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**FORMULATION OF A SHAMPOO WITH SODIUM OLEATE
AS SURFACTANT**

**IZDELAVA ŠAMPONA Z NATRIJEVIM OLEATOM KOT
POVRŠINSKO AKTIVNO SNOVJO**

UN KOZMETOLOGIJA

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Statement

I hereby declare that my bachelor thesis was written independently by me under the supervision of Prof. Odon Planinšek and co-supervision of Prof. Dr. Werner Kunz.

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Abstract

The aim of this work was to develop a formulation of a “two in one” shampoo (2 in 1 shampoo) with sodium oleate (Na oleate) as a primary surfactant. A 2 in 1 shampoo contains not only surfactants but also a conditioning agent. Na oleate and other salts of fatty acids are especially important in developing countries, where the production of artificial surfactants is low. Therefore, the development of a 2 in 1 shampoo with Na oleate would present an important achievement as this product could be potentially available also in countries where the access to the basic products for hygiene maintenance is limited. Na oleate is an efficient surfactant, however, it is not a good candidate for a shampoo formulation due to i) its alkalinity, which disrupts the protective acidic mantle on the skin, and ii) its sensitivity to hard water that leads to the formation of insoluble salts with multivalent ions.

As a part of this thesis, the pK_a value of Na oleate was decreased to 6.2 by adding 3 wt% of *Stevia rebaudiana* extract into solution. The pK_a value refers to a pure Na oleate solution, whereas the apparent pK_a value refers to the pK_a value of Na oleate in a mixture with other ingredients. Then, the effect of cocamidopropyl betaine (CAPB) on the pK_a value of 6.2 was investigated. No significant change in pK_a value was observed. After that, a procedure of preparation of 2 in 1 shampoo was developed, so that the formulation with stable composition was obtained. Further on, the stability of the final 2 in 1 shampoo formulation in hard tap water was evaluated. The sample containing a chelator sodium citrate (Na citrate) remained stable in the following 15 min, however, the precipitates were seen in a sample without chelator. Then, the qualitative size of particles and monodispersity of the colloidal system were evaluated by dynamic light scattering (DLS) at pH values of 6.2, 7.0 and 9.8. The size of the micelles at pH value 9.8 was much smaller compared to the size of the micelles in the other two samples. Moreover, the values of polydisperse index (PI) varied from 0.401 to 0.512, meaning broad size distribution of particles. Last, the viscoelastic properties of the final formulation were evaluated with and without NaCl and Na citrate at pH values of 7.0 and 9.8. The sample with and without salts at pH 7.0 showed a Newtonian behaviour and the sample with salts at pH 9.8 showed a typical shear thinning behaviour. It can be concluded that the 2 in 1 shampoo with sodium oleate as primary surfactant was developed. Of course, more experiments must be carried out to get a stable and potentially saleable product.

Key words: 2 in 1 shampoo, sodium oleate, stevia, pK_a , colloidal system

Povzetek

Namen diplomske naloge je bil razviti postopek priprave “dva v enem” šampona (2 v 1 šampon) z natrijevim oleatom (Na oleat) kot primarno površinsko aktivno snovjo. 2 v 1 šampon je šampon, ki poleg površinsko aktivnih snovi (PAS) v svoji sestavi vsebuje tudi regeneratorski. Na oleat in ostale soli maščobnih kislin so pomembna čistilna sredstva predvsem v državah tretjega sveta, kjer je proizvodnja sintetičnih PAS majhna. Tako bi razvoj 2 v 1 šampona z Na oleatom predstavljal pomemben dosežek, saj bi tak šampon potencialno postal dostopen ljudem v državah, kjer so osnovna higienska sredstva omejena. Na oleat je sicer učinkovito čistilno sredstvo, ki pa se zaradi dveh pomankljivosti dandanes ne uporablja več za izdelavo šamponov. Prvi problem predstavlja bazični pH, ki lahko poškoduje zaščitni lipidni sloj kislega značaja na koži. Kot drugo pa so soli maščobnih kislin občutljive na trdo vodo in tvorijo netopne soli v stiku z dvovalentnimi ioni.

Prvi cilj raziskave je bil znižati pK_a vrednost Na oleata. To nam je uspelo z dodatkom 3 m/m% ekstrakta rastline *Stevia rebaudiana*, tako da je bila končna apK_a vrednost Na oleata enaka 6.2. Izraz pK_a se nanaša na pK_a vrednost čiste raztopine Na oleata, medtem ko se izraz apK_a nanaša na pK_a Na oleata v raztopini z drugimi sestavinami. Prav tako smo preučili vpliv kokamidopropil betaina (CAPB) na apK_a vrednost 6.2. Dodatek te PAS ni bistveno vplival na apK_a . Nato smo razvili postopek priprave 2 v 1 šampona, da je bil končni vzorec fizikalno stabilen. Končno formulacijo smo ovrednotili s spremljanjem stabilnosti izdelka v prisotnosti trda vode iz pipe. Vzorec, ki je vseboval kelator natrijev citrat (Na citrat) je ostal stabilen naslednjih 15 minut, medtem ko se je v vzorcu brez kelatorja pojavila bela oborina. Poleg tega smo s pomočjo metode dinamičnega sipanja laserske svetlobe (DLS) kvalitativno ovrednotili velikost delcev in monodisperznost koloidnega sistema s pH vrednostmi 6.2, 7.0 in 9.8. Najmanjši miceli so bili prisotni v vzorcu s pH vrednostjo 9.2. Vrednosti polidisperznega indeksa (PI) so se gibale med 0.401 in 0.512, kar pomeni široko porazdelitev delcev. Nazadnje smo preverili še viskoelastične lastnosti izdelanega šampona ob prisotnosti in odsotnosti NaCl in Na citrata pri pH vrednostih 7.0 in 9.8. Ugotovili smo, da je vzorec s pH vrednostjo 7.0 predstavljal Newtonsko tekočino, medtem ko je vzorec s pH 9.8 predstavljal tipično pseudoplastično tekočino.

Na podlagi rezultatov lahko zaključimo, da nam je uspelo izdelati prvi 2 v 1 šampon z natrijevim oleatom kot PAS. Seveda pa je potrebnih še veliko nadaljnjih raziskav, da bo tak šampon ne samo dobro čistilno sredstvo ampak tudi fizikalno stabilen izdelek.

Ključne besede: 2 v 1 šampon, natrijev oleat, stevia, pK_a , koloidni sistem

List of abbreviations

2 in 1 shampoo	Two in one shampoo
2 v 1 šampon	Dva v enem šampon
AE	Alkyl ethoxylate
ALS	Ammonium lauryl sulfate
ALES	Ammonium lauryl ether sulfate
APE	Alkylphenol sulfate
AS	Alkyl sulfates
CAPB	Cocamidopropyl betaine
CMC	Critical micelle concentration
DLS	Dynamic light scattering
LAS	Linear Alkylbenzenesulfonates
NaCl	Sodium chloride
Na oleate	Sodium oleate
PAS	Površinsko aktivna snov
PI	Polydispersity index
apK _a	Apparent pK _a
T _{Kr}	Krafft temperature

1. Introduction

Soap is a fatty acid salt prepared by neutralization of fatty acids with alkali. The first recorded evidence of the manufacture of soap dates back to around 2800 B.C. in Ancient Babylon. First it was made of animal fat and ashes. Later on, France, Italy and Spain became soap making centres, because big amounts of vegetable oils were produced there. Society has become aware of the importance of cleaning products for hygiene. In the late 18th century industry started to manufacture bar soaps. Soap was not a luxury item anymore, but was available to the general public as well. It became a daily used cosmetic product. Soap was used for cleaning the body as well as for cleaning hair. At that time soap was the only available hair cleanser. People started to realize that soap is not a suitable cleansing product. It was alkaline, which disrupted the skin acidity. Another problem was sensitivity to hard water. Hence, insoluble fatty acid salts were formed, which left a dull and dry look on hair. These properties made soap a bad candidate for a shampoo formulation. During the World War 2, the first synthetic surfactant was produced. Since, the development of synthetic surfactants has increased significantly due to their great performance and affordable price. In 1933, the first non-alkaline shampoo, called Onalkali was formulated. Nowadays, shampoos and other cleansing products are essential for maintaining cleanliness and attractive appearance of our hair (1, 2).

According to a legend, the word »shampoo« originates from the Hindustan language and it means »to squeeze«. Shampoos are usually liquid, but may also be creams, aerosols or dry. The primary function of shampoos is cleaning hair and scalp (3). However, there are also other very important qualities such as:

1. Quick and abundant foaming
2. Neutral or slightly alkaline pH
3. Conditioning effect
4. Low irritation
5. Pleasant smell and appearance
6. Physical and chemical stability
7. Reasonable price (4-6)

Shampoos usually consist of 10 up to 30 ingredients, including primary surfactants, secondary surfactants, conditioning agents, viscosity builders, pH adjusting ingredients, solvents, opacifiers, colours, fragrances, preservatives, UV absorbers, chelators and

different active ingredients (3, 7, 8). Obviously, surfactants are predominating in shampoo formulations, while other ingredients are added in much lower amounts. First, some general features of surfactants and other ingredients will be presented.

1.1. Surfactants

1.1.1. *Chemical properties of surfactants*

Surfactant is an abbreviation for a surface active agent. Surfactants are amphiphilic molecules, meaning they contain hydrophobic tail and hydrophilic head (9). Therefore, the hydrophilic group interacts with water by hydrogen and dipole-dipole interactions. Conversely, the hydrophobic group interacts only via hydrophobic bonds therefore the self-associating process occurs to lower the high potential energy (10). Hence, surfactant molecules can either adsorb on interfaces or form different aggregates. First, the molecules concentrate at the air-water interface, where nonpolar tails are oriented into the vapour phase. With increased concentration, the surfactant molecules self-assemble so that the nonpolar tails are oriented to each other and the polar heads to aqueous phase. These structures are also known as micelles. The point where the micellization process begins is called critical micelle concentration (CMC). CMC value can be determined by surface tension, conductance or surfactant ion electrode measurement. If the temperature is too low, surfactant molecules can precipitate from solution forming hydrated crystals instead of micelles. The temperature at which micelles start to form is called Krafft temperature (T_{Kr}). Both CMC and T_{Kr} are data which should not be forgotten when formulating a cosmetic product with surfactants. If the concentration of a surfactant increases other structures like liquid crystals are formed.

Surfactants form self-associating aggregates in a solution, therefore, this system is called association colloid. A colloid system is a two-phase system consisting of one substance evenly distributed throughout a continuous phase. In Table 1 some characteristics of colloids, coarse systems and real solutions are compared (11, 12).

Most commonly the surfactants are classified by the nature of hydrophilic head. Four classes should be mentioned: anionic, cationic, amphoteric and non-ionic surfactants. Anionic surfactants carry a negative charge, cationic positive and amphoteric surfactant negative as well as positive charge when ionized. However, non-ionic surfactants always remain uncharged (13).

Table 1. : Classes of dispersed system and their properties

Level of dispersion	Coarse	Colloidal	Molecular
Designation	Suspension	Colloid	Solution
Particle size	> 100 nm	1- 100nm	< 1nm
Visibility	Naked eye/ standard microscope	Electron microscope/ Tyndall effect	Optically homogenous even with electron microscope
Sedimentation	Under gravity	Ultracentrifuge	No sedimentation
Filtration	Paper filter	Some with membrane filters	Not possible

1.1.2. Detergency mechanisms

As the main function of shampoo is cleaning, the mechanisms of detergency should be briefly discussed. Different types of soils can be found in our hair and scalp. Of course, primary soils are lipid soils from sebum and proteins from skin. Also common are soils from hair styling products such as polymers and cationic ingredients. Nevertheless, different environmental soils can be present as well. The most important mechanism is roll-up, which occurs when water diffuses to the soil-fibre interface (14). Roll-up is caused by three interfacial tensions between fibre and oil (γ_{fo}), fibre and water (γ_{fw}) and oil and water (γ_{ow}). That means that the following equation must be positive:

$$\underline{R} = \gamma_{fo} - \gamma_{fw} + \gamma_{ow} \cdot \cos\theta,$$

where \underline{R} presents the combination of a aforementioned interfacial tensions and θ is a contact angle. So hydrophilicity of the hair shaft surface determines the removal of lipid soils from hair. The more hydrophilic the surface, the less lipophilic components will be present on hair shaft. Hair damaged due to bleaching or excessive hair washing is generally more sensitive to lipids removal. Because of the hydrophilic surface, the oily soil removal is more facilitated. However, the removal of soils also depends on the bonding of the particle to the surface. Soil particles which consist of nonpolar components interact with Van der Waals forces. Therefore the removal is much easier than for cationic ingredients. Cationic ingredients bind not only with Van der Waals forces but also with ionic forces (15).

1.1.3. Commonly used surfactants in shampoos

There are several surfactants that are typically used in shampoo formulations. Anionic surfactants are used as primary surfactants. Generally 8 to 20 wt% of primary surfactants are present in shampoos. Primary surfactants possess good cleansing and foaming properties. Most commonly used are sodium lauryl ether sulfates (SLES), ammonium lauryl sulfates (ALS), and ammonium lauryl ether sulfates (ALES) (16). Anionic surfactants can also increase the viscosity of the product when used in combination with salts. Amphoteric and non-ionic surfactants are used as secondary surfactants. Secondary surfactants are added to enhance the action of primary surfactant. They are usually much milder compared to anionic surfactants. Thus, the level of irritancy of a shampoo can be decreased. Amphoteric surfactants are also main ingredients in baby shampoos, where mildness is essential. Non-ionic surfactants are not so frequently used in shampoos. It is known, that they possess good cleaning properties, but the foam is not as stable and dense as when anionic surfactants are used (17).

SLES is found in many shampoo formulations. There are several reasons for its extent application in shampoos. It possesses great cleaning properties and is also a very effective foaming agent. SLES is compatible with hard water and soluble in water also at increased temperature. When used in combination with NaCl it increases the viscosity of a shampoo. SLES is a good choice for formulating high-viscosity and low-pH shampoos. Nevertheless, an important factor for its commercial use is, of course, the low price. However, one disadvantage is the presence of dioxane derivatives as a by-product of the ethoxylation process. The structure of SLES is shown in Fig. 1.

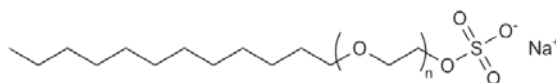


Fig. 1: The structure of SLES

CAPB is frequently used in shampoos as secondary surfactant. It consists of a cationic amine and an anionic carboxylate group (Fig. 2), therefore it is classified as an amphoteric surfactant. CAPB is synthesized from fatty acids hydrolysed from coconut oil and dimethylaminopropylamine. CAPB is not just a good foaming agent, but also enhances the viscosity of the product. It should also be mentioned, that this surfactant is mild and therefore extensively used in baby shampoos. CAPB is also biodegradable and synthesized from renewable materials (17-19).

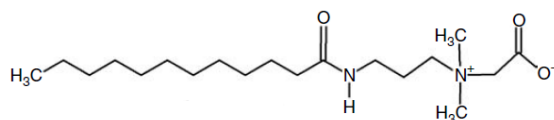


Fig. 2: The structure of CAPB.

1.1.4. Impact of surfactants on environment

Large volumes of shampoos and other products containing surfactants are consumed daily. The environmental awareness notable increased not just among consumers but also by governmental authorities and detergent manufacturers. Therefore sustainable development became an important concept in cosmetic industry as well. After use surfactants are disposed mostly into groundwater. The majority of the groundwater is then treated with different cleaning processes. In some extent surfactants are distributed directly to environment as well (21). First, the degradation process must be considered. Nowadays, most surfactants are biodegradable (Table 2) and also low-toxic to environment. However, the majority is still obtained from petroleum. Beside petrochemical sources, surfactants can be obtained from renewable sources as well. Renewable raw materials showed good biological degradability under all conditions. Thus renewable materials are the most important alternatives for fossil-based raw materials. Key raw materials present fats and oils, carbohydrates and proteins (22).

Table 2: Biodegradability of different surfactants

Surfactant	Aerobic condition	Anaerobic condition
Fatty acid salts	Readily degradable	Readily degradable
Alkyl ethoxylates (AE)	Readily degradable	Degradable
Alkyl ethoxy sulfates (AES)	Readily degradable	Degradable
Alkyl sulfates (AS)	Readily degradable	Degradable
Linear alkylbenzenesulfonates (LAS)	Degradable	Persistent
Cationic surfactants	Degradable	Persistent
Alkylphenol sulfates (APE)	Degradable	Partially degradable

1.1.5. Fatty acid salts

The oil industry has grown and many products containing fats and oils have been developed. Fatty acids are well known materials for soap synthesis. Table 3 illustrates different fatty acids that can be found in oils. Soap is an especially important ingredient in Africa, Asia and

Latin America. There are two main reasons why soap is consumed in much higher levels in less industrialized nations. First, raw materials such as oils and fats are there available in much greater quantities and consequently a significant stock of vegetable-derived materials as well. In addition, the preparation of synthetic surfactants requires sophisticated manufacturing, which is unavailable in most of the less industrialized countries. Thus, soap is an essential cleaning agent for hygiene maintenance in these countries. Even in the industrialized regions, like United States and Europe, soap is widely applied in industry.

In the fat splitting process oil is hydrolysed to fatty acid and glycerol. Further isolation can be done by distillation. Then the fatty acid soap can be synthesized by neutralization of a fatty acid with various bases and that is so called saponification.

The transition of fatty acids to soap increases with an increasing pH. In lower pH, below the pKa value, an undissociated fatty acid dominates the solution. However, in alkaline pH, above the pKa value, carboxylate anions and acid-soap salts are present. A fatty acid shows no surface activity. Inversely, fatty acid soaps possess surface-active properties. If the pH of the solution is too low, a fatty acid form will predominate and no detergency will be achieved due to the lack of soap molecules. Therefore, an appropriate pH must be chosen, to provide a reasonable equilibrium between undissociated and dissociated molecules.

Generally, soaps are alkaline, which disrupts the acidic mantle of skin. Therefore fatty acid salts are not desirable in cosmetic products. The other disadvantage is sensitivity to hard water. It is a well-known fact that soap forms an insoluble salt, also known as soap scum, in presence of multivalent ions. An addition of chelators is therefore essential. These properties make soap a bad candidate for shampoo formulation (20, 22).

Table 3: Typical concentrations of different fatty acids in commercially available oils

	Oleic acid cis C18:1	Palmitic acid C16:0	Linoleic acid cis,cis C18:2
Rapeseed oil	60	6	21
Linseed oil	10	18	14
Sunflower oil	19	12	68
Palm oil	30	55	10
Tallow	40	27	3

1.1.5.1. Sodium oleate

Sodium oleate or sodium 9-octadecenoate is the sodium salt of the oleic acid (Fig. 3). Oleic acid is a monosaturated omega-9 fatty acid with 18 carbon atoms in the structure. It is obtained from triglycerides by a process called fat splitting. Then, the oleic acid is neutralized with sodium hydroxide. Na oleate is a white or slightly yellow powder with a tallow-like smell. It is an anionic surfactant and it possesses good cleansing and foaming properties. In this research, the function of Na oleate was as primary surfactant.

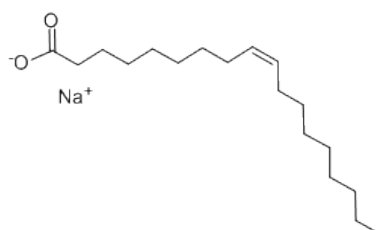


Fig. 3: The structure of Na oleate.

1.1.6. Alkyl polyglycosides

Alkyl polyglycosides are glucose-derived surfactants. The first alkyl polyglycosides were synthesized about 100 years ago. Nowadays, they are synthesized in significant amounts by combining fatty alcohol from vegetable oil and glucose from starch. The structure of alkyl polyglycosides is illustrated in Fig. 4. These non-ionic surfactants are completely naturally-derived and also possess product safety regarding their ecological, toxicological and dermatological properties (23). Beside the ecologically friendly profile, alkyl polyglycosides are not harmful and do not irritate human skin. The main application in cosmetics is in shampoos, where they are used as primary surfactants. Commonly used alkyl polyglucosides are decyl glucoside and caprylyl capryl glucoside. It was shown, that they have been very efficient and mild cleansing agents (24).

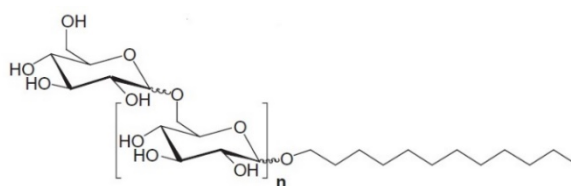


Fig.4: The structure of alkyl polyglucoside

1.1.7. Steviol glycosides

Steviol glycosides are highly sweet compounds extracted from the herb *Stevia rebaudiana* (stevia). Stevia is a herb native to Paraguay. Nowadays, it is cultured in many countries all over the world, including China, Korea, Brazil, Mexico, and Tansania (25). The extract of stevia is 30 to 320 times sweeter than sugar, therefore, it became a very popular artificial

sweetener in the food industry. The typical proportion of major diterpene glycosides is: 9.1% stevioside, 3.8% rebaudioside A, 0.6% rebaudioside C, and 0.3% dulcoside. The structures of stevioside and rebaudioside A are shown in Fig 5. Steviol glycosides can be classified as non-ionic surfactants, due to their amphiphilic properties. The application of stevia extract is wide in food industry however, there are no specific products on the cosmetic market containing this extract (26).

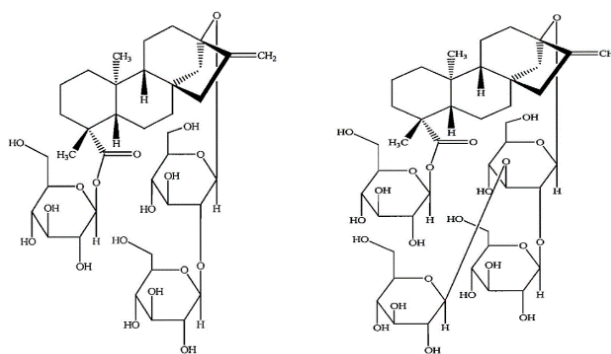


Fig. 5: Structures of stevioside and rebaudioside A.

1.2. Conditioning agents

Nowadays conditioning agents have become increasingly important ingredients in hair care products. They are key elements of conditioners and styling products but have also become an important part of shampoos. Shampoos containing conditioning agents are called »two in one« (2 in 1) shampoos. Frequently used conditioning agents are cationic surfactants, cationic polymers and silicones. One of the most commonly used conditioning polymers in shampoos is polyquaternium-10 also known as polymer JR400. Polyquaternium-10 is a polymeric quaternary ammonium salt of hydroxyethyl cellulose and a trimethyl ammonium substituted epoxide (Fig. 6) (27).

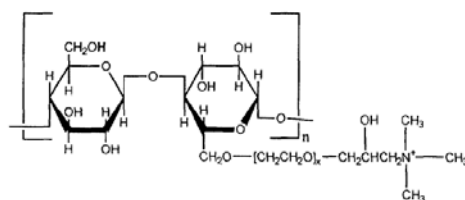


Fig. 6: The structure of polyquaternium-10.

The conditioning agent molecules adsorb on hair shaft surface, forming a thin layer, which gives a nice and shiny look of hair. The key interactions are therefore the one between hair shaft surface and conditioning agents. Three types of bonds should be considered: ionic, covalent, hydrogen bonds and Van der Waals interactions. Of course, this bond classification

is not so rigorous and transition from one to another bond can gradually occur (28). However, silicones like dimethicones interact with hair shaft mostly by hydrophobic bonds, whereas cationic polymers mostly by ionic bonds. Ionic bonds are especially important to the interaction of cationic conditioning agents and hair. These interactions are also the strongest of aforementioned bonds, with bond energies of the order of 50 - 200 kcal/mol. Hydrogen bonds are the second strongest bond, providing bond energies of about 4-10 kcal/mol. Hydrogen interactions are important to the binding of polymers containing polyalcohol or polyamide units to the hair. Van der Waals interactions are the weakest interaction, with bond energy of 1 kcal/mol (29).

It was discovered that unaltered hair shaft surface has an isoelectric point around 3.76, meaning the hair shaft surface will be negatively charged above this pH value. Since the majority of cosmetic hair products possess a pH value above 3.76, cationic conditioning agents will bind to hair surface relatively strong and also show high substantivity to hair, i.e. they would resist removal by water rinsing (30). Cationic polymers are one of the most important conditioning agents used in conditioners and 2 in 1 shampoos.

Formulation of a 2 in 1 shampoos with polyquaternium-10 as conditioning agent can be challenging as the positively charged polymer strongly interacts with negatively charged surfactants. Therefore, the mixture of positively charged polyion and negatively charged surfactant tends to form insoluble precipitates. It was shown that polymer forms association complexes with surfactants in solution (Fig.7). For polyquaternium-10 these interactions occur in two stages when anionic surfactant is in excess. First, the surfactant molecule adsorbs to the polymer. This layer neutralizes the cationic charge on the polymer, which leads to a decrease of solubility. Then, the ratio of negative charges to positive charges increases. Consequently, a second layer is formed by anionic surfactants. Solubility increases as well. To avoid the precipitation due to the net charge, a corresponding ratio between cationic polymer and anionic surfactant must be found.



Fig. 7: Different bindings of polymer and surfactant molecules.

1.3. Additives

Beside surfactants and conditioning agents, there are also other important ingredients that make shampoos stable and appealing to consumers. To formulate a chemically and physically stable shampoo, the addition of preservatives, buffers, chelators, antioxidants, UV absorbers and co-solvents is necessary. Last but not least, dyes, perfume oils, fragrances, and essential oils are added as well. The last mentioned ingredients are especially important to consumers, who usually choose cosmetic products according to their smell. In the following text, only the ingredients that were used in an experiment will be shortly discussed.

The first additive that can be found in many shampoos is NaCl. This salt is added to increase the viscosity of a shampoo. That phenomenon occurs in a combination with anionic surfactants. Micelles are negatively charged and therefore repel to each other. When salt is added, the charge density of the micelles surface is decreased. Micelles can pack more closely together and consequently the solution becomes more viscous (31).

Many surfactants are alkaline or acidic therefore the pH adjustment is very important. For alkaline shampoos, a citric acid is the commonly used substance for pH reduction. Other buffers such as phosphate can also be used.

As many ingredients are sensitive to multivalent ions, the addition of chelator is necessary. In many countries tap water is hard water. It contains multivalent cations such as magnesium and calcium ions. To protect the other ingredients to interact with these ions, the chelators are added to catch them instead.

1.4. Production procedures of shampoos

For clear shampoos, where only aqueous phase is present, the making procedure is simple. Generally, clear shampoos can be made without additional heating. This procedure can be shortly described in four steps:

1. Dissolving surfactants in water
2. Adding fragrances, dyes, preservatives and other additives. Stirring until a homogenous solution is obtained.
3. pH adjustment: adding acid/ alkali
4. Viscosity adjustment: adding salt

If a shampoo also contains oils, the procedure is slightly different. So, for oil in water emulsion the following procedure should be considered:

1. Dissolving hydrophilic ingredients in water (Part X)
2. Mixing and melting solid lipophilic ingredients (Part Y)
3. Part X and Part Y should be heated and added one to another
4. Stirring
5. When cooled, other ingredients should be added
6. pH and viscosity adjustment

When the product is made, some physical parameters such as viscosity and foaming are evaluated (32)

2. Aim of work

A Na oleate is an effective surfactant, however, due to its alkalinity and sensitivity to hard water its application in hair care cosmetic products is limited. In this research, the first precursor of a shampoo with Na oleate as primary surfactant will be developed.

The experiment will be divided into two parts. In the first part, the pK_a value of Na oleate will be decreased and the sample with the most stable composition will be developed. All the ingredients will be added step by step and the stability of the solution will be observed by naked eye.

The sample with the most stable formulation will be then further evaluated by different methods. First, the sensitivity to hard water will be investigated by dilution of the sample with tap water. Then, the DLS measurements will be performed on samples with different pH values. At the end, the rheology of the samples with and without salts at different pH values will be recorded.

3. Materials and methods

3.1. Materials

- Sodium oleate, purity: 82%, Sigma Aldrich Chemie GmbH, Steinheim, Germany
- DEHYTON PK 45 (Cocamidopropyl betaine), purity: 44%, Cognis GmbH, Germany
- Texapon® N 70 (Sodium lauryl ether sulfate), purity: 70%, BASF SE, Ludwigshafen, Germany
- TRUVIA STEVIA RA95 (stevia rebaudiana extract), Cargill, Minneapolis, United States
- Sodium chloride (NaCl), purity $\geq 99.6\%$, VWR, Leuven, Belgium
- Tri-Sodium citrate dehydrate, purity $\geq 99\%$, Merck KGaA GmbH, Darmstadt, Germany
- Citric acid, purity $\geq 99\%$, Sigma Aldrich Chemie GmbH, Steinheim, Germany
- JR400 (Polyquaternium-10), purity $\geq 99\%$, Amerchol Corporation, New Jersey, USA
- Deionised water (Faculty of Chemistry and Pharmacy, Regensburg, Germany)

3.2. Methods

3.2.1. Preparation of a 2 in 1 shampoo formulation

First, the influence of stevia on pK_a of Na oleate was investigated. The amount of each ingredient in samples is indicated in Table 3. In laboratory bottles, 25 g of the solution to be measured were prepared. First, the solid components were weighed and then deionized water was added. All mixtures were stirred until the solutions became clear and homogeneous. The samples were then left to rest for a few minutes to let the foam disappear. After that the samples were titrated and the pK_a values were determined.

Table 3: Preparation of 6 samples with different wt% of stevia.

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Ingredient			<i>wt%</i>			
Na oleate	10	10	10	10	10	10
Stevia	0	1	2	3	4	5
water	90	89	88	87	86	85

Then, the influence of CAPB on the apK_a value of 10 wt% Na oleate/ 3 wt% stevia mixture was investigated. A different amounts of 44 wt% of CAPB solution were added to samples with aforementioned composition. The amounts of Na oleate and stevia remained the same, as seen in Table 4. The CAPB weight percentages in Table 4 refer to the pure CAPB. The total mass of the sample was 25 g. The samples were stirred and left for few minutes that the foam disappeared. These samples were then titrated and the apK_a values were determined.

Table 4: Composition of samples with increased wt% of pure CAPB.

	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6	Sample7	Sample8	Sample9	Sample10	Sample11
Ingredient											
	<i>wt %</i>										
Na oleate	10	10	10	10	10	10	10	10	10	10	10
Stevia	3	3	3	3	3	3	3	3	3	3	3
CAPB _(pure)	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
Water	87	86.8	86.6	86.4	86.2	86	85.8	85.6	85.4	85.2	85

Further on, the stability of prepared solution with composition of 10 wt% Na oleate/ 3 wt% stevia/ 2 wt% CAPB/ 85 wt% water was optimized by addition of SLES. In this case, a 70 wt% SLES solution was used. 10 samples with different ratios of Na oleate and SLES were prepared. The ratio between these two surfactants has varied as follows:

$$0: 10/ 1: 9/ 2: 8/ 3: 7/ 4: 6/ 5: 5/ 6: 4/ 7: 3/ 8: 2/ 9: 1/ 10: 0.$$

The amount of CAPB and stevia remained the same, i.e. 2 wt% of CAPB and 3 wt % of stevia as seen in Table 5.

First, all the surfactants, i.e. Na oleate, stevia, CAPB and SLES, were weighed and then solubilized in water so the total mass of the sample was 25 g. All samples were stirred and pure citric acid was added to each sample, so that the final pH value of the solution was approximately 7. Any changes in stability were then observed in the following 10 days.

Table 5: Composition of samples with different ratio between Na oleate and SLES

Sample1	Sample2	Sample3	Sample4	Sample5	Sample6	Sample7	Sample8	Sample9	Sample10	Sample11
---------	---------	---------	---------	---------	---------	---------	---------	---------	----------	----------

Ingredient	wt %										
	0	1	2	3	4	5	6	7	8	9	10
Na oleate	0	1	2	3	4	5	6	7	8	9	10
Stevia	3	3	3	3	3	3	3	3	3	3	3
CAPB _(pure)	2	2	2	2	2	2	2	2	2	2	2
SLES _(pure)	10	9	8	7	6	5	4	3	2	1	0
Water	85	85	85	85	85	85	85	85	85	85	85

Then, the polymer JR400 was added to 25 g of sample with composition of 8 wt% Na oleate/ 2 wt% SLES/ 3 wt% stevia/ 2 wt% CAPB/ 85 wt% water. The amount of polymer JR400 increased as follows: 0.1/ 0.2/ 0.3/ 0.4/ 0.5 wt% (Table 6). Many different preparation methods were tested. The one described here provided the most stable system: polymer JR400 was added directly to the solutions which were then vortexed for 10 min. The solutions were then put into a water bath and warmed up to 50 °C for 15 min. All the samples were vortexed until the polymer JR400 was completely dissolved. Afterwards, the stability of prepared solutions was visually observed for the following 10 days.

Table 6: Compositions of the samples

Ingredient	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
	wt%				
Na oleate	8	8	8	8	8
SLES _(pure)	2	2	2	2	2
CAPB _(pure)	2	2	2	2	2
Stevia	3	3	3	3	3
JR400	0.1	0.2	0.3	0.4	0.5
Citric acid	1	1	1	1	1
Water	84.9	84.8	84.7	84.6	84.5

Further on, the NaCl and Na citrate were added in 25 g of solutions with the compositions of 8 wt% Na oleate/ 2 wt% SLES/ 3 wt% stevia/ 2 wt% CAPB/ 0.1 wt% JR400/ 84.9 wt% and 8 wt% Na oleate/ 2 wt% SLES/ 3 wt% stevia/ 2 wt% CAPB/ 0.2 wt% JR400/ 84.8 wt% water. As seen in Table 7 the amount of NaCl and Na citrate increased as follows: 1/ 2/ 3/ 4/ 5 wt%. All samples were then stirred until the salts were dissolved. The influence on the stability of the solutions was observed in the following 10 days. The sample with the most stable formulation was then further investigated.

Table 7: Compositions of the prepared solutions after adding salts.

Ingredient	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
	wt%				
Na oleate	8	8	8	8	8
SLES (pure)	2	2	2	2	2
CAPB (pure)	2	2	2	2	2
Stevia	3	3	3	3	3
Citric acid	1	1	1	1	1
JR400	0.1/ 0.2	0.1/ 0.2	0.1/ 0.2	0.1/ 0.2	0.1/ 0.2
Na Cl	1	2	3	4	5
Na citrate	1	2	3	4	5
Water	84.9/ 84.8	84.9/ 84.8	84.9/ 84.8	84.9/ 84.8	84.9/ 84.8

3.2.2. Evaluation of stability of prepared solutions

Each time a new sample was prepared the stability was visually observed. The samples were left in the laboratory for 10 days at 25°C. The samples were clear and homogenous and slightly bluish when prepared. Instability of the sample was seen as a milky solution with precipitates inside.

3.2.3. Determination of apparent pK_a values

Apparent pK_a is a pK_a value of a substance in a mixture, where also other substances are present. On the other side, the pK_a value refers to a pure substance. The titration was carried out with a pH-meter at 25 °C. The solutions prepared of Na oleate, stevia and water and the solutions prepared of Na oleate, stevia, CAPB and water were titrated with a 1 wt% citric acid solution (Table 8). The volumes of the added citric acid solution and pH values were recorded. First, the titration curves were established. The pH values were plotted as a function of volume of added citric acid. Then, the apK_a values were graphically determined.

Table 8: Preparation of 1 wt% solution of citric acid

Ingredient	wt%
Citric acid	1
Water	99

3.2.4. Sensitivity to hard water

10 g of sample with composition of 8 wt% Na oleate/ 2 wt% SLES/ 3 wt% stevia/ 2 wt% CAPB/ 0.1 wt% JR400/ 84.9 wt% were weighed in a bottle. The sample was homogenous, clear and slightly bluish. Then, the sample was diluted with 500 g of tap water at 40 °C. The concentration of Ca²⁺ in tap water was 0.304 mmol/l, therefore, the water used for this experiment was classified as hard water. The changes in stability were observed in the following 15 min. The stable samples remained clear and homogenous when diluted, whereas precipitates were present in unstable samples.

3.2.5. Dynamic Light Scattering (DLS)

DLS, also known as Photon Correlation Spectroscopy, is the most commonly used technique to investigate the presence of structures like micelles or droplets in a solution. It is based on the fact that such structures have a different refractive index than the surrounding media. For example, in an o/w microemulsion, the oil droplets have a different refractive index than the aqueous bulk phase. These objects will scatter an incoming monochromatic light in all directions. The intensity of the scattered beam is then measured at a given angle. As the scattered objects are undergoing Brownian motion due to thermal agitation, the intensity is constantly changing in time. The change in the intensity can be related to the diffusion coefficient and the size of particles. The correlation function, a comparison of the different signals of the scattered intensity, is a useful tool to quickly observe the presence of structures in a system. Moreover, the sphere size distribution, known as polydispersity index (PI), can be calculated as well.

The sample to be measured was filtered through a PTFE-filter in order to remove the dust. The samples were then transferred into cylindrical light-scattering cells of 10 mm outer diameter. This measurement was carried out with temperature controlled vat of toluene of a CGS-3 goniometer system from ALV (Langen, Germany) equipped with an ALV-7004/FAST Multiple Tau digital correlator and a vertical polarized 22 mV HeNe laser

(wavelength $\lambda = 632.8$). All samples were measured for 300 s at a temperature of 25 °C and an angle of 90°. The curves were obtained by software TableCurve 2D v5.01. The curves can be described by the following equation:

$$Y = a_0 + (a_1 + e^{-a_2x})^2$$

Where X is the delay time, a_0 is the constant baseline, a_1 the dynamic part of the amplitude, and a_2 a decay rate.

3.2.6. Rheology measurements

The rheological properties of shampoos are very important. It was reported that typical shampoos containing SLES exhibit a pseudoplastic behaviour also known as shear thinning. That means that the viscosity decreases with increasing shear rate. This behaviour is expected in shampoos, so that by squeezing a bottle the liquid will become less viscous and would run out of the bottle. Moreover, shear thinning behaviour enables an easy distribution of the shampoo to the hair and scalp.

In this research the rheological behaviours of samples with and without NaCl and Na citrate at pH values of 7.0 and 9.8 were evaluated. Rheological properties of samples were measured with a Bohlin CVO 120 rheometer. All samples were measured with a CP4°/4 mm cone. The viscosity measurements were carried out with shear rates from 0.076 to 10 s⁻¹ at 25°C.

4. Results and discussion

4.1. Preparation of a 2 in 1 shampoo formulation

4.1.1. Influence of stevia on the apK_a of Na oleate solution

First, the influence of stevia on the pK_a of a 10 wt% Na oleate solution was investigated. As shown in Fig. 8, the apK_a of Na oleate in water is equal to 9.2. It decreases to 8.8 when 2 wt% of stevia are in the mixture. However, the apK_a reaches a minimal value of 6.2 as soon as the stevia content in the solution is 3 wt%. The apK_a value of Na oleate remains nearly the same with higher stevia content, and equals 6.3 at concentrations 4 or 5 wt% of stevia.

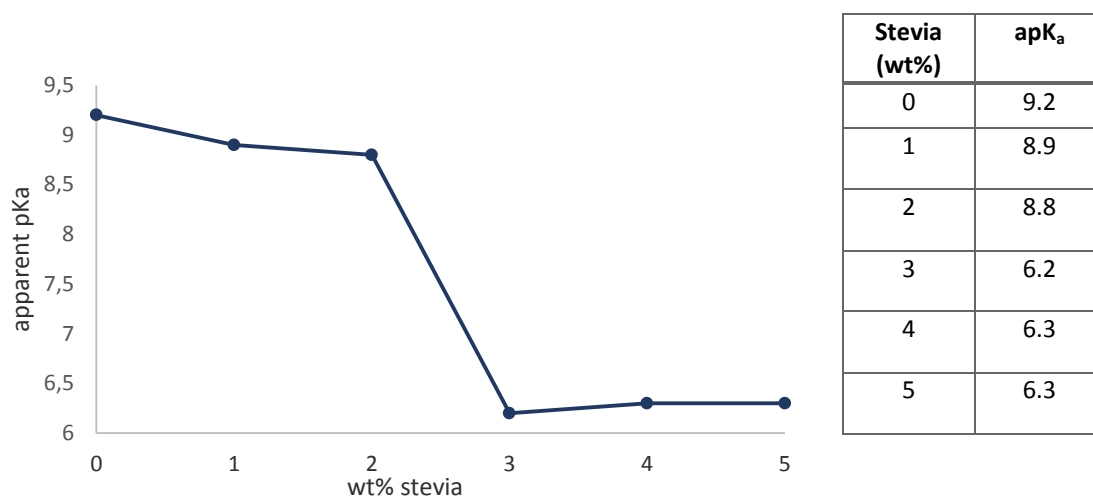


Fig. 8: apK_a of Na oleate as a function of wt% of added stevia at 25°C.

It can be noted that all solutions turned cloudy when the apK_a of the surfactant was reached. For further experiments the following composition was used:

10 wt% Na oleate/ 3 wt% stevia/ 87 wt% water

4.1.2 Influence of CAPB on the apK_a of Na oleate/ stevia system

As the apK_a of Na oleate solution decreased to 6.2 by adding 3 wt% of stevia to the solution, the effect of CAPB on this apK_a value was investigated. As seen in Fig. 9, the values remained nearly the same by increasing the wt% of CAPB. It was concluded that the apK_a value of 6.2 was not strongly affected by the addition of CAPB to the solution. As 2 wt% are usually used in a shampoo formulation, that percentage was chosen for the following formulation.

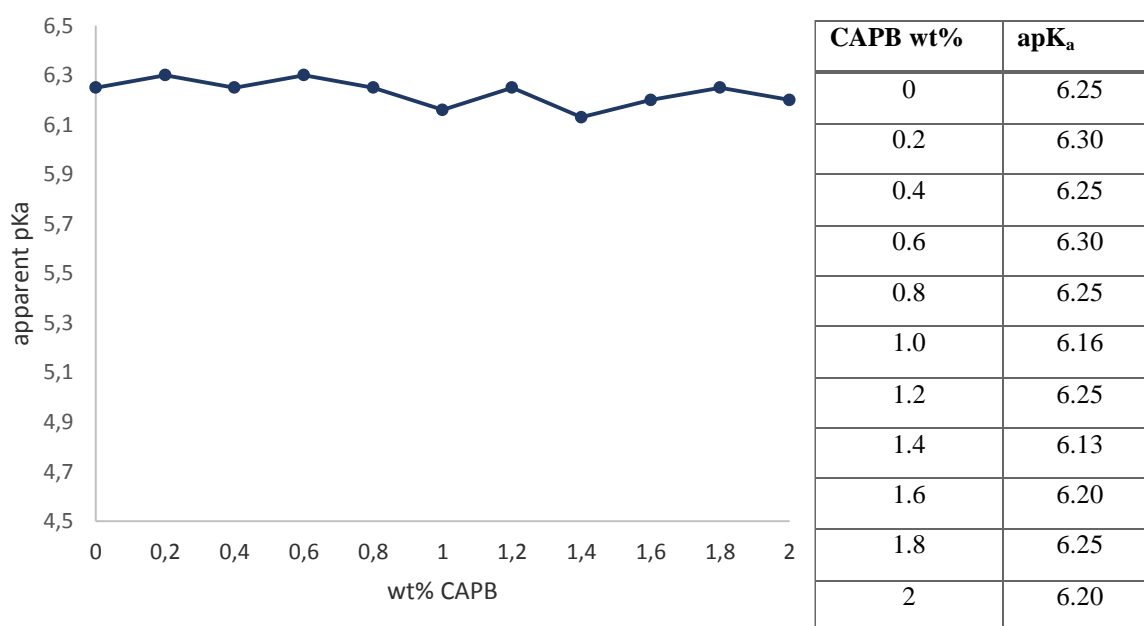


Fig. 9: apK_a of Na oleate/ stevia mixture as a function of wt% of added CAPB at 25°C.

4.1.3. Optimizing the stability of the surfactant mixture

SLES is the most frequently used primary surfactant in shampoos. One of its important physical properties is a low pK_a value of around 1.8. At pH values higher than 1.8, the deprotonated form of SLES dominates in the solution. The higher the pH value the more deprotonated molecules in the solution. On the other hand, Na oleate in combination with stevia has an apK_a value of 6.2. The instability of the system was observed and was due to a lack of charges in the system, as the desired neutral pH 7 is relatively close to the apK_a value of 6.2. Hence, SLES was added to provide more charged molecules in the solution, thereby stabilizing the system. Fig. 10 shows that the samples with 10:0 and 9:1 ratios between Na oleate and SLES were evidently more turbid than the other samples. Moreover, these two

samples became milky after one day as depicted in Fig. 11. However, with an increasing amount of SLES in the system, the samples became clear and homogenous. For further experiments the most stable system containing the highest wt% of Na oleate was chosen:

8 wt% Na oleate/ 2 wt% SLES/ 2 wt% CAPB/ 3 wt% Stevia/ 1 wt% Citric acid/ 84 wt% H₂O



Fig. 10: Prepared solutions with pH 7 after stirring at 25°C. The % on the bottles indicates the amount of Na oleate in the solutions.



Fig. 11: Prepared solutions with pH 7 after one day at 25°C. The % on the bottles indicates the amount of Na oleate in the solutions.

4.1.4. Incorporation of JR400 into the formulation

As JR400 is a positively charged molecule some problems from a stability point of view were expected. After JR400 was dissolved in the solution, the stability was observed in the following 10 days. Instability was detected in the solutions containing 0.3/ 0.4/ 0.5 wt% JR400 already after a few minutes, as the polymer precipitated. However, the samples with 0.1 wt% and 0.2 wt% JR400 remained homogenous, therefore, the stability was observed in the following 10 days. The sample with 0.2 wt% was more turbid than the sample with 0.1 wt% JR400 as depicted in Fig. 12. After 10 days, the polymer JR400 slightly precipitated in both solutions. However, both solutions were clear again when stirred with a Vortex. Hence, these compositions of the two most stable solutions with polymer JR400 were used for further evaluations. The final compositions containing polymer JR400 are shown in Table 9.

Table 9: Composition of Sample 1 and Sample 2 after adding polymer JR400.

Ingredient	wt %	
	Sample 1	Sample 2
Na oleate	8	8
SLES	2	2
CAPB	2	2
Stevia	3	3
Citric acid	1	1
JR400	0.1	0.2
Water	83.9	83.8

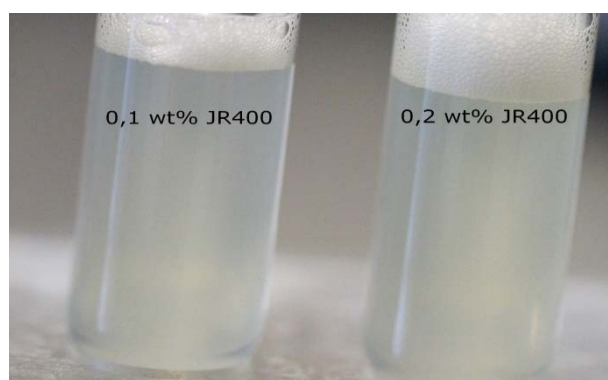


Fig. 12: Test tubes of solutions with 8 wt% Na oleate/ 2 wt% SLES/ 2 wt% CAPB/ 3 wt% Stevia/ 1 wt% Citric acid/ water system. In the first test tube 0.1 wt% JR400 was added and 0.2 wt% JR400 in other test tubes.

4.1.5. Incorporation of salts into the formulation

NaCl was added to increase the viscosity of the shampoo, and Na citrate as a chelator. First, the influence of the salts on the stability of the samples with the composition of 8 wt% Na oleate/ 2 wt% SLES/ 2 wt% CAPB/ 3 wt% Stevia/ 1 wt% Citric acid/ 0.1 wt% JR400/ 84.9 wt% water and 8 wt% Na oleate/ 2 wt% SLES/ 2 wt% CAPB/ 3 wt% Stevia/ 1 wt% Citric acid/ 0.2 wt% JR400/ 84.8 wt% water was observed.

An interesting phenomenon occurred when 1 wt% of both salts were added to the mixture. Both solutions with aforementioned compositions became slightly clearer in combination with 1 wt% of NaCl and 1 wt% of Na citrate. Obviously, the solubility of the polymer JR400 increased due to the higher charge content in the solution. However, with the increasing amount of salts, both solutions became more turbid, which is shown in Fig. 13. Therefore, the compositions containing 1 wt% of NaCl and 1 wt% of Na citrate were chosen for more experiments.

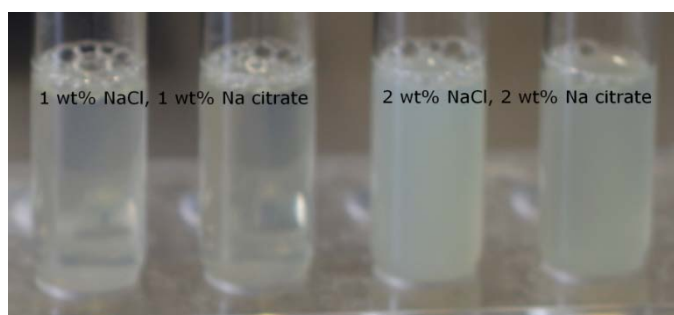


Fig. 13: Samples containing 1 wt% of each salt are much clearer than the samples containing 2 wt% of salts.

4.1.6. The final 2 in 1 shampoo formulation

The first precursor of a shampoo was prepared as described above. The most stable formulation with the highest concentrations of Na oleate and polymer JR400 was chosen for further evaluations. The final formulation is shown in Table 10.

Table 10: The composition of the final formula

Ingredient	wt%
Water	81,2
Na oleate	8

Stevia	3
CAPB	2
SLES	2
Citric acid	1
NaCl	1
Na citrate	1
JR400	0,2

4.2. Evaluation of the final formulation

4.2.1. Sensitivity to hard water

It is a well-known fact that soap forms an insoluble salt in presence of multivalent ions. Therefore, an addition of chelator is essential. In the formulations described above, Na citrate was added to prevent the emergence of insoluble soap salts. The sample was clear and homogenous. When diluted with tap water at 40 °C, the solution remained homogenous in the following 15 min. However, when a sample without Na citrate was diluted, a white precipitate formed. Hence, the addition of a chelator is essential.

4.2.2. DLS measurements

The presence of structures formed by surfactants at different pH values was investigated in the final formulation using DLS. The pH values of the samples were 6.2/ 7.0/ 9.8. In the last sample with pH 9.8 no citric acid was added.

The shape of the obtained curves depicted in Fig. 14 shows that the micelles are present in all three samples. The curve gives also qualitative information about the size of these structures in the solution. The shorter the plateau, the smaller are the structures in the solution. The plateau of the sample at pH 9.8 is significantly shorter than the plateau of the samples at pH 6.2 or pH 7.0, meaning that the structures in this sample are much smaller than in the other two samples. This could be a consequence of high charge content in solution at pH 9.8. Repulsions between the particles prevent aggregation and thus the size of the particles is smaller. More protonated molecules are present in the samples at pH 7.0 and 6.2 and can interact with each other and consequently form larger aggregates. Beside the correlation

functions, a polydispersity index (PI) can be calculated for each sample. PI gives information about the size distribution of the structures in the solution. The lower the PI value, the more monodisperse is the system. Inversely, a high PI value indicates that the sample has a very broad size distribution. As seen in Table 11, the PI of investigated samples are relatively high, and the PI values are decreasing with increasing pH value, i.e. 0.512 at pH 6.2, 0.508 at pH 7.0 and 0.401 at pH 9.8. The high PI values were expected due to the presence of polymer in the sample.

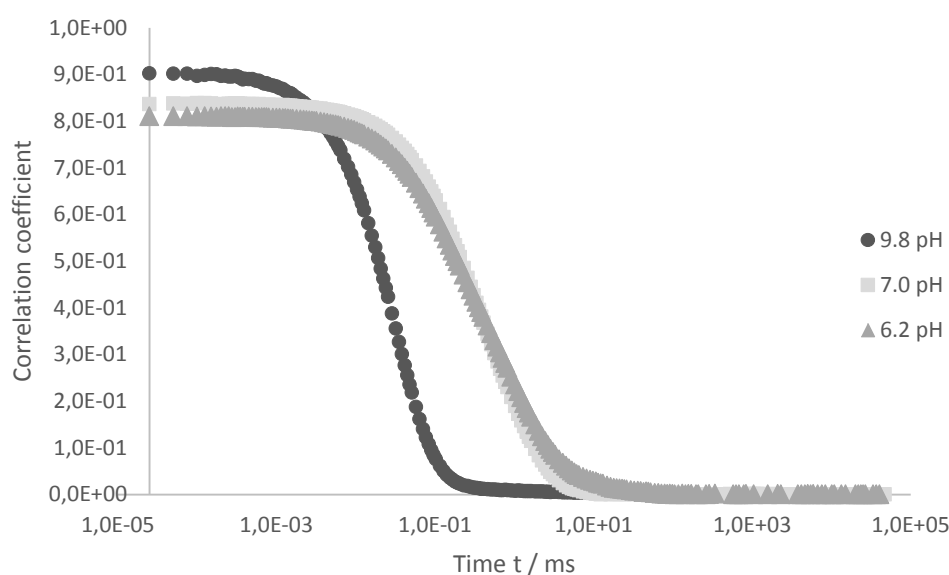


Fig. 14: Correlation functions of samples with different pH values at 25°C.

Table 11: PI values for each sample with different pH value.

	pH 6.2	pH 7.0	pH 9.8
Polydisperse index	0.512	0.508	0.401

4.2.3. Effect of NaCl on the viscosity of the shampoo

It is a well-known fact that the addition of NaCl to an anionic surfactant mixture affects the viscosity of the solution. The sodium ions lower the charge density of the micelle surface. Hence the ability of the micelles to pack closer increases which results in a thicker solution. However, after the maximum viscosity has been reached, the further addition of NaCl lowers the viscosity of the solution. As mentioned above, the sample became clearer when the solution contained 1 wt% of NaCl and Na citrate. The effect of NaCl on the viscosity of the

sample and its rheological properties were investigated. As seen in Fig. 15 and Fig. 16 the flow curves show a Newtonian behaviour, regardless of the presence of NaCl. It can be also seen that the viscosity values of the samples with or without NaCl remain nearly the same.

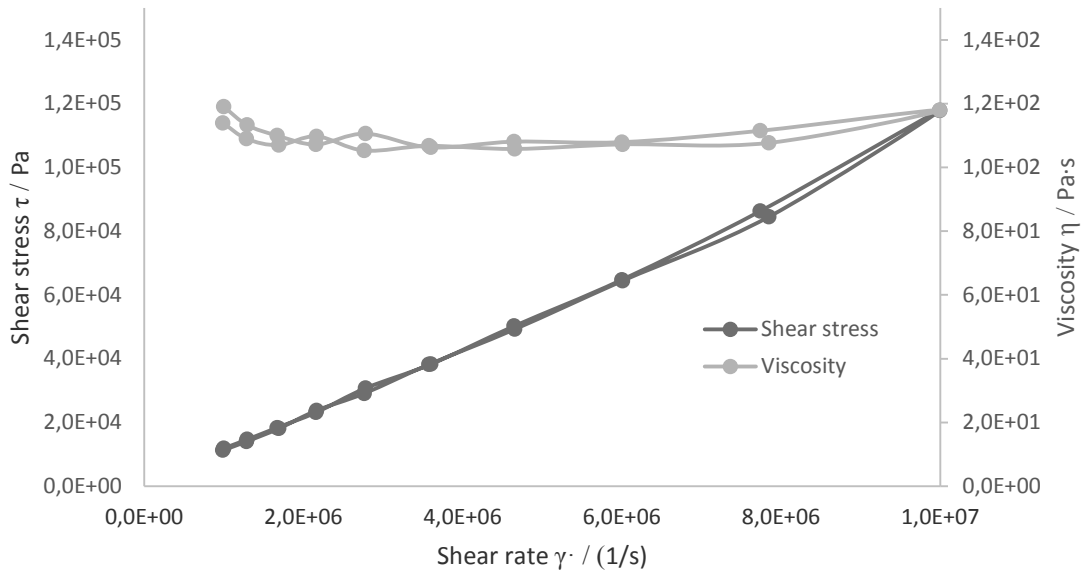


Fig. 15: Viscosity as a function of shear rate and shear stress as a function shear rate in a sample without NaCl at 25°C.

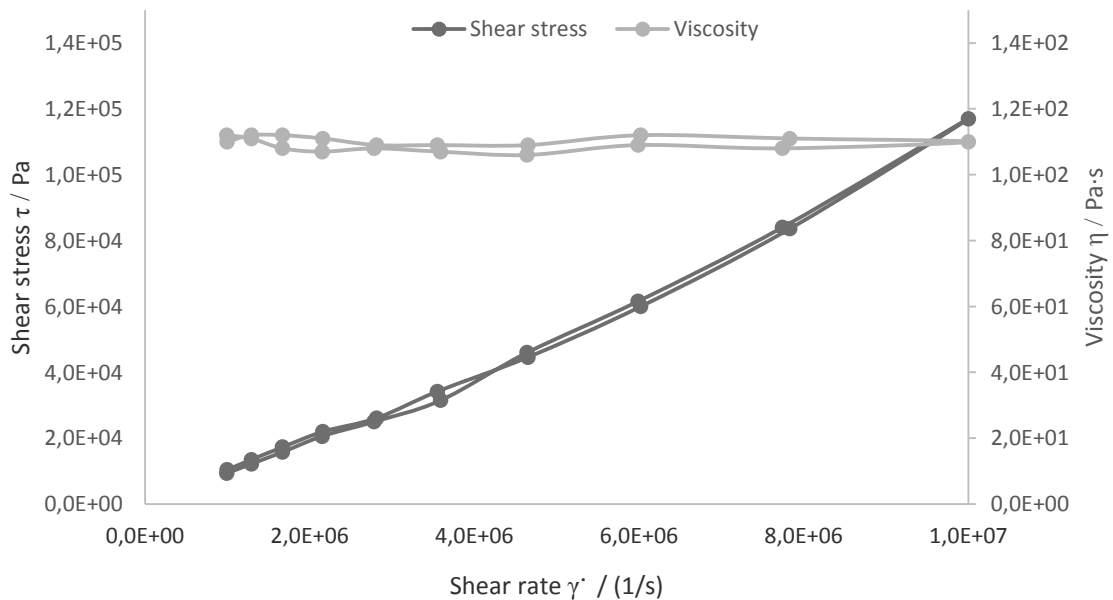


Fig. 16: Viscosity as a function of shear rate and shear stress as a function shear rate in a sample with NaCl at 25°C.

To get a better idea why this phenomenon occurred, the sample at pH 9.8 where no citric acid was present in the solution was prepared and the rheological properties were evaluated as well. As seen in Fig. 17, the sample at pH 9.8 without salt exhibits a Newtonian behaviour. The viscosity of this sample compared to the one at pH 7.0 is higher, i.e. equal to $1.7\text{E}+03$ Pa·s. Then, the sample at pH 9.8 with NaCl and Na citrate was measured. It was visible by the naked eye that the sample became more viscous after adding salts to the solution. Further on, the viscosity decreased with increased shear rate as depicted in Fig. 18. This is also known as shear thinning and is typical for pseudoplastic materials. As already mentioned above, this is a very important property of a shampoo. Because of that, the product can be easily obtained from the bottle and then applied to the scalp. It was suggested that the Newtonian behaviour of the sample at pH 7.0 occurs due to the low charged molecules content in the solution. Inversely, in the sample at pH 9.8 the deprotonate form dominates in the solution. Therefore, more charged molecules are present, and sodium ions can interact with negatively charged soap molecules. Consequently, the viscosity of the solution increases and a pseudo plastic behaviour is observed. Obviously, the addition of salts to the sample at pH 7.0 is not a good choice for viscosity enhancement. Therefore, the viscosity could be increased by adding other thickening agents such as polymers or gums.

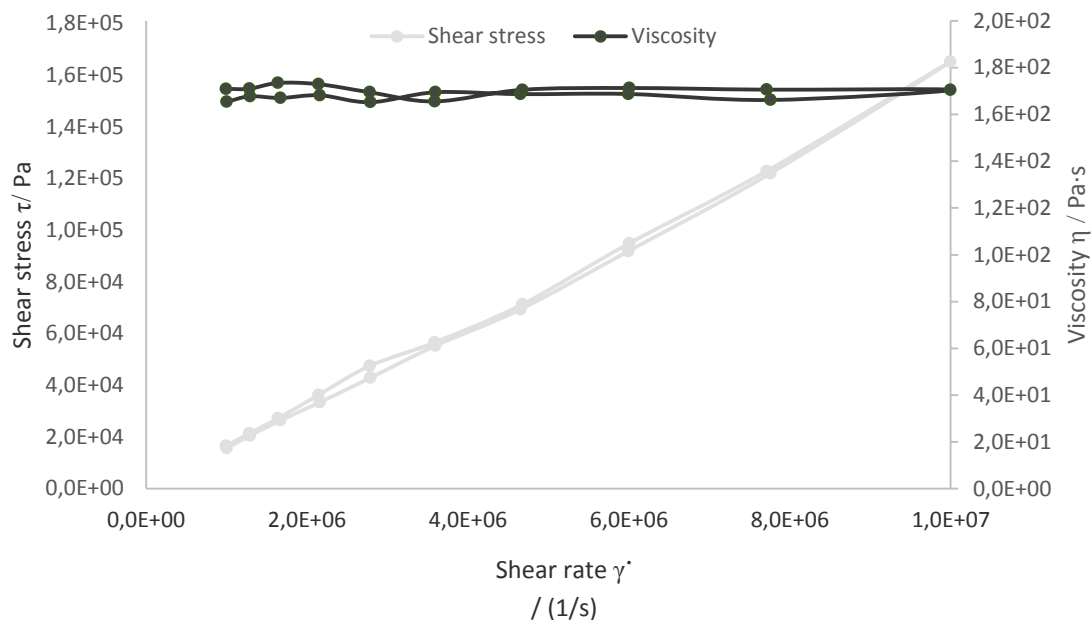


Fig. 17: Viscosity and shear stress as a function of shear rate for a sample at pH 9.8 where no NaCl was involved in the solution at 25°C.

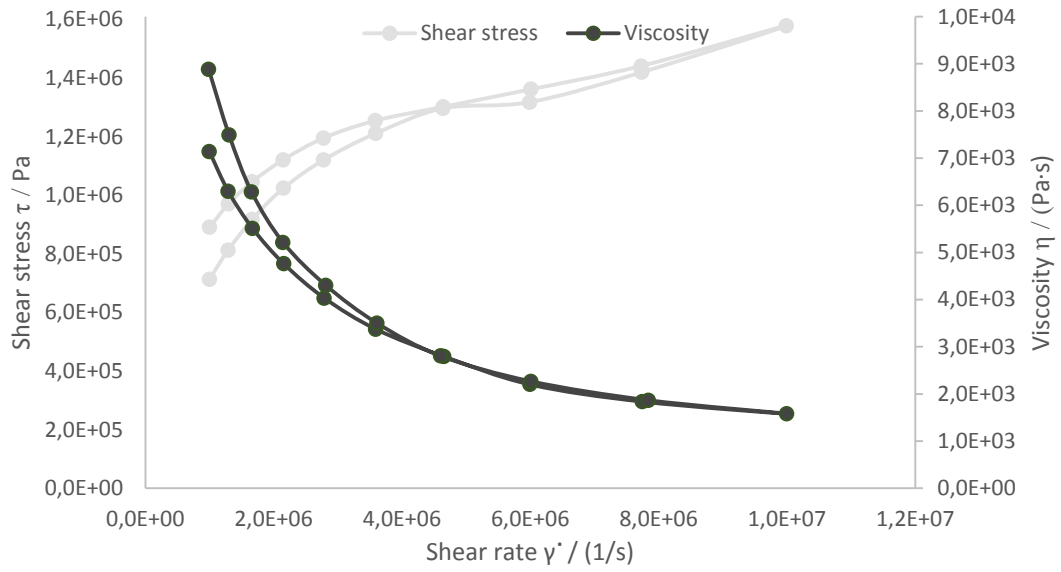


Fig. 18: Viscosity and shear stress as a function of shear rate for a sample at pH 9.8 where NaCl was involved in the solution at 25°C.

5. Conclusion

This work deals with the formulation of a shampoo with Na oleate as a primary surfactant. The first aim of the research was to decrease the pK_a value of sodium oleate. This was achieved by addition of 3 wt% of stevia rebaudiana extract to a 10 wt% Na oleate solution. Different formulations of a 2 in 1 shampoo with Na oleate were investigated. The most promising results were obtained for the following formulation and the following preparation process:

8 wt% of Na oleate, 3 wt% of Stevia, 2 wt% of SLES, 2 wt% of CAPB, and 85 wt% of milipore water were weighed, stirred and put under agitation. When a clear and homogenous mixture was obtained, pure citric acid was being added till the pH value of the solution was decreased to approximately 7. Then, 0.2 wt% of JR400, 1 wt% of NaCl and 1 wt% of Na citrate were added into the sample. The sample was heated up and stirred till a homogenous solution was obtained. After 3 days, some precipitates were present in the sample, however, after shaking the bottle, the solution became homogenous again.

Then, the sample with the aforementioned formulation was evaluated with different experiments. First, the sensitivity to hard water was observed. No precipitates were seen in the solution, meaning that Na citrate was a good choice as a chelator.

The curves obtained by DLS showed that the pH of the solution affects the size of the particles as well as the size distribution.

The rheological properties of the samples with and without salts at different pH values were evaluated. The sample at pH 7 with and without salts showed a Newtonian behaviour and the sample at pH 9.8 with salts showed a typical shear thinning behaviour.

It can be concluded that the precursor of a 2 in 1 shampoo was invented. The final ratio between SLES and Na oleate is 2:8, which is of great importance. As already mentioned, this shampoo would be potentially interesting for the developing countries, where soaps are available in higher stocks. If the new generation of soap-containing-shampoos could be improved, the hygiene conditions in developing countries could be improved as well.

6. References

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