the rheological and solubilization properties of surfactant mixed solutions, the control of the phase of the surfactant system is of crucial importance to the science and technology of soap systems, having to be carefully controlled by the formulator (46).

Micellar aggregates can present different shapes depending on concentration of the surfactant, the pH of the solution, or the presence of salt ions (28).

As the concentration of surfactant in a solution is increased the size of the micelles increases too, while the concentration of monomeric surfactant remains constant, approximately equal to the CMC (33).

With increasing surfactant concentration, the viscosity of the solution it composes increases too, in a non-linear manner, until sometimes it undergoes a sudden decrease, when the lamellar phase is achieved. This phenomenon is due to the changes in the geometry of the surfactant molecules which occur as the concentration is increased. Hence, with the progressive increase of surfactant concentration the presence of several phases, known as liquid crystal or mesomorphic phases are possible to be distinguished (47).

Liquid crystals or mesophases are intermediary states of matter which possess a degree of molecular order intermediate to the one found in solid crystals, and the one found in isotropic liquids where disorder is present (46).

At low concentrations, some surfactants solutions present a geometrical structure of spherical micelles, which consist of micelles of a round shape. Has the concentration is slowly increased rod-like micelles start to form and with the progressive increase in the concentration of surfactant the rod-like micelles are forced to align themselves in the same direction to achieve the required packing density, until the formulation reaches a critical point in which the rod-like micelles adopt a tightly packed hexagonal array, a point in which viscosity increases sharply, and the previously mobile solution sets to a viscous gel known as the hexagonal phase or middle phase. The hexagonal phase is a liquid crystal phase, possessing a high degree of order in the assembly of its rod-like aggregates (44).

With some surfactants, like sodium lauryl sulfate, and surfactant mixtures, if the concentration is increased until 60- 70% there is a sudden drop in apparent viscosity, derived from a switch from a hexagonal phase to a mobile translucent fluid, the lamellar or neat phase. The lyotropic lamellar phase consists essentially of alternate planes of water and hydrocarbon which flow with increasing readiness as the applied shear force is increased (24,46,47).

1.4 Performance characteristics

1.4.1 Detergency

The main function of surfactants is to cleanse, remove particulate and oily soil from surfaces hence the most important attribute of surfactants is their detergency (33). To efficiently cleanse, the surfactants must firstly counteract the interactions established between the soil and the subtract, by establishing stronger interactions surfactant- soil than the subtract-soil and then be redispersed in water (48).

Surfactants are hypothesised to remove sebum through four main mechanisms. The roll-up, in which a lowering in the interfacial tension between the oil and water and the surface tension between the solid surface and water accomplished by adsorption of the surfactant, makes the removal of sebum possible, and so sebum rolls-up into oily droplets and detaches from the solid surface into the bulk solution; spontaneous emulsification is a build-up on the roll-up theory and it hypothesis that the large lipid soil emulsifying through the decrease of interfacial tension of surfactants, penetration of surfactants on the lipid soils, producing liquid crystalline phases at the soil-water interface and solubilization, involves the migration of the soil molecules from the solid surface into the micelles that are adsorbed at the water/oil interface, and the detachment of the filled micelle back into the bulk of the rinse-off product (48).

The lower the CMC the better detergency ability the surfactant possesses. The phase and the switch between phases by the surfactant can have a significant impact on detergency. The presence of liquid crystals has been associate with a increase in detergency and a bigger ease of oil removal (33).

1.4.2 Foaming

Foaming another key performance characteristic in a rinse-off product, since foaming and lathering of the rinse-off product add to the consumer experience and are essential for its acceptance of the product (19). Good foaming properties are usually interpreted by the consumer as an insight into the products cleaning efficiency, hence the achievement of voluminous creamy foam is of furcal importance. However, too much foam is not desirable as it can pose as a rinsing challenge, therefore the control of foam is factor that needs to be studied when developing a formulation (33).

Foam consists of a gas dispersed in a continuous liquid phase. The first foam formed that possess a high water content is normally called wet foam, and presents spherical bubbles. However, as a consequence of drainage of the foam lamellae, the wet foam loses water with time and gives place to the dry foam. Dry foam bubbles are deformed into a polyhedral shape. The polyhedral bubbles are separated from each other by thin liquid films. The intersection of the lamella between three bubbles is called plateau borders, as depicted in Figure 4 (33,49).

Surfactants generate foam because they are able to concentrate at the air/water interface and reduce the surface tension (50). Small air bubbles are formed and preserved by an elastic film made from surfactant molecules, stretching the surface area. Their size and quantity depend on the surfactant monolayer capability of stabilising air/water interfaces. If the surfactant does not adsorb rapidly at the interface, the bubbles break quickly (19,33). Therefore, surfactants with the best foaming ability are those with high CMC, since a plentiful amount of surfactant monomers is necessary to absorb rapidly at the water/air surface, closely packing and forming an elastic film. A fully formed or lamellar foam consists of bubble walls the lamellae (50).

Foaming is always accompanied by an increase in the interfacial area leading to an increase in entropy, hence it is thermodynamically unstable and, therefore, sooner or later destroyed (33). In order to be able to withstand deformation without rupturing, the thin film of the bubble must present some elasticity, a phenomenon explained by the Marangoni and Gibbs. When a surfactant stabilized film undergoes sudden expansion, the expanded portion of the film as a lower degree of surfactant absorption. The expanded portion presents a higher surface tension than the rest of the film. The transport of bulk liquid due to surface tension gradient is termed the Gibbs-Marangoni effect, it re-thickens the think films and prevents foam rupture (51).

Defoaming occurs either by drainage of the liquid phase, gas diffusion to larger bubbles or through rupture of the lamellae. The drainage of water around the foam bubbles occurs due to the force of gravity pushing water in the direction of the bulk of the solution, if the wall of the bubble is too thin or the presence of water is too high it can lead to bubble disruption. Gas diffusion is the diffusion of air from smaller bubbles to bigger ones, this happens due to the effect of osmotic pressure, that is higher in smaller bubbles than in larger ones. The rupture of lamella occurs due to Van der Waals, this occurs because the drainage constantly thins the surface of the bubble walls (19).

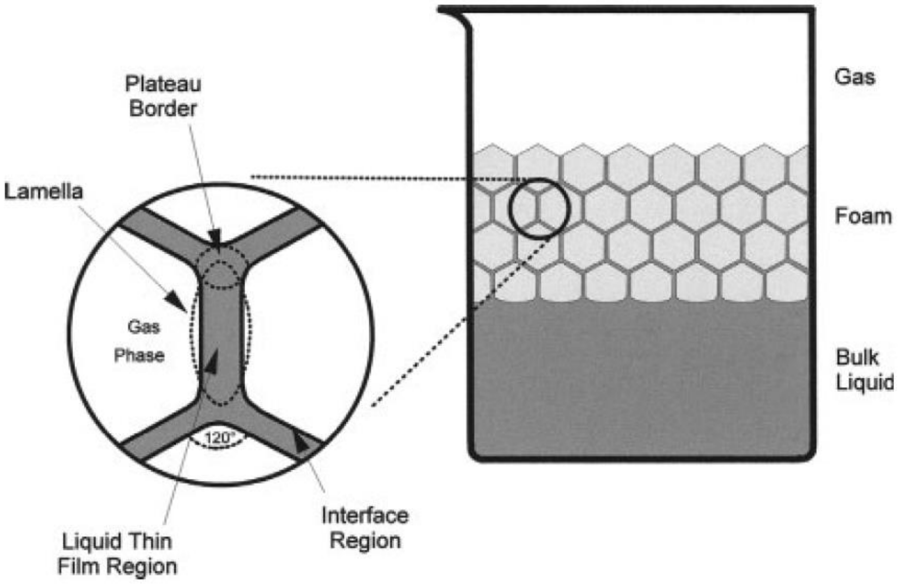


Figure 4. Foam struture. Adapted from: “Emulsions, Foams, and Suspensions” by Laurier L. Schramm.

1.4.3 Mildness

Rinse-off products inevitably come in contact with the skin, eyes and mucous membranes. Mildness to the skin and eyes is another essential aspect that rinse-off products need to deliver to consumers. The choice of surfactant and of surfactant blends is crucial since cleansers affect the lipid and protein contents of the skin, which influences its skin barrier function (52).

There are many ways in which surfactants can interact with the skin when they come in contact with it, and the potential for skin irritancy is very big (32).

Surfactants irritate the skin by adsorbing free surfactant monomers to the proteins of the stratum corneum denaturing proteins them; penetrating through the stratum corneum lipid barrier and solubilizing and disorganizing the intercellular lipidic structures (53).

Once the lipidic barrier has been disrupted surfactant monomers can then diffuse through the stratum corneum and reach deeper layers of the skin where they interact with keratinocytes and Langerhans cells, where they can cause inflammation, alteration of the plasmatic membrane and lysis of the cells (32).

The monomeric surfactant form is the main driver of surfactant irritation; hence the concentration of surfactant monomers present in a rinse-off product is directly correlated to skin and eye irritation (54).

The choice of surfactants is challenging because their cleansing abilities correlate with their irritation potential. The surfactant for optimum detergency is also the one with the highest irritation. However, there are ways to surpass this problem, to counteract the irritational potential of a strong detergent primary surfactant one must mix it with a secondary surfactant of inferior detergency power (32,55).

The first step in the development of a mild rinse-off product is electing the mildest surfactant. Non-ionic surfactants are generally the mildest type of surfactants. Some anionic surfactants are also very mild, it is the case of sulfosuccinate esters. Amphoteric surfactants are usually used as secondary surfactants with anionic primary surfactants, for their decrease in the irritation potential (19).

1.5 Sustainability

Sustainability is built on three main pillars: environment, not depleting or putting it under stress; society; and economy, including equitable sharing of resources and knowledge (56).

Natural resources are not necessarily sustainable, since many natural resources are not renewable at the rate the societies consume them, which makes their use over time, non-sustainable. The demand of consumer for sustainable products, has increased exponentially over the last 30 years, generating a demand from consumers for corporations to take more responsibilities to ensure sustainability in the environment, communities, and economy (56,57).

Making the switch to environmentally friendly alternatives is a race happening in practically every industry. In 2007 it was launched to the US the first double concentrated liquid laundry detergent from Unilever, the “small and mighty”. These concentrated products are low-volume product that use less water, using less volume of product, which leads to a reduction of packaging, less waste packing and less weight of the product and less carbon emissions in transportation, which benefits greatly our environment (58).

Concerns for the environment has provided the impetus to develop this thesis on concentrated rinse-off products. These concentrated compositions have a considerably higher level of surfactant actives than conventional rinse-off products. As a result of the high concentration of actives, these products can be sold in smaller plastic containers and consequently reduce the waste loads of plastic materials. Additionally, the consumer uses less product in each use, bridging saving in the cos of transporting the product and is convenient for the user(59,60).

Most liquid rinse-off products consist of more than 85% water, making shampoo and body washes the highest volume personal care products on the market. The water helps with product with the feel-good and the spread of the product through the increase of the volume of product. But water present huge drawbacks in terms of sustainability, for one its weight. Since water is heavy it increases the overall weight and volume of the product, which reflects in transportation CO_2 emissions and plastic waste in the primary packaging of the product (59,61,62).

Given this panorama the search for more sustainable ideas for rinse-off product has been high, and one of the solutions is decreasing the volume of water in rinse-off products, making it more concentrated. Some of the advantages of a highly concentrated rinse-off product in comparison with their lower active matter counterparts include the reduced transport costs because each product contains more active matter per tonne, a more lasting product, less storage space required; less microbiological contamination due to the reduced content in water and a reduction on the level of impurities on a *pro rata* active matter, since the higher active matter materials gave a less impurities than the lower active matter materials, which them transposes into a more reproductible product with less variability in the adjustments required in terms of viscosity, mildness (24).

The choice in surfactant is another factor that dictates the environmental impact of rinse-off products, and their ecotoxicity and biodegradability have to be taken into consideration. Therefore, it is generally accepted that:

1. The chemical structure of the hydrophobic group is the primary factor controlling biodegradability; high degrees of branching, especially at the alkyl terminus, inhibit biodegradation.

2. The nature of the hydrophilic group has a minor effect on biodegradability.

3. The greater the distance between the hydrophilic group and the polar head group, the greater is the rate of primary degradation (63).

2 AIM AND OBJECTIVES

The aim of this project is to:

Develop concentrated surfactant solutions, in order to create more sustainable rinse-off products.

Each formulation was characterized according to their macroscopic aspect, viscosity, microscopic structure and pH.

Objectives:

- Carry out a literature review on surfactants and their self-assembly behaviour with different formulation variables;
- Identify how to make concentrated surfactant solutions
- Select raw materials widely used and known for their cleansing efficacy;
- Formulate a concentrated surfactant system by combining different chosen surfactants;
- Carry out physiochemical characterisation of the formulations obtained;
- Connect the microstructure of the samples to the rheological response
- Analyse collected data and apply relevant analysis

3 MATERIALS

Plantacare ®1200UP (Lauryl Glucoside), Texapon® N70 LS (Sodium Laureth Sulfate) and Plantapon® SUS powder (Disodium Lauryl Sulfosuccinate) were obtained from BASF, (Germany). Tego Betain® CK D (Cocamidopropyl Betaine) was purchased from Evonik Nutrition & Care GmbH, (Germany).

3.1 Raw-materials properties

As this project focussed on sustainable alternatives to traditional rinse-off products, the environmental impact of the ingredients used.

Plantapon® SUS (Disodium Lauryl Sulphosuccinate) is an anionic surfactant, is a great alternative to sulfate surfactants (Figure 4). It is a disodium salt of ethoxylated lauryl alcohol bonded to sulfosuccinic acid. It presents very good emulsifying and wetting properties. It is widely used as a primary surfactant, and as an alternative for Sodium Laureth Sulfate for its milder properties. It presents good foaming and cleansing properties (8).

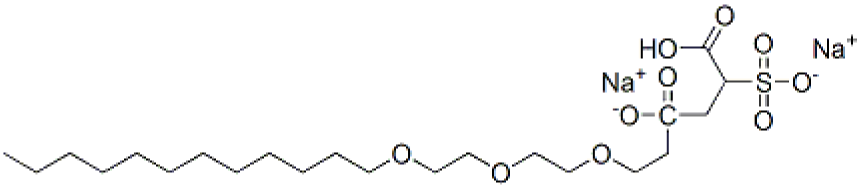


Figure 5. Disodium Lauryl Sulphosuccinate molecular struture. Adapted from https://m.chemicalbook.com/ProdSupplierGNCB32130483_EN.htm.

Texapon® N70 LS (Sodium Laureth Sulfate) is an anionic synthetic surfactant, with excellent detergency power (Figure 5). Sodium Lauryl Sulfate (SLS) is the most researched and documented surfactant, especially in terms of its fate in the environment (64). The ethoxylation SLES presents lends its increased mildness in comparison to SLS, but also reduced detergency performance (65). It is readily biodegradable according to OECD criteria and with the biodegradability criteria as laid down in Regulation (EC) No.648/2004 on detergents (66,67).

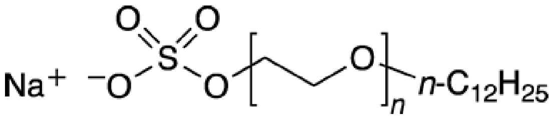


Figure 6. Sodium Laureth Sulfate molecular struture. Adapted from: https://www.acs.org/content/acs/en/molecule-of-the-week/archive/s/sodium-laureth-sulfate.html.

Tego Betain® CK D (Cocamidopropyl Betaine) is an amphoteric surfactant, made from plant-sourced and natural staring ingredients (Figure 6) (68). It is commonly used in formulation to work as a secondary surfactant due to its known ability to reduce the skin irritation potential of alkyl ether sulfates and of alkyl sulfosuccinates. It enhances the overall foaming and mildness performance of the blend when combined with ionic and non-ionic surfactants (69,70). It is Ecocert certified meeting the parameters described in ISO Guide 65 (EN45011) (68).

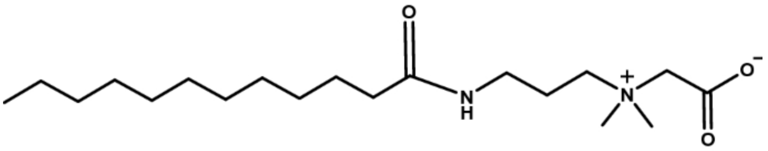


Figure 7. Cocamidopropyl Betaine molecular struture, in its ionized form. Adapted from: **El-Dossoki, F.I., Abdalla, N.S.Y., Gomaa, E.A. et al. An insight into thermodynamic and association behaviours of cocamidopropyl betaine (CAPB) surfactant in water and water–alcohol mixed media**

Plantacare® 1200UP (Lauryl Glucoside) is a non-ionic surfactant with special interest due to its ecological properties. It is a product obtained from the condensation of lauryl alcohol with glucose. It is made by 100% renewable and natural sources, specifically plant-derived feedstock, making it very interesting in terms of sustainability (27,71). It presents a synergetic effect when mixed with anionic surfactants, enhancing their foaming and mildness performance while maintaining the cleansing properties of the primary surfactant (72).

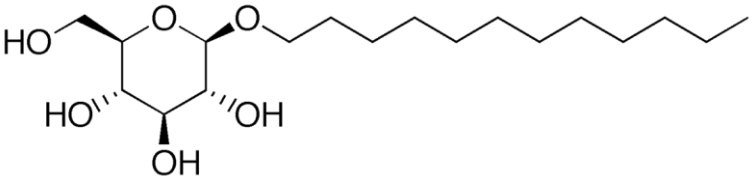


Figure 8. Lauryl Glucoside molecular struture. Adapted from: https://en.wikipedia.org/wiki/File:Lauryl_glucoside.png

Freshly prepared ultra-purified Milli-Q® water.

4 METHODS

4.1 Development of the surfactant formulations

Ternary systems of anionic surfactant, non-ionic or amphoteric surfactant, and water, were studied. Four surfactants were used, sodium laureth sulphate (SLES), disodium lauryl sulfosuccinate (DLS), cocamidopropyl betaine (CAPB), lauryl glucoside (LG).

A range of formulations was prepared by mixing the aforementioned surfactants in specific ratios with water. Samples were prepared by weighing the required amount of surfactant and water using a calibrated scale accurate to ± 0.001g.

Surfactants pairs were mixed in ratios of 1:1, 2:1 and 1:2. The percentage of water was adjusted to 100% for each formulation.

The formulations are shown in Table 1, Table 2, Table 3 and Table 4.

Table 1. Formulation with SLES+CAPB.

	SLES 70 %(w/w)	CAPB %(w/w)	Water q.s
A1	5.00	5.00	100
B1	6.67	3.33	100
C1	3.33	6.67	100
D1	10.00	10.00	100
E1	13.33	6.67	100
F1	6.67	13.33	100
G1	15.00	15.00	100
H1	20.00	10.00	100
I1	10.00	10.00	100
J1	20.00	20.00	100
K1	26.67	13.33	100
L1	13.33	26.67	100
M1	25.00	25.00	100
N1	33.33	16.67	100
O1	16.67	33.33	100

Table 2. Formulation with SLES+LG.

	SLES 70 %(w/w)	LG %(w/w)	Water q.s
A2	5.00	5.00	100
B2	6.67	3.33	100
C2	3.33	6.67	100
D2	10.00	10.00	100
E2	13.33	6.67	100
F2	6.67	13.33	100
G2	15.00	15.00	100
H2	20.00	10.00	100
I2	10.00	10.00	100
J2	20.00	20.00	100
K2	26.67	13.33	100
L2	13.33	26.67	100
M2	25.00	25.00	100
N2	33.33	16.67	100
O2	16.67	33.33	100

Table 3. Formulation with DLS+CAPB.

	DLS %(w/w)	CAPB %(w/w)	Water q.s
A3	5.00	5.00	100
B3	6.67	3.33	100
C3	3.33	6.67	100
D3	10.00	10.00	100
E3	13.33	6.67	100
F3	6.67	13.33	100
G3	15.00	15.00	100
H3	20.00	10.00	100
I3	10.00	10.00	100
J3	20.00	20.00	100
K3	26.67	13.33	100
L3	13.33	26.67	100
M3	25.00	25.00	100
N3	33.33	16.67	100
O3	16.67	33.33	100

Table 4. Formulations with DLS+LG.

	SLES 70 %(w/w)	CAPB %(w/w)	Water q.s
A4	5.00	5.00	100
B4	6.67	3.33	100
C4	3.33	6.67	100
D4	10.00	10.00	100
E4	13.33	6.67	100
F4	6.67	13.33	100
G4	15.00	15.00	100
H4	20.00	10.00	100
I4	10.00	10.00	100
J4	20.00	20.00	100
K4	26.67	13.33	100
L4	13.33	26.67	100
M4	25.00	25.00	100
N4	33.33	16.67	100
O4	16.67	33.33	100

4.2 Formulation Manufacturing Process

All ingredients were mixed under constant stirring and heating at 40º C on a magnetic stirrer with heating plate (IKA, England) until the mixture was homogenous. For the more concentrated formulations an RW 16 Basic overhead stirrer (IKA Oxford, England) with a propeller impeller was used instead of the magnetic stirrer, under the same temperature. The samples were left to cool down to room temperature before testing. The samples were then stored in a borosilicate glass beaker protected with parafilm at ambient conditions in the laboratory. Prior to any experimental studies the samples were manually stirred until homogenous.

4.3 Organoleptic Properties

All samples were evaluated in terms of appearance, homogeneity, colour, and odour.

4.4 Microscopic Analysis

Microstructure of the formulations was assessed by using an Olympus CX40 Biological Upright Phase Contrast optical microscope at a total magnification of 100x, equipped with an Olympus DP80 digital camera, and an Olympus U.GAN gout kit slider Polarizing Kit and U-POT polarizer (Olympus Corporation, Japan). The software CellSens was used for digital imaging acquisition.

Representative images were chosen among at least 4 similar images.

4.5 Viscosity

The apparent viscosity and profile were evaluated using a RV DV2T, SAA Brookfield Rotation Viscosimeter (Brookfield Engineering Laboratories, Inc., Middleborough, MA), at room temperature, ranging from 19,5 to 22,0 º C The shear rate [1/s] versus viscosity [Pa.s] plots were obtained by submitting the samples to a shear rate sweep from 3 to 60 s^{-1} for 30 seconds (73).

4.6 pH

The pH values were determined in triplicate for each formulation with results presented as mean value ± SD, by using a potentiometric method. The pH probe HI-98103 Pocket Checker pH Tester, (Hanna Instruments, United Kingdom) was inserted directly into the formulations at room temperature.

4.7 Data Analysis

Means and standard deviations were calculated using Excel (Microsoft, Redmond, Wash, U.S.A). Ternary phase diagrams were created using OriginPro 2020 (OriginLab Corporation, Northampton, Mass., U.S.A).

5 RESULTS

5.1 Organoleptic Properties

The formulations varied greatly in macroscopic appearance, in terms of colour, opacity, and consistency Table 5 and 6. All samples were homogeneous and had no odour.

5.2 Microscopic Analysis

Optical microscopy is a useful tool when a studying the microstructure of liquid crystal mesophases. Polarised optical microscopy exploits optical properties of anisotropic structures and offers a wealth of information, which is not available with any other optical technique. The idea is to identify the mesophases formed by surfactants since most of the mesophases display unique optical textures.

In a microscope, normal non-polarised light from radiant halogen bulb passes through the polariser to transform it to plane polarised light. There are two polarising filters in a polarising microscope called polariser and analyser. The physical appearance of all compositions was assessed by visual inspection, Table 5 and 6. All samples appeared to be physically stable since there was no visible phase separation after a period of observation of 3 weeks.

Table 5. SLES+CAPB formulation:

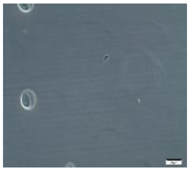
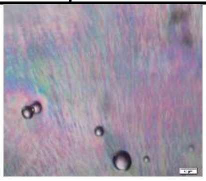
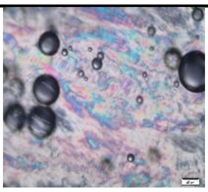
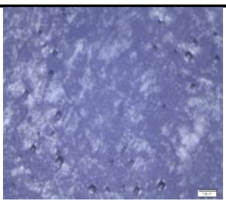
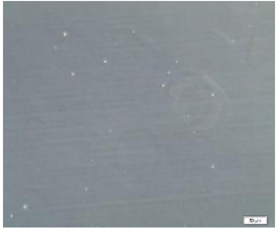
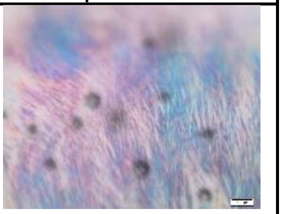
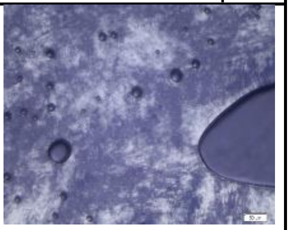
Formulation	% total surfactant	Macroscopic Aspect	Rheological Behaviour	Polarized light aspect X20
A1	10	Transparent liquid solution	Newtonian Flow	 Isotropic solution
B1		Transparent liquid solution	Newtonian Flow	
C1		Transparent liquid solution	Newtonian Flow	
D1	20	Transparent gel like consistency	Shear-thinning Flow	 Isotropic solution
E1		Transparent gel like consistency	Shear-thinning Flow	
F1		Translucent	Shear-thinning Flow	
G1	30	Transparent	Shear-thinning Flow	 Brushed metal aspect with pink and blue iridescence
H1		Turbid, gel-like aspect	Shear-thinning Flow	
I1		Turbid, gel-like aspect	Shear-thinning Flow	
J1	40	Turbid, gel-like aspect	Shear-thinning Flow	 Brushed-metal aspect, pink and blue iridescence
K1		Turbid, gel-like aspect	Shear-thinning Flow	
L1		Opaque with air bubbles entrapped, gel-like	Shear-thinning Flow	
M1	50	Opaque with air bubbles entrapped, gel-like	Shear-thinning Flow	 Mosaic texture
N1		Compact gel with air bubbles entrapped	Shear-thinning Flow	
O1		Compact gel with air bubbles entrapped	Shear-thinning Flow	

Table 6. SLES+LG formulation:

Formulation	% total surfactant	Macroscopic Aspect	Rheological Behaviour	Polarized light aspect X20
A2	10	Transparent liquid solution	Newtonian Flow	 Isotropic solution
B2		Transparent liquid solution	Newtonian Flow	
C2		Transparent liquid solution	Newtonian Flow	
D2	20	Transparent liquid solution	Newtonian Flow	 Isotropic solution
E2		Transparent liquid solution	Newtonian Flow	
F2		Transparent gel like consistency	Newtonian Flow	
G2	30	Transparent gel like consistency	Shear-thinning Flow	 Brushed-metal aspect, pink and blue iridescence
H2		Transparent gel like consistency	Shear-thinning Flow	
I2		Yellowish, gel-like solution	Shear-thinning Flow	
J2	40	Turbid, gel-like aspect with entrapped bubbles	Shear-thinning Flow	 Brushed-metal aspect
K2		Turbid, gel-like aspect with entrapped bubbles	Shear-thinning Flow	
L2		Opaque with air bubbles entrapped, gel-like	Shear-thinning Flow	
M2	50	Turbid, gel-like and foaming at the surface	Shear-thinning Flow	 Mosaic texture
N2		Compact gel with air bubbles entrapped	Shear-thinning Flow	
O2		Yellowish compact gel with air bubbles entrapped	Shear-thinning Flow	

5.3 Viscosity

Continuous shear experiments measure the ability of each system to resist structural breakdown during the standardized shearing procedure. Representative viscosity profiles (viscosity versus shear stress) are shown in Figure 9, 10 and 11.

The shear rate sweep was carried out firstly from low to high values (from 3 to 60 s⁻¹).

In the mixture of SLES with CAPB, the formulations A1, B1 and C1 (dark blue lines) presented a Newtonian flow, all the other formulations presented a flow typical of shear-thinning materials, Figures 9.

In the combination of SLES with LG, the formulations A2, B2, C2 corresponding to 10% total surfactant (dark blue lines), D2, E2, F2 corresponding to 20% total surfactant (yellow lines) presented a Newtonian flow, all the other formulations presented a flow typical of shear-thinning materials, Figures 10.

Lastly in the mixture of DLS with CAPB, the formulations A3, B3, C3 corresponding to 10% total surfactant (dark blue lines) and D3 corresponding to 20% total surfactant (yellow line) presented a Newtonian flow, all the following formulations presented a flow typical of shear-thinning materials of the pseudoplastic type, Figures 11.

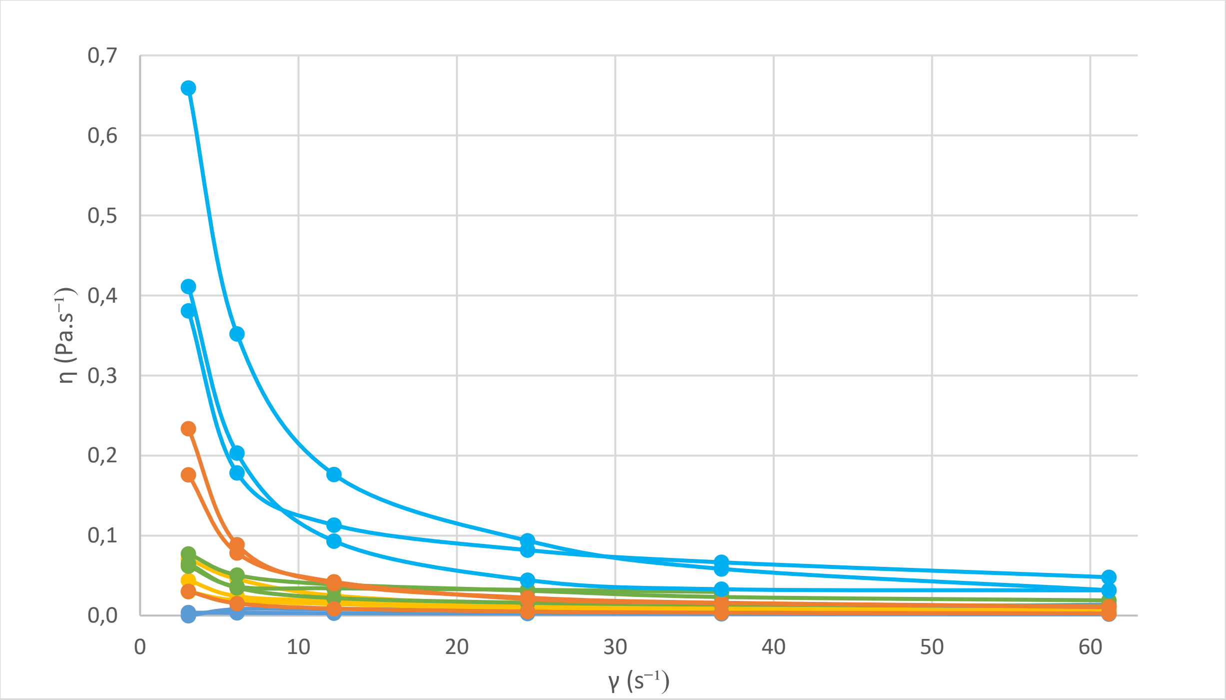


Figure 9. Viscosity profile of SLES with CAPB.

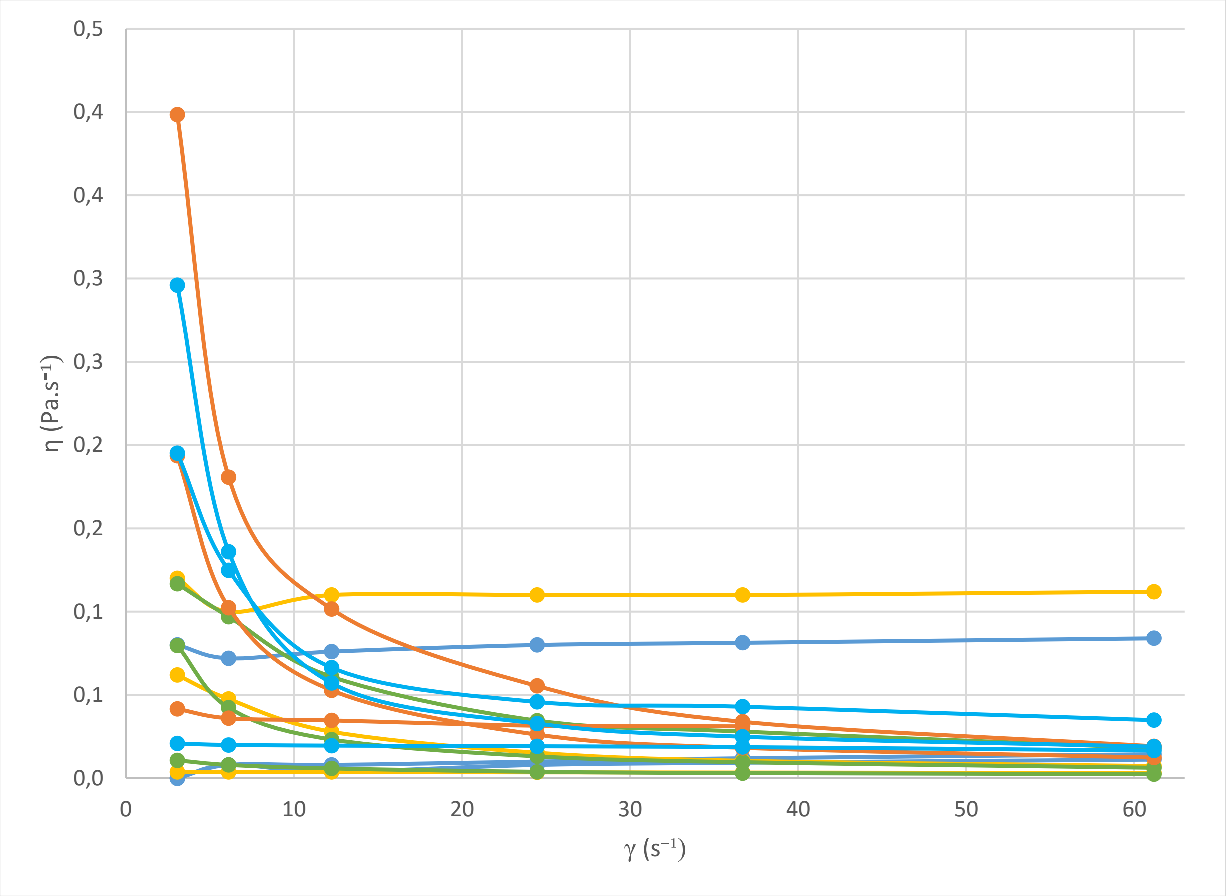


Figure 10. Viscosity profile of SLES with LG.

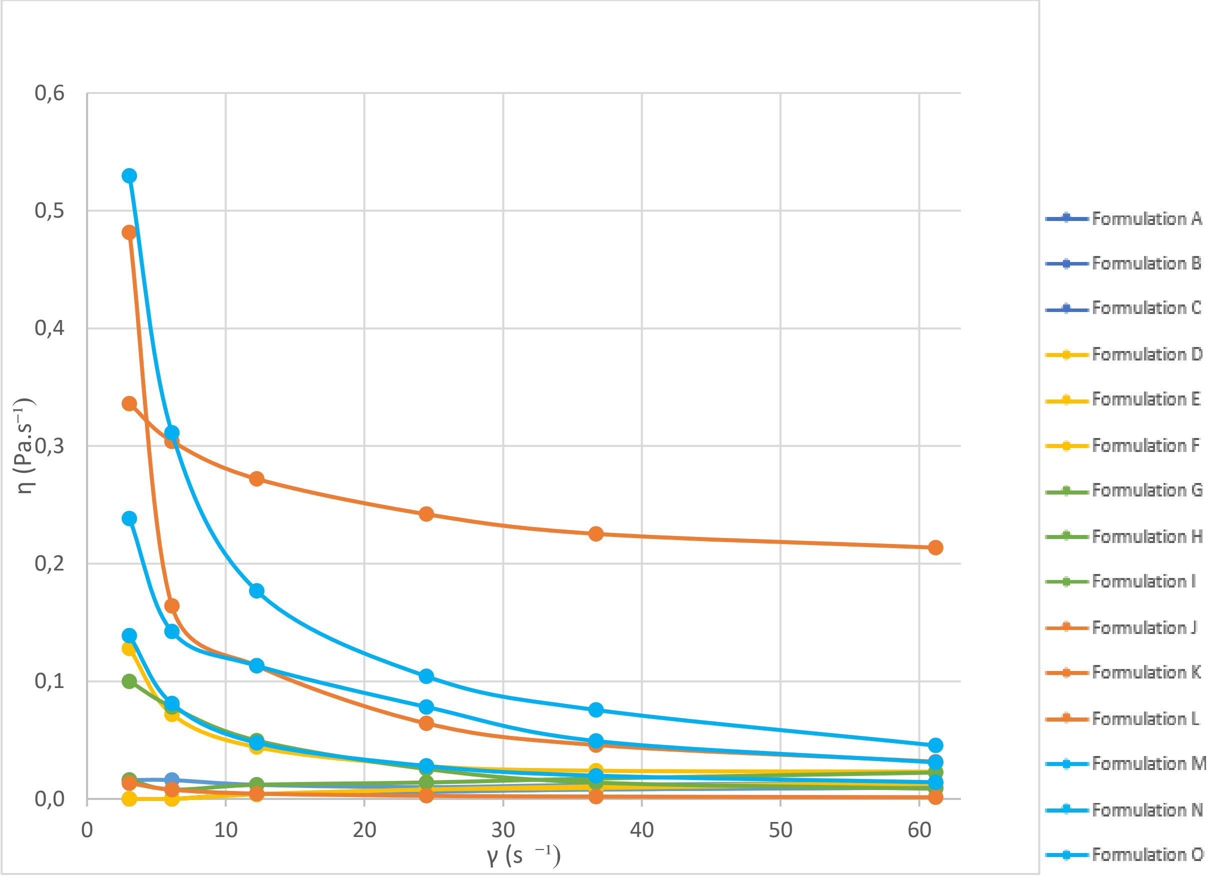


Figure 11. Viscosity profile of DLS with CAPB.

5.4 pH

The pH of rinse-off products has been shown to be important for minimizing the irritation of the eyes and mucous areas of the body and maintain the natural properties of the skin. The products of the combination of SLES with CAPB and of DLS with CAPB had pH that ranged from 5,8 to 6,9 as seen in tables 7 and 8. The combination of SLES with LG and of DLS with LG showed an alkaline pH that ranged from 9,0 to 10,9, as seen in tables 9 and 10 .

Table 7. pH values of the SLES with CAPB

Formulation	% total surfactant	pH
A1	10	6.8 ± 0.1
B1		6.9 ± 0.1
C1		6.2 ± 0.0
D1	20	6.4 ± 0.1
E1		6.7 ± 0.1
F1		6.0 ± 0.1
G1	30	6.2 ± 0.1
H1		6.7 ± 0.0
I1		6.1 ± 0.0
J1	40	6.3 ± 0.2
K1		6.1 ± 0.1
L1		5.9 ± 0.1
M1	50	5.9 ± 0.1
N1		6.4 ± 0.1
O1		5.9 ± 0.1

Table 8. pH values of the SLES with LG

Formulation	% total surfactant	pH
A2	10	9.5 ± 0.1
B2		9.3 ± 0.1
C2		9.5 ± 0.1
D2	20	10.0 ± 0.1
E2		9.9 ± 0.1
F2		10.4 ± 0.2
G2	30	10.5 ± 0.1
H2		10.5 ± 0.1
I2		10.2 ± 0.2
J2	40	10.1 ± 0.1
K2		10.1 ± 0.1
L2		10.9 ± 0.1
M2	50	10.6 ± 0.1
N2		10.2 ± 0.2
O2		10.8 ± 0.1

Table 9. pH values of the DLS with CAPB

Formulation	% total surfactant	pH
A3	10	6.7 ± 0.1
B3		6.9 ± 0.1
C3		6.6 ± 0.0
D3	20	6.6 ± 0.1
E3		6.8 ± 0.1
F3		6.4 ± 0.2
G3	30	6.4 ± 0.1
H3		6.5 ± 0.1
I3		6.4 ± 0.1
J3	40	6.4 ± 0.0
K3		6.4 ± 0.1
L3		6.3 ± 0.1
M3	50	6.1 ± 0.1
N3		6.1 ± 0.1
O3		6.3 ± 0.1

Table 10. pH values of the DLS with LG

Formulation	% total surfactant	pH
A4	10	9.0 ± 0.1
B4		8.8 ± 0.1
C4		9.1 ± 0.1
D4	20	9.2 ± 0.1
E4		9.0 ± 0.1
F4		9.2 ± 0.1
G4	30	9.0 ± 0.1
H4		9.0 ± 0.1
I4		9.3 ± 0.1
J4	40	9.4 ± 0.0
K4		9.3 ± 0.1
L4		9.3 ± 0.1
M4	50	9.2 ± 0.1
N4		9.0 ± 0.2
O4		9.0 ± 0.1

5.5 Ternary phase diagrams

Phase diagrams are another tool that helps in mapping the different mesophases obtained with surfactant mixtures and their properties.

Phase diagrams are useful tools for formulators, as they can give a major contribution in finding the correct compositions to use for a particular product.

The phase diagram of the system of SLES with CAPB and of SLES with LG are shown in figure 10 and 11 respectively.

In the first formulations A1, B1, C1 and D1, a simple clear isotropic liquid can be observed, which is characteristic of a dilute surfactant solution, which is associated with spherical micellar structures. As the surfactant content increases, various liquid crystalline structures can be observed.

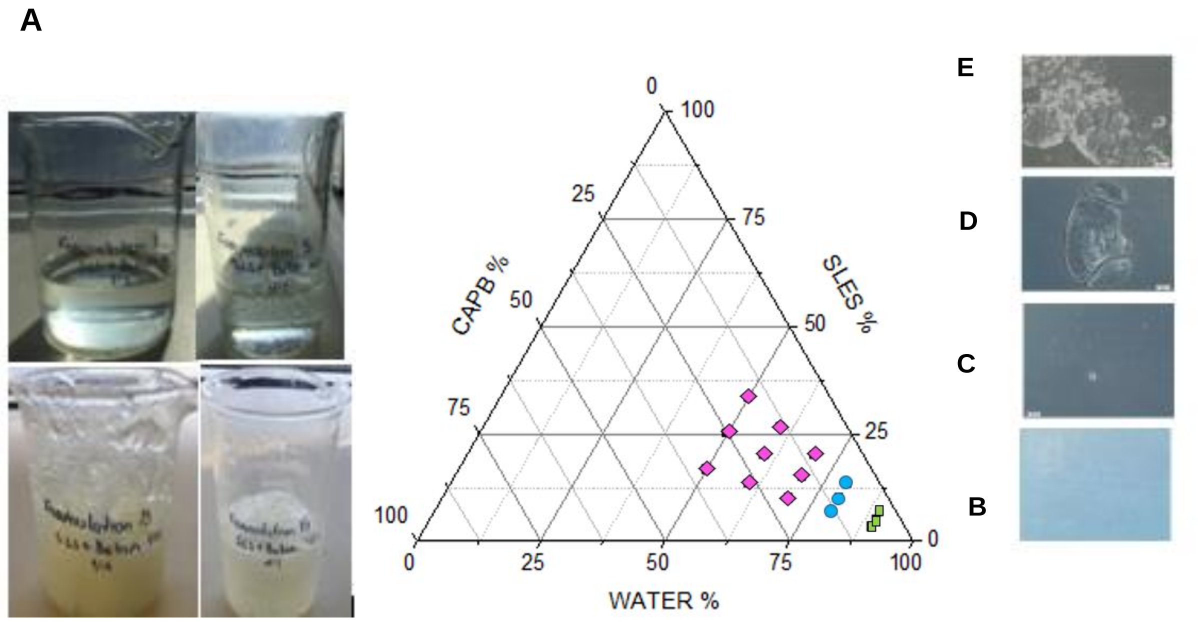


Figure 12. Ternary phase diagram of SLES with CAPB. (A) Images of the mixtures at different concentration ratios. Optical microscopic images of (B) formulation B1 (C) formulation J1(D) formulation L1 (E) formulation O1. The scale bar is 50µm.

Green (🟩): Low viscosity with no crystalline structures under polarised light.

Blue (●): High viscosity with no crystalline structures under polarised light.

Pink (◆): High viscosity showing crystalline structures under polarised light

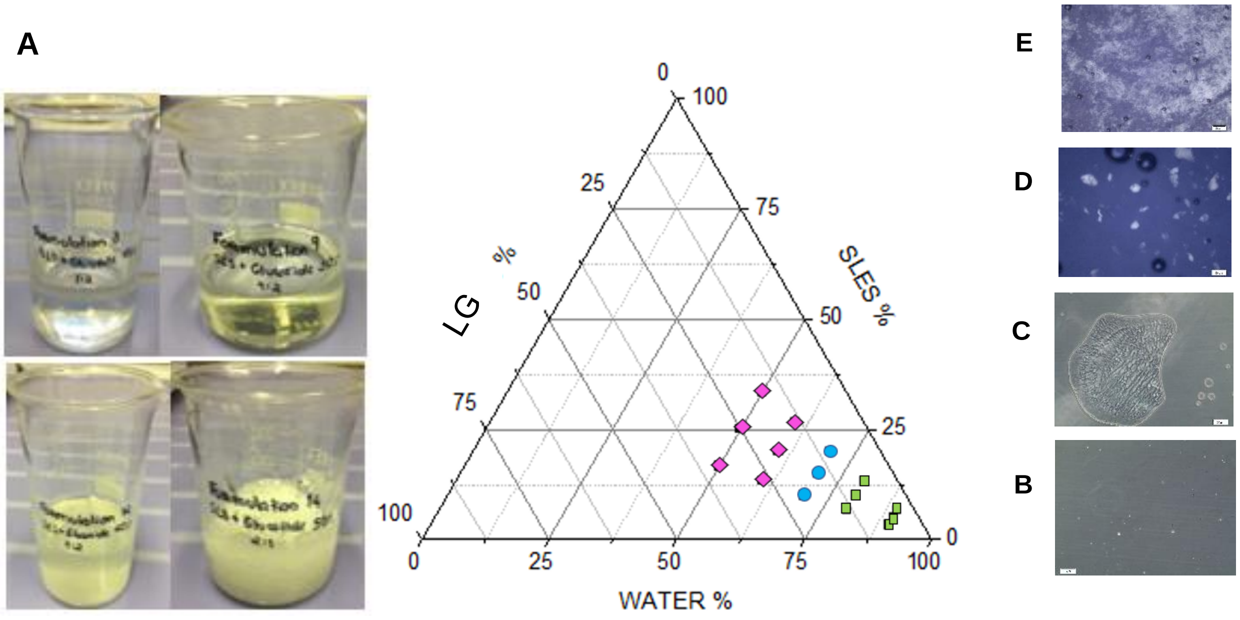


Figure 13. Ternary phase diagram of SLES with LG. (A) Images of the mixtures at different concentration ratios. Optical microscopic images of (B) formulation B2 (C) formulation J2(D) formulation M2 (E) formulation O2. The scale bar is 50µm

Green (🟩): Low viscosity with no crystalline structures under polarised light

Blue (●): High viscosity with no crystalline structures under polarised light.

Pink (◆): High viscosity showing crystalline structures under polarised light

6 DISCUSSION

Subtle changes in the system properties can lead to transformation of micellar aggregation from one type to another, such as: changes in the concentration of surfactants, addition of an electrolyte, changes in the pH of the solution, changes in the temperature of the system or even changes in the solvent composition. This project focussed mainly on the impact that the increase of surfactant has on the microstructure and overall properties of the formulation, having the goal of achieving easy to use concentrated cosmetic rinse-off products (43).

The type of surfactants used was the first aspect that had to be discussed, in order to understand better the surfactant interactions, and the difference between blends. Two types of anionic surfactants were used, SLES the ethoxylated version of SLS, and DLS belonging to the sulfosuccinate family, that for their good detergency and foaming properties are often exploited in rinse-off products.

Both anionic surfactants contain a hydrophobic moiety of twelve carbons, so the hydrophobic chain length has no influence on the difference between their CMC, detergency, or mildness performance differences. Therefore, the main differences between these two anionic surfactants reside in their polar group. SLES has the advantage of being far less irritating to the skin and eyes than SLS, because of its ethoxylation. The multi counter ion valences of DLS also grants it a lower CMC than those of monovalent anionic surfactants, and therefore a good foaming ability and low irritational potential. A trade-off is always present between more aggressive surfactant, resulting in better cleansing performance but also leading to more skin and eye potential irritational behaviour (14,74).

Liquid crystal phase behaviour of mixed surfactant systems and their relation to physical characteristic of the final product needs to be considered, since the microstructure of mesophases influences their properties such as rheology, texture, and physical appearance.

The first aspect to take into consideration when analysing the blends formulated is their microstructure. The most important technique to identify the presence and type of liquid crystal is polarising optical microscopy, since all mesophases are birefringent and display a unique texture when viewed under crossed polarises. Liquid crystalline phases show a variety of optical patterns when observed under a polarized microscope, that are particular to the state of molecular order prevailing in that mesophase, such as mosaic texture, oily streaks and Maltese crosses present in lamellar phase, or the presence of fan-like units in hexagonal phases (9,46,75).

The relationship between rheology and microstructure is of decisive importance in a rinse-off product. The consumer opinion is often swayed by the viscosity of the product, where thicker formulations are considered to be richer and more luxurious, because of their improved ease of application and overall cosmetic appeal. Rinse-off products can have many types of primary packing, the preferred ones being bottles, possibly fitted with a pump, or in a squeezable tube. Rinse-off products are generally formulated to achieve the viscosity of a gel-like material, with shear-thinning flow, allowing the easy flow of the rinse-off product out of the bottle trough the exertion of pressure either on the bottle or on its pump, as well as allowing an easy distribution though the skin's surface (14,59). Therefore, viscosity has the potential to make or ruin the overall functionality and availability of the product, since if it does not possess the right flowing properties it cannot be used. In this way, products should appear thick and creamy while sitting on the palm of the hand but still be easily managed once applied (14).

Microstructural changes that happen when total surfactant concentration is increased in the system is directly related to the rheological behaviour of the formulation (74).

Considering each of the optical microphotos exhibited in Table 5 and 6 as a typical representation of the sample overall aspect. The SLES and CAPB formulations with total surfactant concentration of 10% presented an isotropic aspect under polarised light demonstrating the same optical properties when manipulating the polarizer, which can indicate the presence of simple surfactant aggregates such as micelles (76). This is corroborated by the viscosity flow, since these formulations presented viscosities close the water flow, possessing a Newtonian flow behaviour, which can be associated with spherical micellar aggregations being present in solution.

For the formulations of D1, E1, F1 (20% total surfactant) a Newtonian flow and isotropic aspect was obtained, but the apparent viscosity were higher than the ones seen in the 10% total surfactant blends, this coupled with be absence of crystalline structures, can suggest the presence of rod or worm-like micelles in solution (Figure 10).

However above 20% total surfactant, for the SLES with CAPB blend, a higher order self-assembly of surfactant starts to appear, made clear by the presence of birefringence, a phenomenon observed in both hexagonal and lamellar phases, and the solution becomes anisotropic. The microscopic appearance of the optical micrographs for the 30 to 50% total surfactant clearly shows the existence of liquid crystalline phases in concentrations above 30% total surfactant, and indications of hexagonal phase were present at samples with 50% total surfactant that presented a brushed metal or mosaic texture. However we cannot say with certainty if the lamellar phase was indeed achieved, since the optical patterns associated with this phase, such as maltese crosses or oily streaks were not present (77,78). These findings are supported by the flow behaviour exhibited. Above 30% total surfactant apparent viscosity increased significantly, and the solution started presenting a non-Newtonian shear-thinning behaviour, where the viscosity of the solution decreases significantly with increasing shear rate which suggests the possibility of a hexagonal phase being present in solution, Figure 9.

Similarly, for the SLES with LG blend with concentrations from 10 to 20% were optically clear and present a Newtonian flow, with low apparent viscosity, which indicates the possibility of spherical micelles, Figure 11 (9). For the formulations of 30% total surfactant a Newtonian flow was present, but the apparent viscosity were higher than the more verified for the 10% and 20% total surfactant blends, and no crystalline structures were present, which can suggest the presence of rod or worm-like micelles in solution.

With the addition of more surfactant to the system, a higher packing value is achieved and micellar curvature is decreased (42). Therefore, above the 30% concentration of total surfactant, optical microscopy under polarised light suggests the existence of liquid crystals, clear by the presence of birefringence in those samples and so it can be hypothesised that lyotropic liquid crystalline phases were present, this coupled with the fact that the formulation appears to behave as clear ringing gels with shear-thinning behaviour, it can be extrapolated that we were in the presence of an hexagonal phase (59). However, in order to arrive to a more conclusive decision samples should be observed and analysed by Small Angle X-ray Scattering (SAXS), to determine with certainty the structural features present (33).

The shear-thinning behaviour of high-viscosity rinse-off gels is indispensable. The reduction of viscosity with the increase of shear rate, indicates that the formulas will allow for a quicker distribution of the product through the area (skin or hair) increasing the rate of dilution and allowing for a quicker adsorption of the surfactant, which leads to a rapid foaming. Furthermore, this flow behaviour allows full use of the concentrated product, reducing to the minimum the amount of product stuck in the primary packaging (59,79). Lamellar phase if the most attractive liquid crystal phase due to its flow properties, allowing to achieve a creamier and less water-like feel product. From a performance perspective the lamellar phase is the most appealing liquid crystal phase, since in comparison with the hexagonal phase it presents, in theory, lower apparent viscosities, which make for an easy product use, similar to the ones present in classical rinse-off products.

Foam quality if another important aesthetic consideration. While not strictly part of the technical functionality, consumers have come to expect a rich creamy foam. The high viscosities of this concentrated formulations can present as an advantage in the slowing of water drainage, and improve the stabilization of foam (50).

The presence of co-surfactants in the formulation is essential when it comes to foamability and the control of foam, so LG and CAPB are very important to reduce the overall CMC of the surfactant system since they reduce the ionic repulsion forces and steric hindrance of the anionic moieties of SLES and DLS making the mixed micelles more stable, and maintaining it inside the Marangoni window essential for the elasticity of the solution and for its foam stabilization ability. So that there is a balance between having enough free monomers but not exceedingly that the Marangoni stabilizing effect is lost (50).

To allow good lathering ability rinse-off products are formulated with a total surfactant concentration greater that the CMC, allowing for the excess surfactant to be available to interact with air upon use and form lather. The most commonly used foam boosters are betaines, such as CAPB. So, it would be expected to observe a more stable and longer-lasting foam, on the formulations that contain this secondary surfactant. The cylinder shake or the perforated disc beating method would have to be performed in order to evaluate with certainty the foaming ability of this formulations (80–82).

A logical concern that could surface when designing and formulating a concentrated rinse-off product is its skin irritation potential, in order words, its mildness behaviour. From a purely theorical perspective one could be tempted to think that higher concentrations of surfactant, a potential skin and eye aggressor, would lead to a harsh rinse-off product, that could lead to serious skin conditions in the long run. However, research has proven this theory wrong, since surfactant monomers seem to be the cause of most skin irritation potential in surfactants, the higher packing of surfactant when in concentrated formulations, leads to the aggregation of surfactant molecules into non-irritating micellar phases. Since surfactant are aggregated into micellar structures, they are not available in the monomer form, and hence are not available to adsorb at the surface of the skin, causing its impairment (52,83).

Secondary surfactants such as CAPB and LG play an essential role in reducing the irritational potential of the primary anionic surfactants SLES and DLS, since they stabilize the micellar aggregates by lowering the repulsion forces between the polar head to anionic surfactants with each other, and hence decrease the relative proportion of monomers in the solution. Micelles composed of mixtures of surfactants such as an anionic surfactant with an amphoteric surfactant or a anionic surfactant with an non-ionic surfactant lead to a bigger micelle radius making it difficult for it to penetrate through the lipidic membrane of the stratum corneum due to steric hindrance (32). Hence, the addition of a secondary surfactant leads to stabilization of the micelles and a decreased penetration of the mixed micelles because of an increase in their size (54,84). Although sufficient literature can be reassuring of the mildness performance for concentrated surfactant formulations, research should be done to assess transdermal water loss (TEWL) testing, that measures skin hydration, a factor affected by skin impairment, the Zein test, which measure protein absorbance of the surfactant, and/or corneosurfametry for skin irritation. (14).

The higher the pH rises, the more irritant is the rinse-off product (85). The formulations with LG as a secondary surfactant had the inconvenient of being extremely alkaline (pH 8.8-11.0) and rinse-off products with these pH ranges generally cause irritation, skin dryness and scaling. Soap cleansers that exhibit a high pH have been consistently shown to perturb the skin barrier (19). Therefore, the correction of the formulation's pH is of fulcra importance in rinse-off products.

The blends that possessed CAPB has a secondary surfactant, had dramatic increase in the packing factor of mixed micelles due to the ionic attraction between the positively charged betaine, since CAPB isoelectric point is at 6,25; and the negatively charged sulfate groups. This leads to the formation of wormlike mixed micelles and confers a higher viscosity the solution. Since the pH of the formulation of CAPB was slightly acidic in most samples, which means that the CAPB was in its acidic form, and the formation of large stable micelles is favoured. The mix of SLES with CAPB generates a significant synergetic enhancement in surface-active properties such as detergency and foaming (62). The fact that the pH varies so much from blend to blend of surfactant might point to differences in the syntheses processes of these surfactant being the pH attributed to the raw material itself and its manufacturing process, being its corrections for the achievement of mildness a process that should occur later on.

Concerns for the environment has provided the impetus to develop this thesis on concentrated rinse-off products. These concentrated compositions have a considerably higher level of surfactant actives than conventional rinse-off products. As a result of the high concentration of actives, these products have smaller volumes allowing them to be sold in smaller containers and consequently reduce the waste loads of primary packaging. Additionally, the consumer uses less product in each use, bridging saving in the storage area needed as well as in cost of transporting. The lower weight and volume of the product, due to less water content decreases the emissions of CO_2 and other greenhouse gas during transport, because less trips are made for the distribution of the product (59,60). Less water content can also be associated with a lower growth of microorganisms, this can, if studying, allow the decrease or total omission of preservatives. The omission of preservatives would provide numerous advantages by avoiding the risks associated with the addition of preservatives, such as disturbances of the normal skin microflora, skin irritations, or skin allergies (59). The need for preservatives should be assessed through Preservative Efficacy Test (86).

By developing rinse-off products alternatives with less water content, one can take advantage of all the benefits that would come from the less weight and volume of the finished product, benefits demonstrated in other product such as the “Small and Mighty” laundry detergent or Guhl concentrated shampoo (58,59).

7 CONCLUSION

One of the main focus of the beauty market nowadays is the development sustainable and environment-friendly products without compromising their performance.

The concentrated surfactant formulations studied on this project have the advantage of being more ecological than most commercial rinse-off products, since they can be presented in a smaller format. Therefore, volumes of transported products would be significantly decreased, which reduces the emissions of CO_2 during transport, and in the consumption of plastic, since the product bottles would be a lot smaller.

However, it is not enough for a product to be more sustainable than the traditional options and concentrated rinse-off products have to present the same performance characteristics as the classical product. They should have appropriate viscosity, an acceptable foaming ability and a reasonable shelf-life, which properties that must be assessed further in future studies. Studies in terms of mildness like TWEL and zein test are important next steps in order to assess the products harshness. In terms of the cosmetic properties of concentrated surfactant formulations, these should be assessed through simple sensorial analyses with volunteers, in order to assess texture, skin feel and evaluate the overall consumer appeal, results that can then be compared with corneometry and other performance tests.

The concentrated formulations presented in this work had liquid crystalline structures in their compositions, as shown by the viewed by polarised light microscopy.

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