Achieving optimum viscosity on challenging surfactant compositions by understanding the thickening mechanism

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Abstract

Background: Moving away from sulfate-based surfactants and at the same time avoiding PEG-derivative thickeners opens a new world of challenges in Personal Care. In order to succeed in achieving the desired viscosity in each formulation, we believe that understanding the mechanism behind a thickener is the best way to proceed.

Methods: The techniques used in this study are Dynamic Light Scattering to characterize the size distribution of surfactant aggregates and Small-Angle X-Ray Scattering to determine the shape and structure of the aggregates. A Brookfield Viscosimeter has also been used to measure viscosity.

Results: A thickening mechanism has been identified for NaCl and Lauryl Lactate in different surfactant compositions. A correlation has been identified between the surfactant aggregates shape and size for different compositions that can be thickened with NaCl. Finally, different aggregate structures have been identified according to the ratio between anionic, amphoteric and non-ionic surfactants.

Conclusion: The thickening mechanism of NaCl has a low influence on modifying the internal aggregate size. On the contrary, Lauryl Lactate has a high influence on modifying the internal shape and size of the aggregates. An increase of the aggregate size has been identified while increasing the % of Lauryl Lactate and therefore while increasing viscosity.

Also, is has been concluded that, within ellipsoidal models, the surfactant compositions with oblate shape are more likely to be thickened with NaCl than those with prolate shape, which are hardly thickened with NaCl.

Keywords: sulfate-free surfactants; associative thickeners; viscosity; thickening mechanism

Introduction

When using personal care products, consumer perception depends on many aspects such as texture, odor and color. The texture of a personal care product can be related, among other properties, by the viscosity, which has a big influence on how a product looks and feels in-use. Therefore, when designing a product it is highly important to obtain desirable viscosity levels in order to achieve products well perceived for consumers.

For many years, Sodium Lauryl Sulfate (SLS) and Sodium Laureth Sulfate (SLES) have been the mainstay surfactants in personal care cleansing formulations. However, there is a move to replace these and other sulfate-containing surfactants with sulfate-free alternatives. Consumer health awareness has increased the demand for safer ingredients and mild cosmetics products.[1]

The cheapest and simplest way to thicken a surfactant formula is to use NaCl. The addition of electrolytes reduces the electrostatic repulsion between the ionic head groups and the micellar surface charge density.[2] However, it is well known that many of the sulfate-free surfactants currently available on the market are often very difficult to be thickened with NaCl.

In this context, it is needed to look for alternative thickeners in order to achieve good viscosity profiles. Natural polymers may be a good option, but in some cases they may provide unappealing textures, PEG-derived surfactants can be a very good alternative offering effective thickening outcomes in Sulfate-Free compositions; however, many costumers also prefer to move away from PEG-derived ingredients due to petrochemistry origin or because they could contain undesirable impurities. So, in conclusion, achieving viscosity in today's personal cleansing formulations in not an easy requirement to fulfill for cosmetic formulators.

The structure of micelles is one of the factors, among others, that influences the final product viscosity. Micelle shapes have been widely discussed in the literature and many studies report that a viscosity increment is often attributed to a micellar growth from spherical shapes to larger micelles.[4]

Although different studies related to the thickening mechanism have been published, we believe that the thickening mechanism of sulfate-free formulations with PEG-free surfactant thickeners is still poorly understood[5]. In order to close this gap, the general objective of this study is to understand the thickening mechanism of different surfactant formulations. The thickening agents selected have been NaCl, which is commonly used, and also a PEG-Free surfactant thickener, Lauryl Lactate, which can build up viscosity in most of sulfate and ethoxylate free compositions.

These results will help succeed in achieving the desired viscosity in different surfactant formulations, while predicting good stability and nice sensory feelings for sulfate-free cleansing products.

Materials and Methods

Materials

The compositions evaluated during this study include aqueous surfactant formulations based on a mixture of three surfactants of anionic, amphoteric and non-ionic nature. The anionic surfactant used as reference surfactant is Sodium Laureth Sulfate (LES) and the selected sulfate-free and EO-free surfactants are Sodium C14-16 Olefin Sulfonate (AOS), Sodium Lauryl Glucose Carboxylate (LGC) and Sodium Cocoyl Glutamate (CG). The amphoteric surfactant is Cocamidopropyl Betaine (CAPB) and the non-ionic surfactant Lauryl Glucoside (APG). The thickening agents used for studying the mechanism and increasing the viscosity of the formulations are the NaCl as the most common electrolyte and Lauryl Lactate as a non-ionic surfactant thickener. All of the formulations have been adjusted to a pH value within 5.0 – 5.5 using Citric Acid or Sodium Hydroxide. All of the surfactants are widely used in Personal Care formulations.

Methods

Dynamic Light Scattering (DLS) measurements were performed to evaluate the size distribution of the aggregates formed in aqueous solution using a Zetasizer (Nano Series, Malvern Instruments, UK). The scattering angle was 173° and the measurements were performed at 25 ± 0.1 °C. The detector is placed at 90º. A 1-cm-path-length quartz cuvette was used for the measurements. Before the measurements, samples were run through a 2μm filter and allowed to equilibrate for 2 min in the DLS optical system chamber. An average of 6 measurements were collected as experimental data and micelle size was calculated by using Malvern DTS software.

Small-Angle X-Ray Scattering (SAXS) studies were carried out in the beam-line BL11-NCD-SWEET of ALBA Synchrotron light source facility (Cerdanyola del Vallès, Barcelona, Spain). Samples were loaded into a glass capillary of 2.0 mm and placed in a non thermo-stated ladder for 38 capillaries. SAXS diffraction patterns were collected using a photon counting detector, Pilatus 1 M (pixel size 172x172 µm2), placed at 2.67 m from the sample. The data output was absolute scattered intensity I(Q), vs. scattering vector Q, where Q is the scattering vector defined as $Q = 4\pi \sin \theta/\lambda$. SAXS data was analyzed using a model-based fitting procedure through SasView software.

Viscosity measurements were performed at 20 °C with a Brookfield Viscosimeter LVT.

Results

Surfactant aggregate size by DLS

The first approach of the study was to perform an initial characterization of the size of the surfactant aggregates by means of DLS. The measurements were done with a formulation containing 6% anionic, 3% CAPB and 3% APG in which the anionic component was varied between LES, AOS, LGC and SCG. All of the formulations were adjusted to pH=5.0-5.5 and all had a clear liquid appearance.

The result obtained by DLS is the Z-average value (Z-av), which corresponds to the hydrodynamic diameter of an aggregate having the same translational diffusion coefficient than an spherical particle.

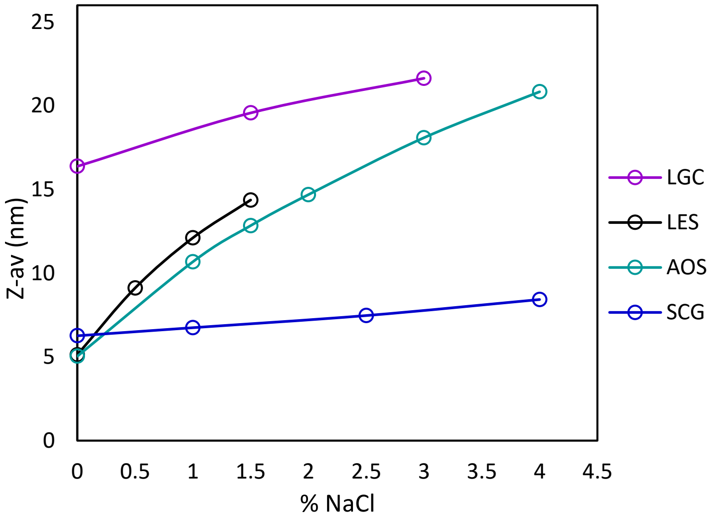

Figure 1. Z-average evolution with the addition of NaCl in formulations containing 6% Anionic : 3% CAPB : 3% APG. Measurements were done at 1:3 dilution.

Figure 1 shows that with the addition of NaCl hydrodynamic diameter increase for all compositions, indicating that the NaCl thickening mechanism responds to an increase of the surfactant size aggregates. Moreover, two types of growth can be identified: formulations prepared with LES and AOS have a greater slope in comparison with formulations prepared with LGC and SCG. The correlation between this effect and the viscosity will be discussed in a later section.

Surfactant aggregate shape and size by SAXS

Figure 2 shows the scattering data obtained by SAXS for formulations of 6% Anionic : 3% CAPB : 3% APG in which the anionic surfactant has been varied between LES, AOS, LGC and SCG. A core shell ellipsoid model with a structural factor fitting model has been applied for all formulations. On the left, a schematic drawing of the core-shell ellipsoid model is represented, which has been used for the calculation of the aggregate sizes shown in Table 1. The inner diameter is calculated by the sum of thick_shell and Requat_core parameters, and the equatorial diameter by the sum of the product of x_core by Requat_core and x_polar_shell by thick_shell.

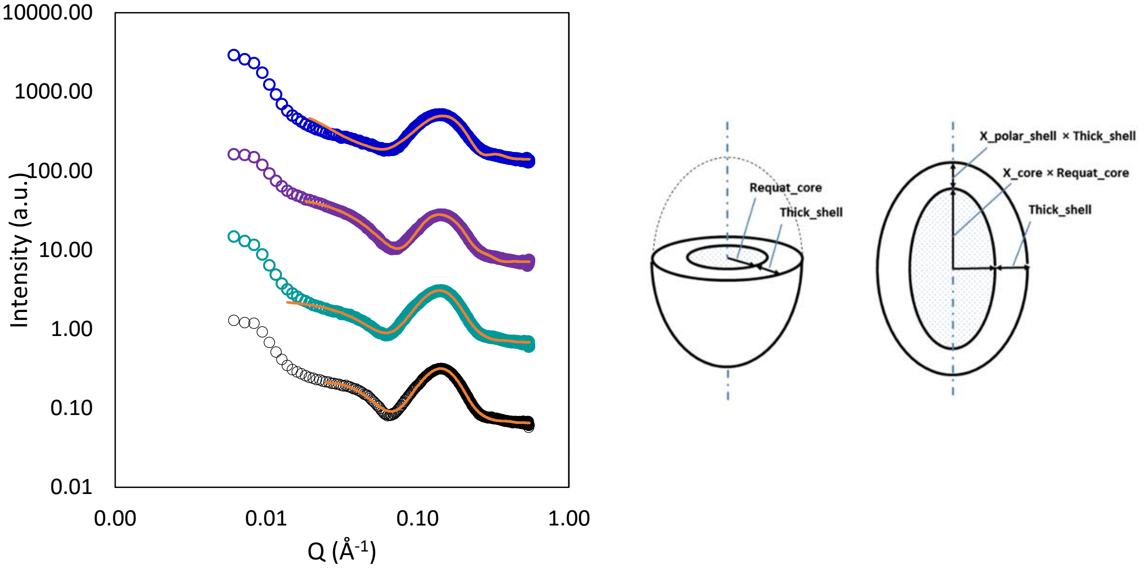

Figure 2. Scattering data obtained by SAXS for LES (black), AOS (green), LGC (purple) and SCG (blue) and core-shell ellipsoid fit (orange) of each formulation. 2D schematic drawing of the core-shell ellipsoid model obtained from SASView 5.0.3 software (www.sasview.org, accessed on 12 July 2022).

Table 1. Size results by means of SAXS of the aggregates obtained for a formulation of 6% Anionic : 3% CAPB : 3% APG.

Anionic surfactant	Equatorial diameter (Å)	Inner diameter (Å)
LES	26	76
AOS	21	78
LGC	408	64
SCG	234	54

As it can be observed in Table 1, significant differences can be observed between the anionic surfactant studied. From one side LES and AOS show lower equatorial diameter than inner diameter, whereas LGC and SCG show clearly a longer equatorial diameter than inner diameter.

As the best fitting models correspond to an ellipsoid shape for all of the surfactant systems, from now on all the results will be analyzed by SAXS.

Surfactant aggregate shape and size evolution by thickening addition

The second approach of the study was focused on studying the evolution of the aggregate shape and size with the addition of a thickener ingredient. On the one hand, NaCl was chosen as the most commonly used electrolyte in the market and, on the other hand, Lauryl Lactate, 100% natural and effective thickener in most of the systems, was chosen as a PEG-free surfactant.

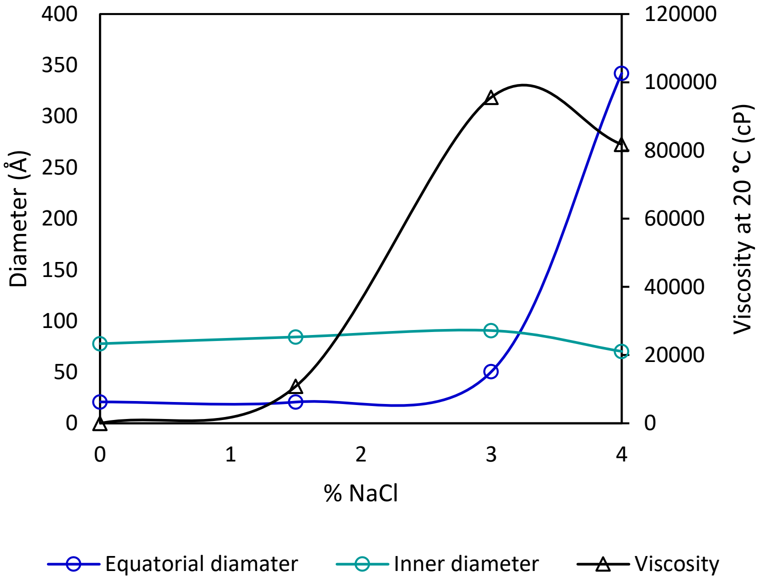

Figure 3. Aggregate surfactant size and viscosity evolution with the addition of NaCl in a formulation of 6% AOS : 3% CAPB : 3 % APG. SAXS fitting correspond to a core shell ellipsoid model with a sticky hard sphere structure factor.

The surfactant AOS is known to be easily thickened with NaCl in a basic formulation with an amphoteric surfactant. Therefore, the formulation developed in this study, 6% AOS : 3% CAPB : 3% APG, has been thickened with the addition of NaCl and the viscosity increase is shown in Figure 3 (black line). Additionally, the evolution of the size of the aggregates has been represented. As it can be observed, the thickening mechanism of NaCl does not respond to a strong change on the aggregate size, as the shape and size of the aggregate remain constant up to 3% of NaCl. The dramatic change of the aggregate size was observed at the % of NaCl in which the viscosity already started to decrease, therefore indicating a clear destabilization of the aggregate structure system.

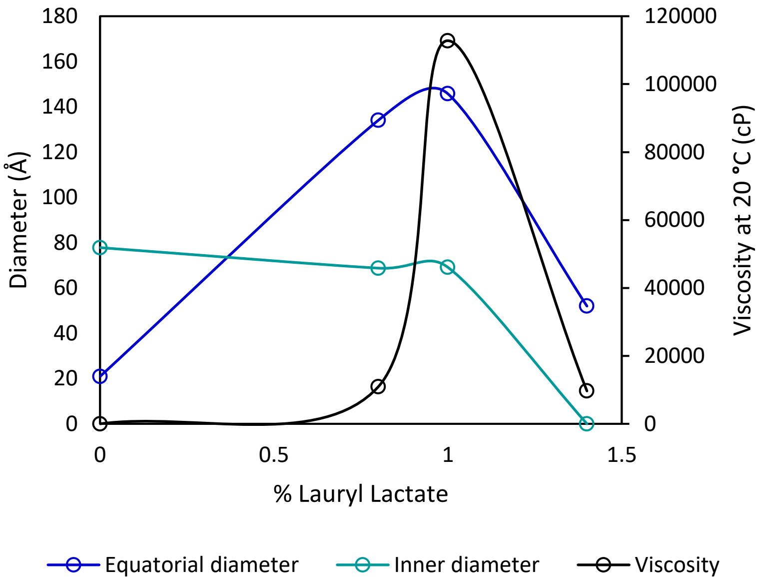

Figure 4. Aggregate surfactant size and viscosity evolution with the addition of Lauryl Lactate in a formulation of 6% AOS : 3% CAPB : 3 % APG. SAXS fitting correspond to a core shell ellipsoid model with a sticky hard sphere structure factor.

With the aim to compare the thickening mechanism of NaCl and Lauryl Lactate, Figure 4 shows the evolution of the size of the aggregates in the same basic formulation 6% AOS : 3% CAPB : 3% APG. As it can be observed, the thickening mechanism of Lauryl Lactate is linked to a modification of the surfactant aggregate size. With the increase of % of Lauryl Lactate in the formulation, an increase of the equatorial diameter is seen, while viscosity increases. Once the maximum point of viscosity is overstepped, above 1% of Lauryl Lactate, a clear decrease can be observed in the aggregate size, both for the equatorial diameter and inner diameter, indicating a break on the surfactant aggregate system.

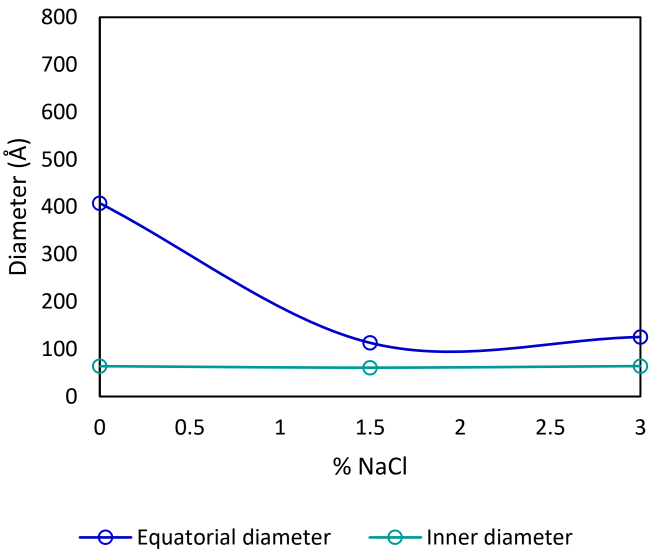

Figure 5. Aggregate surfactant size evolution with the addition of NaCl in a formulation of 6% LGC : 3% CAPB : 3% APG. SAXS fitting correspond to a core shell ellipsoid model with a sticky hard sphere structure factor.

LGC is known for not being easily thickened with NaCl in common formulations. Figure 5 shows how aggregate size is modified with the addition of NaCl in a formulation of 6% LGC : 3% CAPB : 3% APG. Viscosity results have not been represented because no viscosity increase has been achieved within this % NaCl range. As it can be observed in Figure 5, the size of the aggregate decreases with the addition of NaCl, which indicates that the addition of NaCl to this system is therefore unlikely to have an increase effect on viscosity.

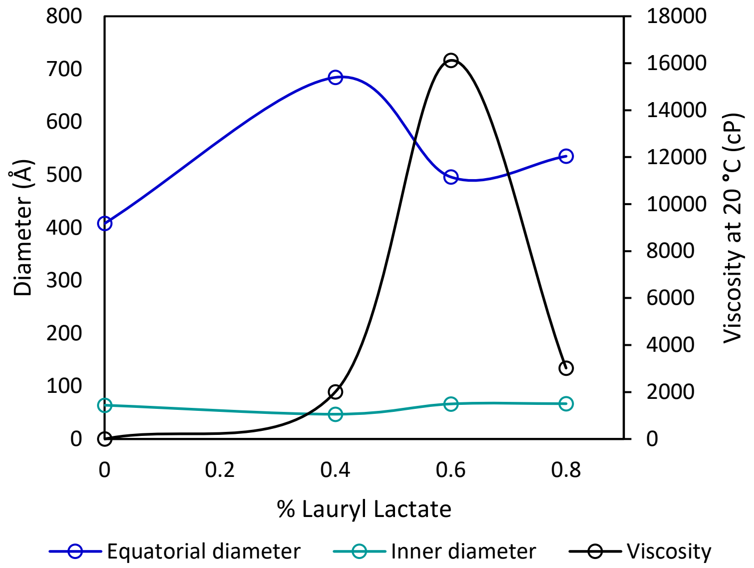

Figure 6. Aggregate surfactant size and viscosity evolution with the addition of Lauryl Lactate in a formulation of 6% LGC : 3% CAPB : 3% APG. SAXS fitting correspond to a core shell ellipsoid model with a sticky hard sphere structure factor.

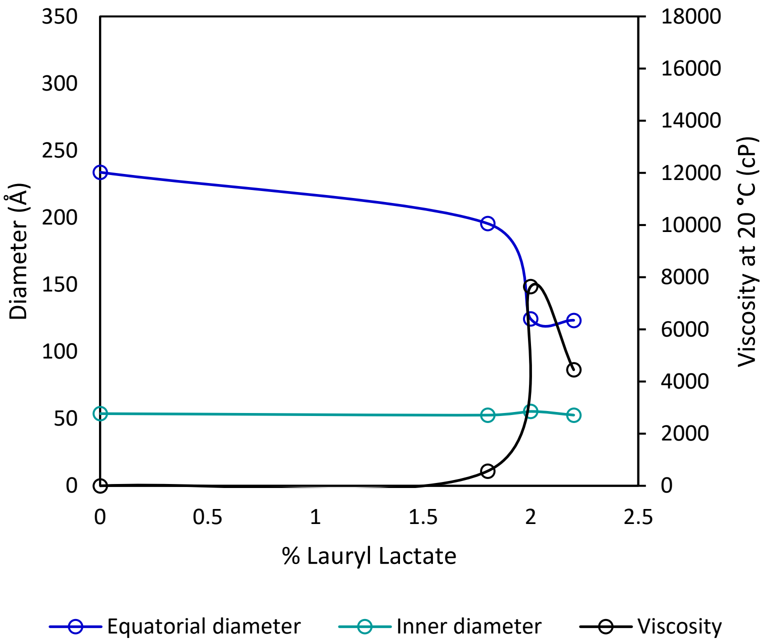

Figure 7. Aggregate surfactant size and viscosity evolution with the addition of Lauryl Lactate in a formulation of 6% SCG : 3% CAPB : 3% APG. SAXS fitting correspond to a core shell ellipsoid model with hayter_msa structure factor.

Figures 6 and 7 show the surfactant aggregate size and viscosity evolution in a formulation of 6% LGC : 3% CAPB : 3% APG and 6% SCG : 3% CAPB : 3% APG, respectively. As it can be observed, for the LGC formulation, the aggregate size evolution increases with the addition of Lauryl Lactate up to the % in which Lauryl Lactate cannot be solubilized in the system and viscosity drops down, also observing a decrease in aggregate size. On the other hand, it can be observed on SCG formulation that viscosity does not reach a maximum value as high as in the other surfactant systems, and it can also be observed that the size of the surfactant aggregates in not so significantly increased with the addition of Lauryl Lactate.

Surfactant aggregate shape and size evolution by surfactant composition variation

Another key aspect that influences the viscosity of a surfactant formulation is the ratio between anionic, amphoteric and non-ionic surfactant. According to this, different amounts of thickener are required and also the peak of the viscosity curves varies.

Figure 8 shows the evolution of viscosity with the addition of Lauryl Lactate at different surfactant ratios of LGC : CAPB : APG.

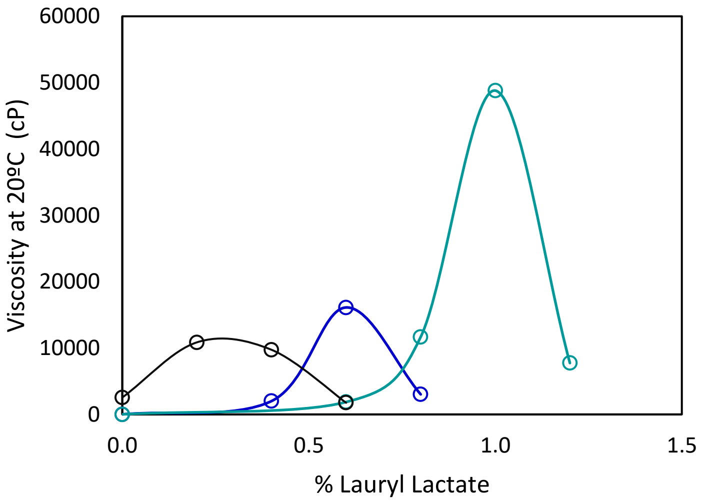

Figure 8. Viscosity evolution with the addition of Lauryl Lactate of different surfactant formulation ratios: 6% LGC : 3% CAPB : 3% APG (blue), 3% LGC : 3% CAPB : 6% APG (green) and 3% LGC : 3% CAPB : 6% APG (grey).

These formulations were analyzed using SAXS and the aggregates size and shape was obtained by fitting a core shell ellipsoid or a core shell cylinder model to the experimental scattering data.

When the surfactant formulation contains 6% LGC : 3% CAPB : 3% APG the shape of the aggregates resemble an ellipsoid with an equatorial diameter of 408Å and an inner radius of 32 Å. To thicken this formulation around 0.6% of Lauryl Lactate is required.

The maximum viscosity is achieved in the formulation of 3% LGC : 6% CAPB : 3% APG, reaching around 50,000 cP. The aggregates in this second case fit properly with a core shell cylinder model, having a length of 306 Å and a radius of 30 Å.

In the third case, where APG predominates, we can observe that the maximum viscosity is achieved with only a low amount of thickener but not exceeding 10,000 cP. Core shell cylindrical model provide the best fit to the micelle scattering data obtaining a length of 210 Å and a radius of 31 Å.

Surfactant aggregate shape and size evolution by active matter variation

Finally, regarding the active matter of the aqueous surfactant formulations, samples with a 10%, 12% and 15% of total surfactant active matter has been prepared, excluding the % of thickener.

In this case the amount of non-ionic thickener to reach the maximum viscosity peak is the same, but the higher the surfactant concentration, the higher the viscosity value achieved, from 8,000 cP to 21,000 cP.

Using SAXS micelle shapes and sizes were determined. The scattering date fits properly with a core-shell ellipsoid in all three cases. As the concentration of surfactant is increased it is observed that the aggregates have the same radius of around 30 Å and the equatorial diameter is 171 Å, 204 Å and 210 Å, respectively.

Discussion

We have studied how the effect of the surfactant aggregate size can have a correlation with the further possibility of increasing viscosity with an electrolyte or a non-ionic surfactant. It is well known that basic surfactant compositions prepared with SLES or AOS surfactant together with an amphoteric surfactant and optionally with a non-ionic surfactant like APG can be easily thickened with electrolytes or other surfactant thickeners. Otherwise, surfactant compositions prepared with carboxylate surfactants or amino acid based surfactants are commonly known to be hardly thickened with NaCl but can be thickened with the non-ionic surfactant Lauryl Lactate.

Figure 1 shows that with the addition of NaCl to a surfactant composition the aggregates size increases by hydrodynamic diameter. However, it has been identified two types of increments: formulations prepared with LES and AOS experiment a higher aggregate size increment than formulations prepared with LGC or SCG. At this point it can be concluded that there is a correlation between the slope at which a surfactant aggregate increases and the ability of this surfactant aggregate to increase viscosity.

When comparing the evolution of the aggregates by means of SAXS measurements between the addition of NaCl and Lauryl Lactate, it has been observed in Figure 3 that NaCl has a small influence on the shape and size of the surfactant aggregate for the formulation 6% AOS : 3% CAPB : 3 % APG while viscosity increases. This correlates with the hypothesis that the thickening mechanism of NaCl for increasing viscosity is more related with increasing the external size of the aggregate or by modifying the electrostatic repulsion between aggregates. On the contrary, the thickening mechanism of Lauryl Lactate is more related with the modification of the shape of the surfactant aggregates. As shown in Figures 5 and 6, the size of the surfactant aggregate increases when viscosity is increased with the addition of Lauryl Lactate, specially elongating the equatorial diameter of the ellipsoidal aggregate. In the case of the formulation 6% SCG : 3% CAPB : 3% APG it would be needed some additional points to confirm an aggregate size modification while increasing viscosity, as in this case the only clear effect observed is the decrease on the aggregate size once viscosity starts to decrease.

Figure 9 shows the ellipsoidal diameters of the different formulations prepared without any thickener addition, all of them corresponding to a core shell ellipsoidal model. From this graph it can be concluded that formulations with a oblate ellipsoidal shape, medium inner diameter (Ø ≈ 70-80 Å) and low equatorial diameter (Ø ≈ 20-30 Å), can be easily thickened with NaCl and also Lauryl Lactate. Rather, formulations with a prolate ellipsoidal shape, lower inner diameter (Ø < 65 Å) and a larger equatorial diameter (Ø ≈ 200-400 Å), will be hardly thickened with NaCl.

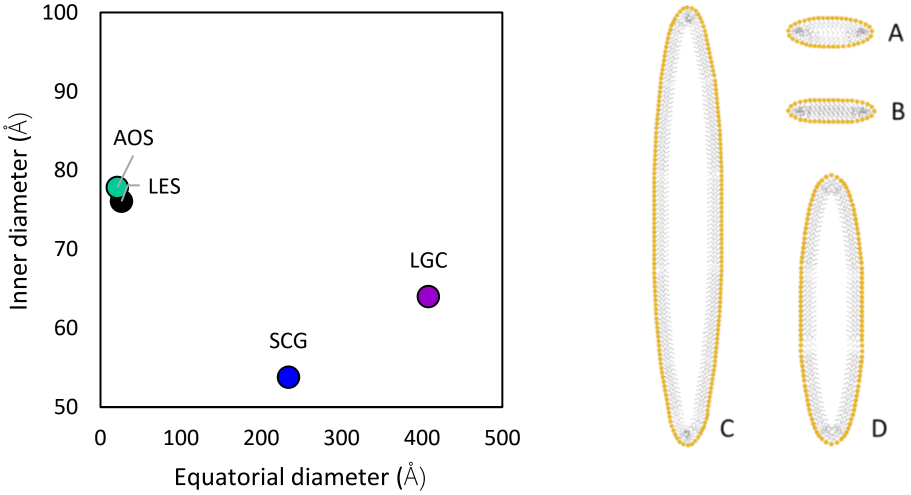

Figure 9. Ellipsoidal equatorial and inner diameters (Å) of surfactant formulations without thickener addition. Schematic 2D representation of aggregate surfactant size and shape of LES (A), AOS (B) , LGC (C) and SCG (D).

Regarding how surfactant aggregates shape and size depend on the ratio between anionic, amphoteric and non-ionic surfactants, it can be observed that in all three cases the radius is almost the same, and the difference that causes different viscosity curves is the length of the aggregates. It can also be concluded that, if high viscosities are required, the amphoteric surfactant percentage should be increased.

Finally, taking into account surfactant concentration, it can be concluded that, the higher the percentage of active matter, the higher the viscosity achieved.

Conclusion

The surfactant aggregate structures of different surfactant compositions have been analyzed. The study formulations at a ratio of 6% anionic : 3% CAPB : 3% APG fit to a core shell ellipsoidal model; with alkyl chains comprising the core, and a compact shell formed by the head groups. Based on the observed evolution of the ellipsoidal model when increasing viscosity, the thickening mechanism of NaCl and Lauryl Lactate has been identified.

The thickening mechanism of NaCl has a low influence on modifying the internal aggregate size. On the contrary, Lauryl Lactate is incorporated internally into the micelles, causing a modification in the shape elongating the equatorial diameter of the ellipsoidal aggregates.

A correlation has been found between the aggregate shape and the feasibility to thicken the formulation with NaCl. It has been concluded that, within ellipsoidal models, the surfactant compositions with oblate shape are more likely to be thickened with NaCl than the once having prolate shape, which are hardly thickened with NaCl. The different shapes and sizes found in the surfactant compositions can be attributed to the differences between the polar head groups of the anionic surfactants.

Furthermore, the highest viscosities are reached in formulations where the amphoteric surfactant percentage is higher or when the total active matter is increased.

As a whole, this study represents a progress in understanding the thickening mechanism in a wide range of sulfate-free personal cleansing formulations which can lead to the design of more effective formulations while fulfilling green market requirements.

Conflict of Interest Statement

The authors declare no conflict of interest.

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