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Shampoo Science: A Review of the Physicochemical Processes behind the Function of a Shampoo

Courtney J. Thompson, Nick Ainger, Pierre Starck, Oleksandr O. Mykhaylyk, and Anthony J. Ryan*

The components of a shampoo are selected specifically to carry out important roles within the formulation. They must be carefully considered as not only do they act to carry out their own function but they also influence the function of the other components through complexation and other physicochemical interactions. This review focuses on the four principal components in a commercial shampoo formulation: surfactant, deposition polymer, structuring polymer, and viscosity modifiers. The most common molecule types used commercially to carry out the specific roles are discussed, with each of their fundamental functions outlined in detail. The mechanisms by which these molecules can perform these roles are reviewed. Further consideration is taken to outline how components could interact with one another to hinder or facilitate processes.

important of the four, the surfactant. The surfactant carries out the shampoo's primary cleaning role while also aiding the foaming capabilities and contributing to the formulation's interaction with the skin.^[1] Second, it reviews the deposition (or conditioning) polymer which acts to condition and aid the deposition of other beneficiary agents onto the hair.^[2] The third component described in the article is the structuring polymer, incorporation of which prevents phase separation through either an associative or nonassociative mechanism dependent on its chemical nature.^[3] Finally, viscosity modifiers, which tune the viscosity of the shampoo to the correct level of flowing performance to facilitate applications and meet the customer requirements.^[4]

1. Introduction

An industrially formulated shampoo contains many different molecules all with a distinct, but equally important role in the formulation. The self-interactions and interactions between these molecules are important to consider when defining the shampoo's function and efficacy, as they can trigger a complex response of the system under certain conditions defined by changing temperature, moisture, and pH. Thus, the loading of the components must be carefully considered, to allow the shampoo to carry out its function correctly during the different stages of the washing process. This article contains a detailed review of four of the main ingredients in a shampoo formulation and how they function within it. First, it discusses the most

2. Surfactants

The surfactant is the driving force behind a significant number of the functional processes that occur within a shampoo. Its main role is to carry out the cleansing mechanisms, acting to remove dirt and soils from the hair. However, it also contributes toward the shampoos foaming capabilities, the solubilization of active agents and components, viscosity moderation and suspension of additives.^[5,6]

The intrinsic physicochemical activity of the surfactant gives it a governing role in the shampoo formulation through its amphiphilicity driving structural organization at interfaces. Having dual function within a singular molecule allows both the hydrophilic and hydrophobic benefits to be exploited. This amphiphilic nature is what dictates the surfactants orientation at various interfaces (**Figure 1**), ultimately resulting in the formation of larger self-assembled objects, the most common of which are micelles (**Figure 2**).

Adsorption of the surfactant molecules at an interface is the process that acts to lower the surface tension of a system.^[7] The cohesive forces experienced by the phases in the absence of surfactant are strong, as like–like interactions are more favorable and the net force pulls into the respective phase. The addition of the surfactant disrupts these cohesive forces, acting as a mediator between the two phases.^[7] Ultimately this lowers the surface tension and stabilizes the interface. The population of the interface with surfactant molecules and the resultant reduction in the surface tension between the two phases only proceeds up to a physical limit. Once the interface becomes saturated with

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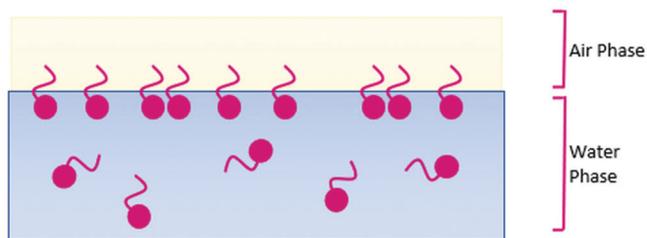


Figure 1. A schematic of surfactant molecule interaction at the air–water interface, the molecules align at the interface to maximize the favorable interactions between the hydrophilic head groups and water and the hydrophobic tail groups and air. The surfactant molecules are shown in pink.

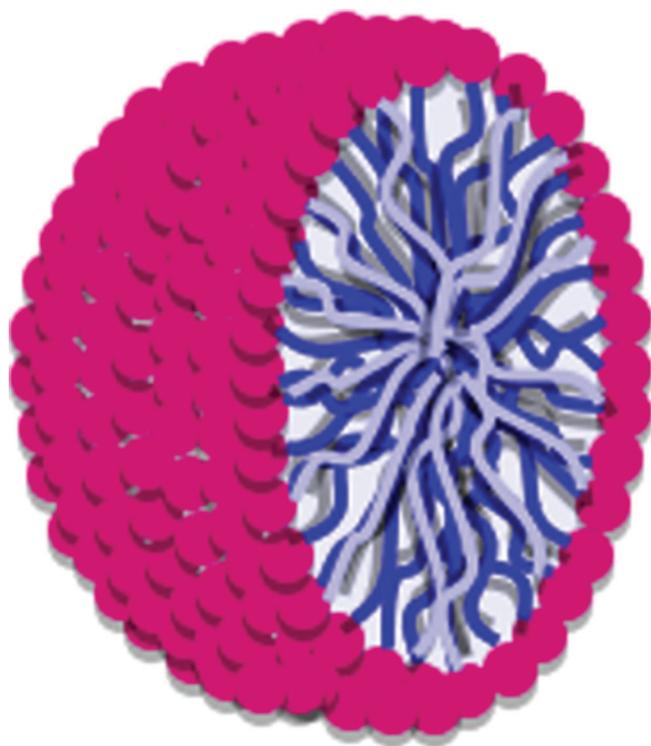


Figure 2. The cross-sectional structure of a spherical micelle with the head groups shown in pink forming the hydrophilic micelle shell and tail groups are shown in blue forming the hydrophobic micelle core.

surfactant the formation of micelles in the solution begins. The minimum concentration of surfactant required for this spontaneous phenomenon to be observed is known as the critical micelle concentration, or the CMC.^[18]

As the concentration of surfactant in a system increases, the molecules can form more complex self-assembled morphologies (**Figure 3**).^[9–14] The geometry of the self-assembled surfactant aggregate is defined by the critical packing parameter, $p = v/a_0l$.^[11,13,15] The packing parameter (p) is a function of the volume of the surfactants hydrophobic tail (v) the length of its tail (l) and the surface area of the surfactant head group at the interface (a_0). The value of p dictates the self-assembled morphology that the surfactant molecules can pack into. Increasing toward a value of one, the packing parameter accommodates the formation of spherical micelles, worms, vesicles, and finally lamellar.

2.1. Cleansing Role

The principal role of the surfactant is to carry out the cleansing mechanisms. It is widely reported that there are four individual mechanisms of soil removal, each rely on the amphiphilic nature of the surfactant molecule, and each is supported to varying degrees by literature.

The first of these is known as “the roll-up” mechanism (**Figure 4**), introduced by Adam et al.^[16] Simply defined, this mechanism relies on the increase in the contact angle between the soil and the hair, leading to complete detachment. This mechanism is evidenced well by Poce-Fatou,^[17] Muherei et al.,^[18] and Childs et al.,^[19] defining the Young equation which describes the contact angle requirement to overcome the work of adhesion, and the resultant reduction in interfacial tension experienced by the soil. Surfactant begins to adsorb at the oil/water interface, reducing the interfacial tension for this phase boundary (Figure 4). This leads to a gradual increase in contact angle between the soil and the hair, from 0° to 90° (Figure 4, particle 1) and eventually 180° (Figure 4, particle 2), when the soil particulate is removed completely as the adhesive forces are overcome (Figure 4, particle 3). The “roll-up” removal is further promoted by the repulsive forces experienced between the soil and the surfactant head group. The soils then remain solubilized as all desirable absorption surfaces are wet or wetted with surfactant. This removal mechanism is the most reported in literature, making it the most widely accepted mechanism.^[17–25]

The second mechanism is known as spontaneous emulsification (**Figure 5**). This mechanism is often reported in parallel with the “roll-up” mechanism in literature and is evidenced by Muherei et al.^[18] and Childs et al.,^[19] again defining the Young’s equation and the changes in interfacial tension facilitate the soil removal. This mechanism works much like an extension of the “roll-up” process, being driven by low interfacial tension at the soil/water interface. However, in this case the contact angle is not high enough to result in complete soil detachment. Instead, the soil film deforms over time due to surfactant interaction, leading to the formation of “bud-like” particles emulsified by lipids (Figure 5, particles 2 and 3). These droplets can then be easily broken up by general agitation (Figure 5, particle 4), the force of which is greater than the cohesive forces attaching the soil to the hair. In this case some oil residue can be left behind on the hair.^[5,7,8,10–12]

The third mechanism, referred to as the penetration mechanism or “soil-softening” (**Figure 6**). The mechanism is experimentally evidenced by Lawrence et al.,^[26] Cox,^[27] and Evans et al.,^[28] in which dissolution and submersion experiment were conducted to monitor rate and extent of the penetration of the surfactant into the soils. “Soapy” Lawrence,^[29] demonstrated how the hydrophobic effect had driven surfactants to penetrate insoluble, hydrophobic soils. The penetration is controlled by favorable hydrophobic interactions between the soil and the tail group and reduces interfacial tension at the soil/water interface. An interfacial liquid-crystalline phase forms (Figure 6, particle 2), which is then agitated and removed (Figure 6, particle 3), leaving behind some exposed soil. This process is repeated until complete soil removal is achieved.^[4,10,26–28,30]

The fourth and final mechanism is the solubilization mechanism, which is sometimes referred to as the micelle mechanism or encapsulation (**Figure 7**). The solubilization mechanism is

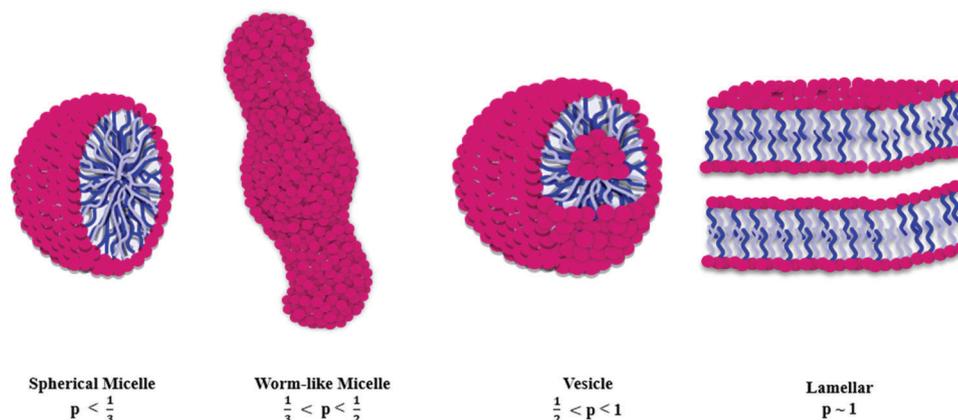


Figure 3. A schematic drawn based on information in Feng et al.,^[11] depicting the observed relationship between the critical packing parameter, p and the self-assembled surfactant aggregate morphology



Figure 4. A schematic diagram of the roll-up mechanism of surfactant aided soil removal, drawn based on information in Muherei et al.,^[18] Lochhead^[24] and Childs et al.^[19] The soil is shown in yellow and the surfactant molecules are shown in pink. Particle 1 depicts an initial stage when a soil particulate forms a 90° contact angle with the surface (human skin). Particle 2 depicts an intermediate stage when the contact angle is 180° . Particle 3 depicts a fully removed soil particulate.

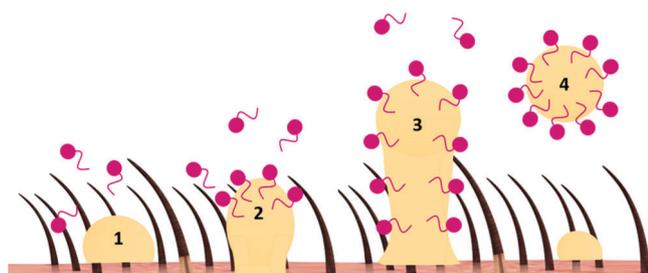


Figure 5. A schematic diagram of the spontaneous emulsification mechanism of surfactant aided soil removal, drawn based on information in Muherei et al.,^[18] Lochhead,^[24] Miller et al.,^[25] and Childs et al.^[19] The soil is shown in yellow and the surfactant molecules are shown in pink. Particle 1 depicts the soil particulate on the hair. Particles 2 and 3 depict the formation of "bud-like" particles via emulsification. Particle 4 shows the soil removal by agitation.

evidenced experimentally by Poce-Fatou,^[17] Childs et al.,^[19] Bajpai et al.,^[22] Kabin et al.,^[23] and Carroll.^[31] The experimental evidence uses techniques to monitor the solubilization of soils at high surfactant concentrations and interfacial tension measurements. This mechanism relies on the surfactants ability to form micelles at the CMC (Figure 7, particle 1). It harnesses the hydrophobic core of the micelle to remove soils directly and is mediated by the finite (but vanishingly small) solubility of oil in water

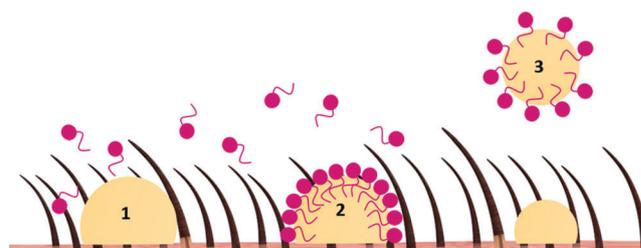


Figure 6. A schematic diagram of the penetration mechanism of surfactant aided soil removal, drawn based on information in Evans et al.,^[28] Cox,^[27] Lochhead,^[24] and Cornwell.^[20] The soil is shown in yellow and the surfactant molecules are shown in pink. Particle 1 depicts the soil on the hair. Particle 2 depicts the formation of the interfacial liquid-crystalline phase. Particle 3 depicts the agitation and partial removal of the soil.

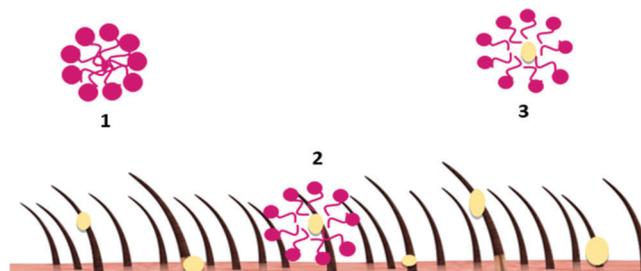


Figure 7. A schematic diagram of the micelle (solubilization) mechanism of surfactant aided soil removal, drawn based on information in Cornwell,^[18] Lochhead,^[24] Carroll,^[31] and Carbonell et al.^[23] The soil is shown in yellow and the surfactant molecules are shown in pink. Particle 1 depicts the surfactant micelles formed in the bulk. Particle 2 depicts the encapsulation of the soil particulate in the hydrophobic core of the micelle. Particle 3 depicts the removal of the soil particulate.

and the formation of a depletion layer. The micelles encounter the hydrophobic soils as they adsorb at the soil/water interface (Figure 7, particle 2). The soil particles are enveloped by the hydrophobic core and subsequently removed with rinsing (Figure 7, particle 3).^[4–12,31,32]

At low surfactant concentrations the CMC is not met and soil removal occurs mostly by the "roll-up" and emulsification mechanisms (Figures 4 and 5, respectively). Once the concentration of

surfactant exceeds that of the CMC, solubilization begins to take precedence (Figure 7).

2.2. Foaming Role

While the foaming capability of the surfactant in the shampoo does not affect its ability to carry out its primary cleansing role, it does however govern the perception of the product and a greater degree of lather is viewed by consumers as an indicator of good performance and more aesthetically pleasing.^[33–35]

When air is introduced into the shampoo during the lathering process the surfactant can aid the production and stabilization of the foam. Adsorbing at the newly formed air/water phase boundary, the surfactant both stabilizes and lowers the surface tension of the interface. The stabilization of the interface allows more air to be introduced, as the liquid membrane expands around it with an increasing surface area. This phenomenon occurs as a result of the Gibbs-Marangoni effect, which essentially defines the movement of mass along a gradient, the gradient being that of surface tension and the mass being surfactant molecules.^[36,37] The reduction in surface tension of the phase boundary aids the longevity of the foam, a high surface tension would lead to popping and bubble collapse as the water would preferably form cohesive interactions with the net force pulling inward.

The main features of a surfactant stabilized foam are the lamellar film and the plateau borders.^[38–40] The lamellar film defines the region in which two bubbles meet. The term lamellar is used as the structure is to a degree layered, with identical thin film interfaces being parallel and in proximity to one another. The plateau borders occur once the foam has adopted a stable polyhedral structure and can be defined as points at which three or more bubble coalesce.

The degradation of the foam occurs via two mechanisms individually known as liquid drainage and lamellae puncture. The liquid drainage is initiated at the plateau borders as they exhibit a lower Laplace pressure. The Laplace pressure^[41–43] of a liquid is inversely proportional to the curvature of its interface, which at the plateau point is at its maximum. As a result, the liquid in the wet foam drains from the lamellar film regions of higher pressure to the plateau borders to reach an equilibrium. Ultimately this drainage means the thin films become thinner until the internal pressure of the trapped air can no longer be supported and the bubbles collapse. Lamellae puncture refers to the act of other environmental stresses resulting in lamellae rupture, leading to the coalescence and collapse of the bubbles.^[44–46]

2.3. Skin Mildness

Ideally, a shampoo will remove soils from the hair without also leaving behind skin irritation and dryness. Unfortunately, surfactant molecules are nondiscriminatory when cleansing the hair and scalp, often resulting in beneficial proteins and lipids being removed or adversely affected as a consequence.

Such detrimental interactions can occur in several ways. First, surfactant molecules can interact with proteins found in the hair and scalp, forming protein–surfactant complexes, and preventing these proteins from binding, and holding water molecules to

their usual extent, this results in a feeling of dryness once the washing process is over. The swelling action that results from these protein–surfactant interactions has also been seen to facilitate surfactant penetration into the dermis which can trigger biochemical responses such as inflammation and irritation. In addition to this, the charge density of the micelles formed can act to denature the proteins leading to further irritation. The shampoo surfactants can also interact with essential lipids leading to solubilization of the lipids inside the formed micelles. It has been reported that the charge associated with the surfactant enables it to penetrate and adsorb to the lipid bilayers in the cell wall, thereby destabilizing them and triggering adverse biochemical responses.^[47–52]

Skin mildness is a term adopted by the personal care industry to refer to the degree to which such surfactant mixes impart the above response when used, those that impart a lesser response are known as milder on the skin. However, it is possible to improve the skin mildness of a surfactant in several ways, some of which are outlined in this review.

2.4. Surfactant Selection

Surfactant selection is an important process dependent on the tailored properties of the shampoo. Specific surfactants are designed to carry out certain roles within the formulation, from effective lathering to skin mildness and even in more recent years the dreaded “sulfate-free” cleansing.^[20] For this reason, it is most common for a shampoo to contain a primary and a secondary surfactant (or cosurfactant) to allow the beneficial properties of both to be exploited while also considering other external factors such as cost and processability (Table 1).

Generally, the surfactant type defines the properties that the surfactant brings to the shampoo formulation. Anionic surfactants provide good foaming and cleansing properties and are usually the cheapest to source, however they often contain sulfate groups and can lead to skin and scalp irritation.^[50–52] Cationic surfactants are usually used in conjunction with other surfactants to provide other benefits in addition to cleansing, such as antiseptic or antibacterial properties and/or conditioning properties; however, they are often expensive and thus not often used as the primary surfactant.^[5,20,24,53] Zwitterionic surfactants are also often used as the cosurfactant in a shampoo formulation, enhancing such properties as foaming, thickening, and emulsification. However, their cleansing ability is not as pronounced as other surfactant types and, in some cases, use of a zwitterionic surfactant at high concentrations can result in skin-sensitization.^[24,33,35,53–55] Nonionic surfactants are great stabilizers, acting to boost the foaming and viscosity of the formulation, while also being “milder” on the skin. However, they are less effective cleansers than the other surfactant types and owing to their lack of interaction with ‘hard water are more often used in hard surface cleaning products and laundry detergents.^[5,20,22,24,53]

2.4.1. Primary Surfactant

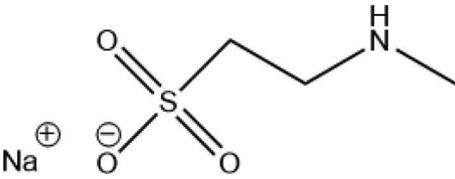
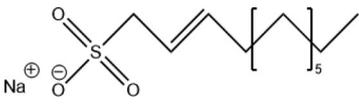
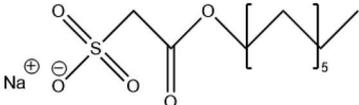
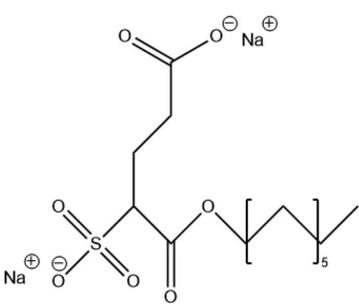
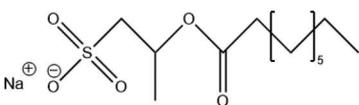
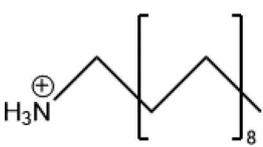
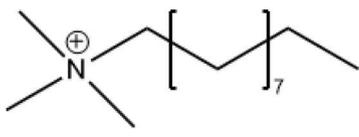
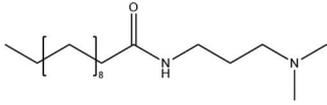
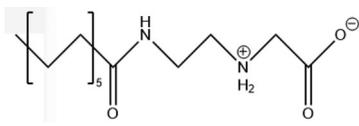
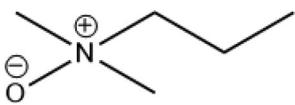
As the name suggests, the primary surfactant carries out the bulk of the surfactant’s role within the formulation and is present in the largest quantity, usually up to 10% w/v.

Table 1. Examples of the most common surfactant within each surfactant type classification used in commercial products, with details of their chemical structure, acronyms, physical form as supplied and molecular weight.

Surfactant type	Chemical structure	Common acronyms	Physical form as supplied	Molecular weight [g mol ⁻¹]
Anionic		Sodium lauryl ether sulfate, ^[56] SLES, sodium laureth-2 sulfate, α -sulfo- ω -(dodecyloxy) poly(oxyethylene) sodium salt, sodium; 2-dodecoxyethyl sulfate	70% Liquid in deionized water	332.43
Anionic		Sodium dodecyl sulfate, ^[57] SDS, SLS, sodium lauryl sulfate, sodium 2-dodecoxyethyl sulfate, sodium laureth sulfate, dodecyl sodium ethoxysulfate	> 99% Solid	288.38
Anionic-		Sodium methyl palmitate sulfonate, ^[58] MES, palmfonate methyl ester sulfonate, methyl palmitate, sodium 1-methoxy-1-oxohexadecane -2-sulfonate	> 95% Solid	372.50
Anionic		Sodium coco monoglyceride, ^[59] sodium cocomonoglyceride sulfate, coconut oil monosulfated sodium salt, sodium coconut monoglyceride sulfate	85 – 95% Solid	≈ 381.50
Anionic		Ammonium lauryl sulfate, ^[60] ALS, azana dodecyl hydrogen sulfate, ammonium dodecyl sulfate, dodecyloxy sulfonic acid amine	30% Liquid in deionized water	283.43
Anionic		Monoethanolamine (MEA) lauryl sulfate, ^[61] MEA-lauryl sulfate, 2-aminoethanol dodecyl hydrogen sulfate, 2-hydroxyethyl ammonium dodecyl sulfate	98% Solid	327.48
Anionic		Sodium laureth carboxylate, ^[62] AEC (alkylpolyethoxy carboxylate), sodium lauryl glucose carboxylate, sodium laureth-(No) carboxylate, sodium laureth carboxylic acid, laureth carboxylic acid	100% Solid	310.40
Anionic		Sodium lauroyl glutamate, ^[63] sodium N-lauroyl glutamate, monosodium N-lauroyl L-glutamate, sodium hydrogen N-1-oxododecyl L-glutamate	20 – 40% Liquid in deionized water	351.40
Anionic		Sodium lauroyl sarcosinate, ^[64] sarkosyl, N-lauroyl sarcosine sodium salt, sodium N-lauroyl sarcosinate, sodium 2-dodecanoyl(methyl) amino acetate	> 95% Solid	293.38

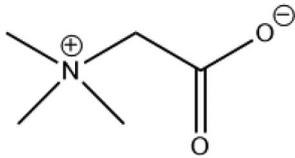
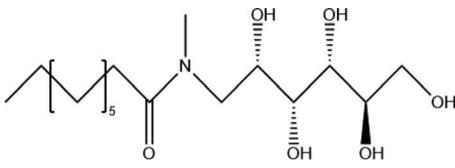
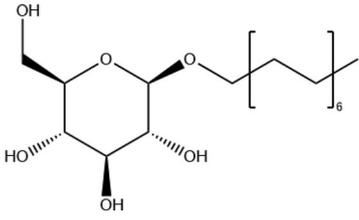
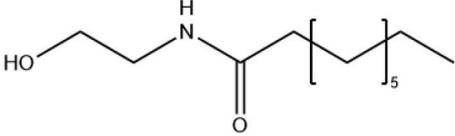
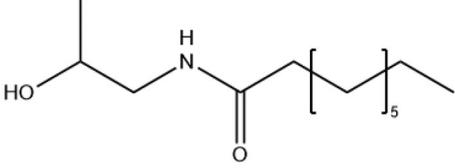
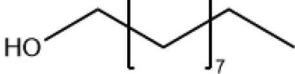
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Table 1. (Continued).

Surfactant type	Chemical structure	Common acronyms	Physical form as supplied	Molecular weight [g mol ⁻¹]
Anionic		Sodium methyl taurate, ^[65] sodium 2-methylamino ethane sulfonate, <i>N</i> -methyl taurine sodium salt, ethane sulfonic acid 2-methylamino monosodium salt	70–80% Liquid in deionized water	161.16
Anionic		Sodium olefin sulfonate, ^[66] sodium c14 olefin sulfonate, 2-tetradecene 1-sulfonic acid sodium salt, sodium tetradec-2-ene 1-sulfonate	80–90% Solid	298.42
Anionic		Sodium lauryl sulfoacetate, ^[67] SLSA, lathanol, nacconol, sodium 2-dodecoxy 2-oxoethane sulfonate	85% Solid	330.42
Anionic		Disodium lauryl sulfosuccinate, ^[68] DLS, sodium monododecyl sulfosuccinate, disodium 5-dodecoxy 5-oxo 4-sulfonatopentanoate	95% Solid	424.50
Anionic		Sodium lauroyl methyl isethionate, ^[69] SLI, sodium 2-dodecanoyloxy propane 1-sulfonate, dodecanoic acid 1-methyl 2-sulfoethyl ester sodium salt	60 – 99% Liquid in deionized water	344.40
Cationic		Cetyl trimethylammonium bromide, ^[70] CTAB, Alkyl trimethylammonium salt, cetrimonium bromide, hexadecyl (trimethyl) azanium; bromide	>99% Solid	364.40
Cationic		Cetrimonium chloride, ^[71] CTAC, hexadecyl trimethyl ammonium chloride, cetyl trimethyl ammonium chloride, hexadecyl trimethyl azanium chloride	30% Liquid in deionized water	320.00
Cationic		Stearamidopropyl dimethylamine, ^[72] stearamidopropyl dimethylamine stearate, octadecanoic acid <i>N</i> -3-dimethylamino propyl octadecanamide	> 99% Solid	653.10
Amphoteric		Cocamidopropyl betaine, ^[73] CAPB, coco betaine amphoretic L, lauroylamide propylbetaine, 2-[3-(dodecanoylamino) propyl-dimethylazaniumyl] acetate	30% Liquid in deionized water	342.50
Amphoteric		Alkyl dimethyl amine oxide, ^[74] APAO, dimethyl propyl amine <i>n</i> -oxide, <i>N,N</i> -dimethyl propan-1-amine oxide	45% Liquid in deionized water	103.16

(Continued)

Table 1. (Continued).

Surfactant type	Chemical structure	Common acronyms	Physical form as supplied	Molecular weight [g mol ⁻¹]
Amphoteric		Betaine, ^[75] Bt, alkyl betaine, glycine betaine, oxynurine, lycine, 2-trimethyl azaniumyl acetate	100% Solid	117.15
Nonionic		Lauroyl methyl glucamide, ^[76] N-methyl N-pentahydroxyhexyl dodecanamide, N-lauroyl meglumine	50% Liquid in deionized water	377.50
Nonionic		Lauryl glucoside, ^[77] dodecyl glucoside, dodecyl b-D-glucopyranoside, (2R,3R,4S,5S,6R)-2-dodecoxy-6-(hydroxymethyl)oxane-3,4,5-triol	60% Liquid in deionized water	348.50
Nonionic		Cocamide MEA, ^[78] lauramide MEA, laurylethanolamide, N-2-hydroxyethyl dodecanamide, copramyl, lauric acid monoethanol amide	> 90% Solid	243.39
Nonionic		CocamideMIPA (monoisopropanol amine), ^[79] coco isopropanolamide, monoisopropanol amine coconut acid amide, cocamide monoisopropanol amine	> 95% Solid	215.34
Nonionic		Cetyl alcohol, ^[80] hexadecane-1-ol, palmityl alcohol, cetanol, 1-hexadecanol	> 95% Solid	242.45

The primary surfactant in a shampoo formulation is typically anionic, as they have the greatest cleaning power owing to their strong amphiphilicity imparted by the negatively charged head group.^[53,81] The most common of the anionic surfactants are those containing sulfate groups such as sodium lauryl sulfate (SLS) or sodium lauryl ether sulfate (SLES) (Table 1). For the latter, the addition of ethoxylate groups helps to increase the surfactant skin mildness providing some mitigation for the irritation caused by sulfates.^[20] However, the ethoxylation leads to an increase in molecule solubility resulting in less viscosity build up within the system due to the suppression of worm-like micelle formation. Thus, a balance must be struck between skin mildness and viscosity when considering the degree of ethoxylation appropriate.^[20]

In more recent years there has been a drive to reduce or even eliminate the use of sulfate containing surfactants in formulations. This is due to their skin irritation properties and intensive cleansing abilities that can often lead to hair stripping.^[50–52,82]

However, they are still unmatched in their ability to deliver functionality at a low production cost.

Surfactant synergy also plays a part, while a decision to use binary mixtures of surfactants in shampoo formulations is made. It has been reported widely in literature that certain ratios of surfactants in binary mixtures allows a lower surface tension to be achieved due to such synergistic affects.^[83–86] Achieving a lower surface tension from a binary surfactant mixture rather than a pure surfactant can further reduce the cost of production.

2.4.2. Cosurfactant

The addition of a cosurfactant into a shampoo formulation acts to enhance the properties of the primary surfactant. This allows the primary surfactant to be selected based on its ability to carry out the fundamental cleaning role without the shampoo being

compromised in its other roles, such as foaming and skin mildness. Cosurfactants are usually present in formulation at 1–5% w/v.

Typically, cosurfactants are amphoretic (zwitterionic) in nature meaning they are more accommodating of pH alterations, with a tunable net charge.^[37,87] The most frequently used amphoretic surfactants are known as betaines, with the most common of all being cocamidopropyl betaine (CAPB) (Table 1), which can be extracted from coconut oil.^[88]

CAPB is synergistic with anionic surfactants present in formulation and thus can act to improve the surfactant properties via the formation of micelles with mixed surfactant composition in solution. Owing to the zwitterionic nature, CAPB lowers the micelle charge density, which reduces the shampoos irritation potential.^[47,49] The mixed micelles formed also possess the potential to adopt worm-like micelle formations due to charge screening interactions, this leads to the shampoo viscosity build-up.^[55] In some cases the shampoo viscosity can be controlled solely through the loading of cosurfactant. In addition to this, amphoretic surfactants provide foam enhancing properties.^[54] The dual charge nature allows for the surfactant molecules to pack closer together at the air–water interface, as a result the interfacial tension is lowered, and foaming is enhanced.^[54]

It has been reported in more recent years that cocamidopropyl betaine has led to some minor cases of contact dermatitis and sensitization.^[89,90] The source of the irritation is believed to be 3-dimethylaminopropylamine (DMAPA) and cocamido propyl dimethylamine (“amidoamine”), both of which are impurities often found in CAPB as a result of the manufacturing process.^[90] Although their presence in commercial CAPB is believed to be below 0.002% w/w for DMAPA and below 0.3% w/w for amidoamine, in a study carried out by the International Contact Dermatitis Research Group the impurities triggered an allergic response in 39% of patients with no allergic response being triggered for those tested with pure CAPB.^[91]

3. Deposition Polymers

The deposition polymer is used in shampoo formulations to facilitate the deposition of beneficiary agents onto the hair. More colloquially, it can be referred to as the conditioning polymer. The selected beneficiary agents define the additional function of the shampoo, amongst which are conditioning, dandruff reduction, and “antifrizz.”^[92] Thus, the deposition polymer has a vital role in the formulation.

The polymers most used to carry out this role are cationic in nature with water soluble backbones.^[3,92] These polymers are often derived from biopolymers such as cellulose or guar gum (Table 2). This means they can be made synthetically or obtained from renewable sources.^[93,94] The latter is the preferred route as most companies move toward more renewable product sources.

3.1. Role in the Formulation

The deposition of cationic conditioning polymers onto the hair is fundamentally what occurs when a shampoo containing such polymers is used. Cleverdon et al.^[95] and Hossel et al.^[2] using

observations of complex precipitation, measurements of charge potentials associated with the formed complexes and the direct measurement of absorption forces have demonstrated that the conditioning process could be subdivided into three definitive steps. In the first step the deposition polymer complexes electrostatically interact with the surfactant micelles while in the undiluted bulk formulation (Figure 8). The charge along the polymer chain can act as a nucleation site for the micelle formation, allowing for hemimicelles to develop along the polymer creating a “string of pearls” complex. This complex is fully solubilized by its interaction with the excess anionic surfactant.

In the second stage the “string of pearls” complex is broken down as it is diluted. The dilution results in surfactant dissociation from the complex and the resultant formation of a further complex that is perfectly charge balanced. The polymer is no longer solubilized by the excess surfactant and the new complex precipitates out of solution. The surface of the polymer in this charge balanced state becomes hydrophobic owing to the surfactant tail groups, this hydrophobicity is shared by the hair’s surface making it a favorable interaction.

The charge balanced polymer–micelle complex is entrapped by the hair allowing for the third stage to be completed. This third stage involves the further dilution of the complex via rinsing. This additional dilution pushes the surfactant concentration below the CMC and leads to further dissociation from the complex. The polymer can then form electrostatic interactions with the anionic hair strands while in close proximity, depositing itself onto the hair.^[2,3,92,95,96]

Secondary to its own deposition onto the hair the cationic polymer also aids the deposition of other beneficiary agents, most commonly silicone used for its conditioning properties, either as solid particles or oil droplets. The polymer adsorbs to the surface of the beneficiary agent, coating it (Figure 9). The surfactant is then able to complex with the cationic polymer in the same manner as outlined above, however with the silica particle being at the core of the coacervate complexes. Once the precipitation stage is reached both the cationic polymer and the silicone particles or droplets are able to be deposited onto the hair.^[3,92,96] The presence of coacervates in solution has been mapped experimentally by Lochhead et al.^[96] via absorbance measurements and infrared wavelength shift mapping.

The role of the deposition polymer is not greatly affected by the specific chemical structures of the polymer backbones; however, they should be water soluble and cationically charged to maximize the electrostatic interactions with the surfactant molecules.

4. Structuring Polymers

With modern shampoo formulations containing a multitude of different components each with differing chemical and structure properties, coacervation and spontaneous phase separation of formulation components can often be encountered.^[98–105] The addition of what is known in industry as a structuring polymer can help to combat such issues. The structuring polymer interacts with the system in either an associative or a nonassociative manner, depending on its chemical composition, acting as a molecular emulsifier (Table 3).

Table 2. Examples of the most common cationic deposition polymers used in shampoo formulation. The polymers are categorized based upon their polymer backbones as cellulose based, other biopolymer derivatives, synthetic copolymers, “polyquaternium” and others. The polyquaternium category refers to a range of cationic polymers that exist specifically for the personal care industry and all contain a quaternary ammonium center.

Category	Industry examples
Cellulose based ^[3,24,92,96]	Cocodimonium hydroxypropyl oxyethyl cellulose Stearidimonium hydroxyethyl cellulose Stearyldimonium hydroxypropyl hydrolyzed oxyethyl cellulose Cationic hydroxyethyl cellulose Hydrophobically modified cationic hydroxyethyl cellulose
Other biopolymers ^[2,3,24,92,96]	Guar hydroxypropyl trimonium chloride Chitosan Cocodimonium hydroxypropyl hydrolyzed collagen Cocodimonium hydroxypropyl hydrolyzed keratin Cocodimonium hydroxypropyl hydrolyzed wheat protein Starch hydroxypropyl trimonium chloride Lauryldimonium hydroxypropyl hydrolyzed collagen Lauryldimonium hydroxypropyl hydrolyzed wheat protein
Synthetic Copolymers ^[2,3,24,92]	VP/DMAA acrylate copolymer PVP/dimethyl aminoethyl methacrylate copolymer PVP/dimethyl aminoethyl methacrylate polycarbamyl PVP/dimethiconylacrylate/polycarbamyl polyglycol esterVP/vinyl caprolactam/DMPA (dimethylol propionic acid) acrylates copolymer
“Polyquaternium” ^[2,3,92,97]	Polyquaternium-2—poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] Polyquaternium-4—hydroxyethyl cellulose dimethyl diallyl ammonium chloride copolymer Polyquaternium-5—acrylamide/quaternized dimethylammonium ethyl methacrylate copolymer Polyquaternium-6—poly(diallyldimethylammonium chloride) Polyquaternium-7—acrylamide/diallyl dimethyl ammonium chloride copolymer Polyquaternium-8—methyl and stearyl dimethyl amino ethyl ester of methacrylic acid/quaternized dimethylsulfate Polyquaternium-10—quaternized hydroxyethyl cellulose Polyquaternium-11—vinylpyrrolidone/quaternized dimethyl amino ethyl methacrylate Polyquaternium-16—vinylpyrrolidone/quaternized vinyl imidazole Polyquaternium-17—adipic acid/dimethylaminopropylamine/dichloroethylether copolymer Polyquaternium-18—azelaic acid/dimethylaminopropylamine/dichloroethylether copolymer Polyquaternium-22—acrylic acid/diallyldimethylammonium chloride copolymer Polyquaternium-24—quaternary ammonium salt of hydroxyethyl cellulose/lauryl dimethyl ammonium substituted epoxide Polyquaternium-27—Block copolymer of “polyquaternium-2” and “polyquaternium-17” Polyquaternium-28—vinylpyrrolidone/methacrylamidopropyl trimethylammonium copolymer Polyquaternium-31—N,N-dimethylaminopropyl-N-acryl amidine quaternized with dimethylsulfate and bound to polyacrylonitrile Polyquaternium-39—acrylic acid/acrylamide/diallyldimethylammonium chloride terpolymer Polyquaternium-43—acrylamide/acrylamidopropyltrimonium chloride/2-amidopropylacrylamide sulfonate/dimethylaminopropylamine copolymer Polyquaternium-44—3-methyl-1-vinylimidazolium methyl sulfate-N-vinylpyrrolidone copolymer Polyquaternium-46—vinyl caprolactam/vinylpyrrolidone/quaternized vinyl imidazole terpolymer Polyquaternium-47—acrylic acid/methacrylamidopropyl trimethylammonium chloride/methyl acrylate terpolymer Polyquaternium-53—acrylic acid/acrylamide/methacrylamidopropyl trimonium chloride terpolymer Polyquaternium-55—vinyl pyrrolidone/dimethylaminopropyl/methacrylamide and methacryloylaminopropyl lauryl dimethyl ammonium chloride random copolymer
Other ^[24,92]	Amodimethicone Trimethylsiloxamodimethicone Ioneners Polyglycol ester Poly(vinylpyrrolidone-dimethyl amido propylmethacrylamide)

4.1. Role in the Formulation

Structuring polymers have two main roles within a shampoo formulation, viscosity tuning and acting as a suspending agent to prevent phase separation. While the interaction between surfactants and structuring polymers is well defined in

literature,^[106–108] their function as part of a multicomponent shampoo formulation is not.

Intrinsic viscosity build-up occurs within the system because of the formation of elongated (worm-like) micelle structures. These worm-like micelles form self-entanglements.^[11,12,109] The rheological profile associated with the surfactant (spherical)

Table 3. Examples of the most common structuring polymers used in shampoo formulation, categorized by the mechanism by which they function and their respective acronyms.

Type	Name	Example
Associative Nonionic	HMHEC: ^[3,115,116] hydrophobically modified hydroxyethyl cellulose	Cetyl hydroxyethyl cellulose
Associative Nonionic	HEUR: ^[3,92,115,116] hydrophobically modified ethoxylated urethane	Polyethylene glycol/isocyanate copolymer Polypropylene glycol/isocyanate copolymer Polybutylene glycol/isocyanate copolymer
Associative Anionic	HASE: ^[3,92,115,116] hydrophobically modified alkali swellable emulsion polymer	Methacrylic acid/ethyl acrylate/methacrylic ester with long chain alkoxylation terpolymer
Associative Nonionic	HMPE: ^[115,116] hydrophobically modified polyether	Polyacetal/polyether copolymer with a long chain hydrophobe Polyketal/polyether copolymer with a long chain hydrophobe
Nonassociative	ASE: ^[115,117,118] alkali swellable emulsion polymer	Polyacrylate copolymer Polyacrylic acid copolymer
Nonassociative	HEC: ^[115,118] hydroxyethyl cellulose	Cellulose/ethylene oxide copolymer

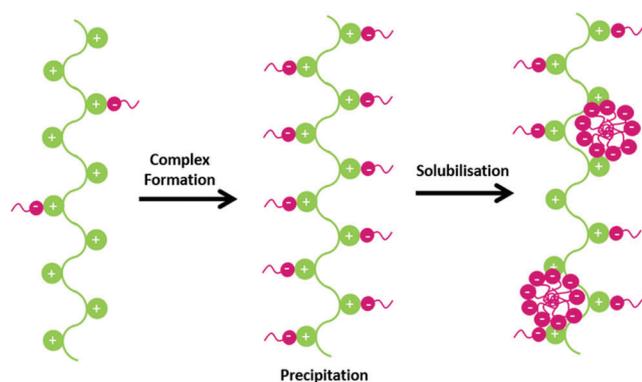


Figure 8. A schematic diagram drawn based on information in Hossel et al.,^[2] Cleverdon et al.,^[95] and Lochhead,^[3,92,96] showing the complexation between the cationic deposition polymer, shown in green and anionic surfactant, shown in pink, with increasing surfactant concentration (left to right).

micelle formation corresponds to Newtonian fluid which can be problematic during product handling processes and exhibits poor particle and droplet suspension properties. The most desirable rheological profile for a shampoo formulation is pseudoplastic.^[34] A pseudoplastic system is able to exhibit shear-thinning behavior, this allows the system to flow when a certain level of shear is reached (e.g., pouring) owing to the breakdown of any network formation.^[110] The transition from Newtonian fluid to a pseudoplastic rheological behavior of the system can be achieved by the introduction of the structuring polymer, initiating the network formation is initiated.

The viscosity build-up as a direct result of structuring polymer addition is defined by the formation of polymer-micelle networks and polymer entanglements. This process occurs via two differing mechanisms, dependent upon the type of structuring polymer used within the formulation. The nonassociative mechanism usually occurs when alkali swellable emulsion (ASE) polymers are incorporated into the formulation, and the associative

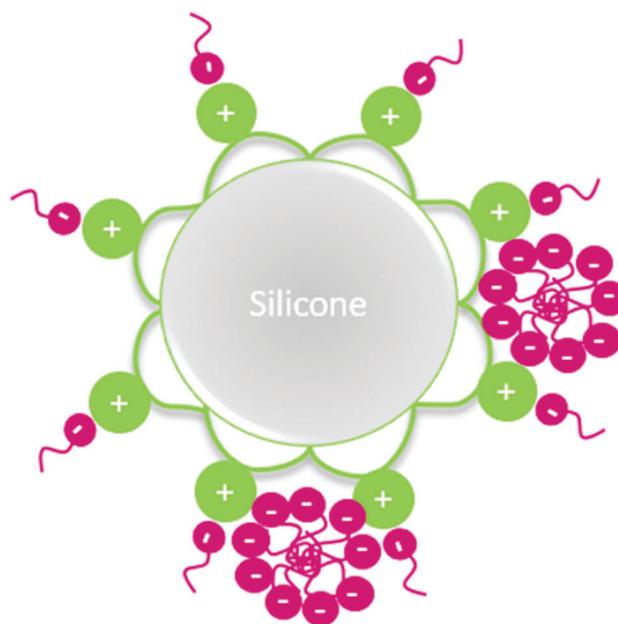


Figure 9. A schematic diagram drawn based on information in Lochhead,^[3,92,96] showing a polymer-micelle coacervate coating a beneficiary agent (silicone), with the micelles depicted in pink and the cationic polymer depicted in green. The beneficiary agent will be deposited onto the hair via the dilution-deposition mechanism.

mechanism takes precedence when hydrophobically modified alkali swellable emulsion (HASE) polymers are used.

The structuring polymer's additional role within the formulation is to act as a suspending agent, preventing the spontaneous phase separation process. The suspension properties stem from the polymer aiding the production of a continuous phase through its network formation and self-entanglements. For the associative structuring polymers these properties are furthered through their ability to form positive associations with both hydrophobic and hydrophilic components in the formulation, acting as phase mediators.

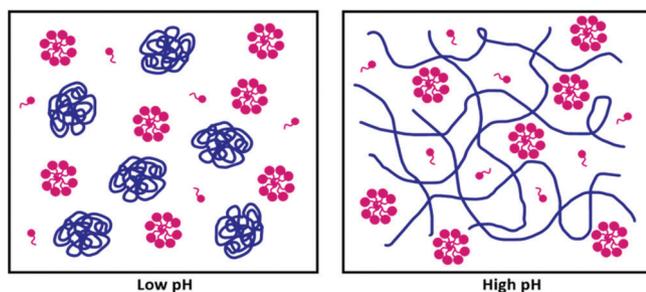


Figure 10. A schematic drawn based on information in Wolfe et al.^[111] and Xian,^[112] depicting the swelling action of the ASE polymer (shown in blue), resulting in nonassociative thickening in the presence of micelle and surfactant (shown in pink). At low pH (left drawing) the ASE polymer exists as coiled particles and at high pH (right drawing) the particles are neutralized and swell into chains.

4.2. Types of Structuring Polymer

4.2.1. Nonassociative

The nonassociative mechanism of thickening and suspending occurs when ASE such as acrylic polymers are used in the formulation. These processes can effectively be observed via dynamic and static light scattering experiments outlined by Wolfe et al.^[111] Under acidic conditions the nonassociative polymers exist as tightly coiled polymer particles (**Figure 10**, low pH). As the pH of the system increases beyond the pKa ~ pH 7 the acid groups on the long acrylic chains are ionized allowing the uncoiling process to begin (**Figure 10**, High pH). Eventually, with further alkali addition the chains become water-soluble allowing for the elongation and “swelling” action to drive chain entanglements in the system. The thickening processes is furthered as the swellable polymers occupy a large effective volume in the system, limiting the motion of other components, specifically bound water.^[111,112]

4.2.2. Associative

The use of HASE polymers leads to the associative mechanism of thickening and suspending. These HASE’s are in essence acrylic polymers, however they contain long chain hydrophobes that are pendant to the polymer backbone (**Figure 11a**). The hydrophobes act as nucleation points for hemimicelle (**Figure 11b**) formation which ultimately drives the formation of the hydrophobic network (**Figure 11c**). The formation of the hydrophobic networks, as a result of the polymer swelling action is usually studied by rheology and relaxation time measurements as demonstrated by Lochhead,^[3,92] Tam et al.,^[113] and Johnson et al.^[114] Under acidic conditions the polymer exists in its contracted, particle like coiled state. As the pH is increased, above pH 7, the acid groups along the polymer backbone are neutralized. The polymer chain is solubilized, and the alkali initiated “swelling” behavior is observed. The uncoiling of the polymer backbone exposes the hydrophobic groups, allowing them to form an associative hydrophobic network. The network forms as the hydrophobic groups interact with one another and other hydrophobic components in the system (such as surfactant) bridging together chains (**Figure 11**). The network self-entangles leading to viscosity build-up.^[3,92,112–114]

5. Viscosity Modifiers

Viscoelastic properties of a shampoo are governed initially by the micelle and polymer components.^[4,98,100,106] Polymer chain entanglements, the formation of physical crosslinks and networks all drive the viscosity of the shampoo up, however competitive relaxations, such as reptation, sliding of contact points and micelle breakage all act to lower the shampoo viscosity.

Micelle formation leads to viscosity build up via entanglement of wormlike micelles and the formation of physical crosslinks between the polymer components to produce networks, be that hydrophobically or electrostatically (shown in **Figures 10 & 11**). Equally, when shear is imparted onto the system, micelle breakage and the movement of branching points can result in an overall viscosity decrease. This process is defined physically as shear thinning behavior.

Polymer chains can form self-entanglements and can be bridged by micelles to form larger networks resulting in viscosity increases (shown in **Figures 10 and 11**). Conversely, polymer chains can disentangle, and networks can be broken down when the formulation is under shear flow. Adjustments to the pH of the formulation also affects the way the system interacts, owing to the pH swellable nature of some of the polymer components.^[106] These adjustments either facilitate network formation or hinder it.

For these reasons alone viscosity modifiers are essential to tune the system viscoelastic properties, allowing it to achieve the optimum level.

5.1. Role in the Formulation

Common salts, such as sodium chloride, are the most used viscosity modifier in the personal care industry, owing to its low cost.^[119] Its incorporation in a shampoo formulation at varying concentrations allows for the overall viscosity of the system to be tuned according to the desired function.

The production of a “salt curve” is essential to determine the correct loading of sodium chloride for optimum viscosity tuning in a specific system (an example of which is shown in **Figure 12**). Generally, with an increase in salinity a shampoo formulation initially generates a steep increase in viscosity. The viscosity plateaus slightly before exhibiting a decrease when salinity levels are at a maximum before becoming saturated. From this curve the level of salt loading can be determined to suit the desired result.^[120,121]

The steep increase in viscosity observed at initial loading concentrations is mostly attributed to a process known as charge screening. The packing parameter of a micelle is defined and limited by the degree of head group repulsion exhibited by the surfactant molecules and the micelle’s charge density.^[13] When sodium chloride is introduced into an aqueous system it breaks down into its constituent ions, Na⁺ and Cl⁻ (**Figure 13**, ion dissociation). These free ions can interact electrostatically with the surfactant head groups, screening their charge and reducing the micelle charge density. With a reduced charge density and with screened individual charge the surfactant molecules can pack closer together. As the packing parameter increases a transition in micelle shape is observed. Micelles become less spherical or ellipsoidal and more cylindrical or wormlike (**Figure 13**, Charge Screening). Once a wormlike or cylindrical micellar structure is

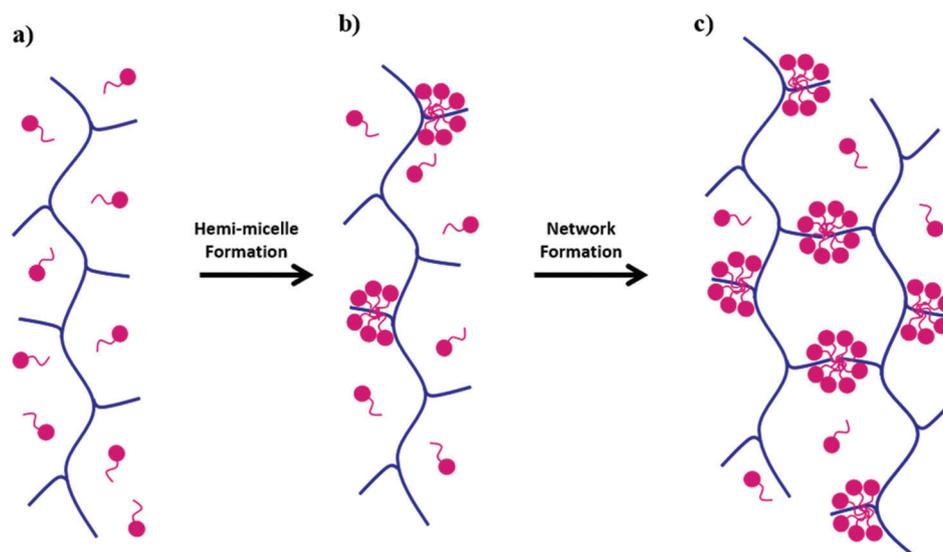


Figure 11. A schematic diagram drawn based on information in Tam et al.^[113] and Lochhead,^[3,92] depicting a) the structuring polymer, with its pendent hydrophobes and surfactant in solution, b) the pendent hydrophobes acting as nucleation points for the formation of hemimicelles, and c) the formation of the hydrophobic network via the bridging of neighboring polymer chains by the micelles. The HASE structuring polymer is shown in blue and the surfactant micelles are shown in pink.

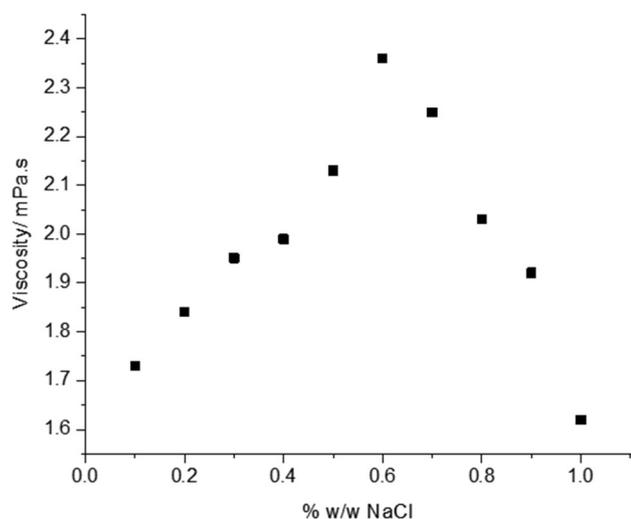


Figure 12. An example salt curve depicting the effect of NaCl on the viscosity of binary surfactant micellar solutions of CAPB and SLES (2:8 at a total of 10% w/w) diluted with deionized water, at 25 °C.

achieved, the viscosity builds as entanglements occur (Figure 13, Entanglement).^[122,123]

The plateau in viscosity is achieved once charge screening has reached its full potential in the micelle elongation processes. From this point on increase salinity acts to decrease viscosity gradually. Further introduction of Na^+ and Cl^- ions disrupts the balance of the system. The ions compete with the surfactant molecules to interact with water, this leads to the breakdown of the microstructure of the system and disrupts the micelle's ability to form viscosity building entanglements.^[124–126] The observation of entangled network formation can be mapped experi-

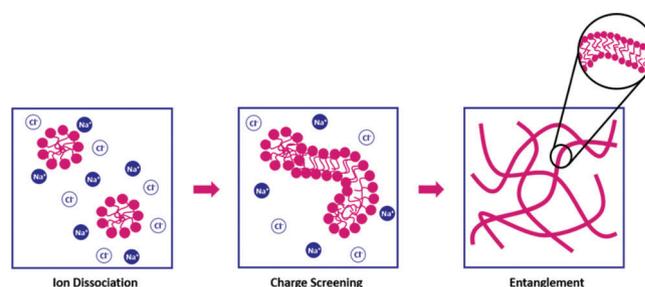


Figure 13. A schematic diagram drawn based on information in Kern et al.^[122] and Kralchevsky et al.^[124] depicting the mechanism of viscosity build up through ion dissociation of NaCl (shown in blue and white), charge screening of surfactant head groups (shown in pink), leading to micelle elongation and entanglement.

mentally via zero-shear viscosity measurements and the characteristic times for micelle breakage and reptation, outlined in Kern et al.^[122] and Kralchevsky et al.^[124]

6. Conclusion

This review successfully outlines the main components of a shampoo formulation, describing their roles and how they function, as well as providing examples of the most common of each component currently being used in the personal care industry.

The surfactant is the main cleaning components of the shampoo, carrying out this role via four different mechanisms: “roll-up,” spontaneous emulsification, penetration, and solubilization. Further to this surfactants aid forming by tuning the interfacial tension leading to bubble stabilization. Surfactant selection is crucial, allowing for the enhancement and introduction of specific properties to the formation, with the use of a primary and

complimentary secondary (cosurfactant) surfactant being commonplace in the personal care industry.

The deposition polymer aids the deposition of beneficiary agents (such as silicone which has conditioning properties) onto the hair, while also acting as conditioning agents itself. The deposition polymer selection requires a water-soluble, cationic polymer backbone; however, other functional groups can be selected as per the formulation requirements.

The structuring polymer prevents the micro- and macrophase while simultaneously leading to viscosity build-up. There are two main classes of structuring polymer, those that interact associatively in the formulation and those that interact nonassociatively in the formulation. The viscosity build-up can be tuned to allow for the perfect “bottle-viscosity” to be achieved. The most common viscosity modifier used in the personal care industry is salt, NaCl, owing to its low cost and charge screening abilities. A “salt curve” is constructed to allow for the correct concentration of NaCl to be added to a formulation to achieve the ideal viscosity.

The future of shampoo science is progressing with a look to being more sustainable in its manufacturing processes, its formulation, and its lasting effects on the environment after use. Shampoos that are kinder to the hair and skin, for example sulfate-free formulations, and kinder to the environment, for example minimizing microplastic contributions, are on the rise. This review article has outlined the principal components used in modern day shampoo formulations including surfactants, deposition polymers, structuring polymers, and viscosity modifiers. In addition to this the component functions are explained in detail along with the physiochemical processes by which they can perform these functions. It is hoped that the information outlined in this article will in some way aid the understanding behind the physiochemical process by which a shampoo functions, with a view to developing more sustainable shampoo formulations in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

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cleansing, conditioning, deposition, foaming, polymer, shampoo, surfactant

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