In vitro method to evaluate the cleansing performance of surfactants dedicated to micellar water formulations

Roso, Alicia[1]; **Cuq-Arnaud, Elodie**[1]; Cavaillès, Maïté[1]; Dumaine, Marion[1]; Laubé, Florian[1].

[1] Research & Innovation, Seppic, France.

* Cuq-Arnaud, Elodie, 127 chemin de la poudrerie – BP 90128, 81105 Castres, France
, (+33) 563726969, elodie.cuqarnaud@airliquide.com

Abstract

Background: Choose suitable surfactants or combinations to create effective micellar waters needed to measure their cleaning properties in real condition, especially to clean make-up on the face. The aim of this work was to develop a simple *in vitro* method to evaluate the cleaning power to guide the development of the formulation.

Methods: A mechanical cleaning protocol, close to the micellar water routine, has been put in place to evaluate the effectiveness of surfactant solutions in removing a standard foundation film. Colorimetric measurements were made before and after cleaning and the percentage of efficiency was calculated by the ratio of the parameter L* before/ after.

Results: The optimized method was able to distinguish the ability of surfactants to remove foundations with a long-lasting hold, at low dose (with a maximum standard deviation of 6%), thus facilitating the worktop of micellar water formulation.

Conclusion: In addition to the emphasis placed on the choice of an effective surfactant, this work shows the importance of studying the influence of other ingredients and combinations to optimize the make-up removal performance of micellar waters.

Keywords: Make-up removal; Foundation; Method; Surfactants; Micellar waters;

Introduction.

An easy way to formulate gentle skin cleansers is to reduce the dose of surfactants, as is the case in micellar waters. However this poses the challenge of finding a good compromise with the cleansing properties, especially for makeup removal. Surfactant characteristics such as CMC (Critical Micellar Concentration) [1], wetting properties, help in comparison but the measurement condition is far from the final formulation combining them with other ingredients. A method closer to the application condition is needed. This work aimed to develop a simple tool that provides a quick and reproducible answer to select effective cleansing ingredients for micellar water at an early stage of formulation development. Another interest of this *in vitro* tool is the ability to guide the development of new cleansing structures that can not be tested *in vivo*, pending comprehensive safety assessment and risk analysis processes. Well-known mild surfactant solutions and essential additives in micellar water compositions were tested at realistics use levels. The results were compared to negative controls and micellar water benchmarks to challenge the method and its ability to discriminate the cleansing performance.

Materials and Methods.

Make-up removal performance evaluation was based on colorimetric measurement (L*,a*,b*) on a standard film of foundation before and after mechanical cleansing. The protocol has been adapted to be representative of the final micellar water routine. Two inverse emulsion foundations benchmarks claiming non-transferable efficacy (i.e. Water-in-Oil: W/O and Water-in-Silicone: W/Si with different pigment compositions) were selected for their difficulty in being cleaned.

A foundation film at standard thickness was made on a white carrier (in-house made) and then dried 12h to 24h at 40°C. Measurements of L* parameters (clarity) were firstly made, on the dry calibrated foundation film, using a chromameter (CR400 from Minolta company), in 5 different places of the film: these values represented the "make-up" values. A standard amount, 1g, of ingredient solution (or benchmark formulas) was evenly dotted on a cotton pad attached to a cylindrical cleaning head. The cotton was applied to the film by 17 rotations for 30 seconds and L* measurements were again performed on the film in the same manner and represented the values "after make-up removal". Cleansing performance was calculated by a ratio between the "makeup" and " after makeup removal" values and expressed in % (average of 5 places on the film and 3 to 5 replicates).

% of make-up removal= [L* (with make-up)- L* (white control)] - [L* (after cleansing)- L* (white control)] / [L* (with make-up)- L* (white control)].

Results were compared to cotton alone (mechanical effect due to rubbing) and cotton wetted by 1g of hard water (adjusted to 30° french hardness). An oil applied on a third W/Si benchmark composition was fixed as a positive control to validate the experiments (Caprylic/ Capric Triglyceride).

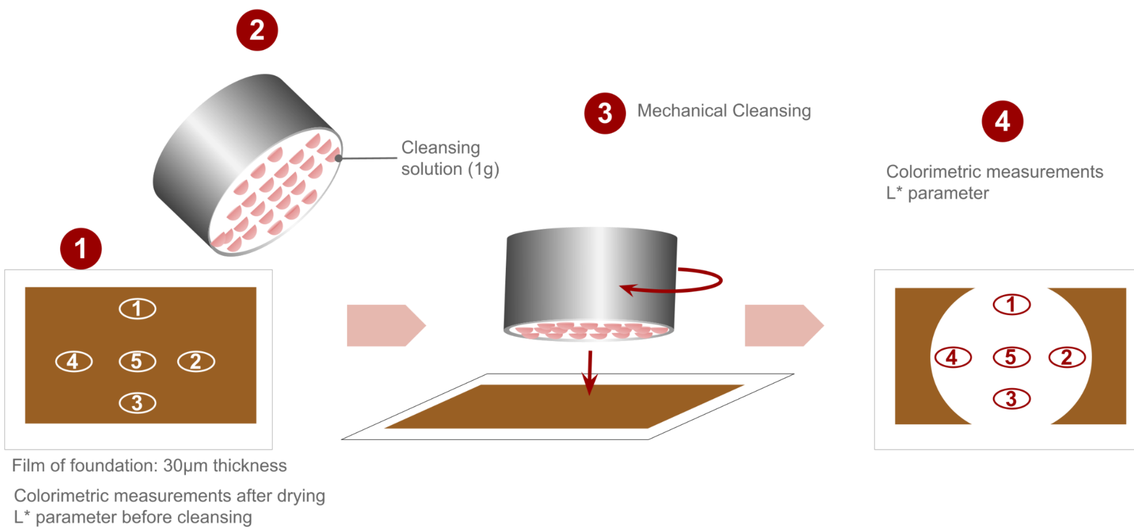
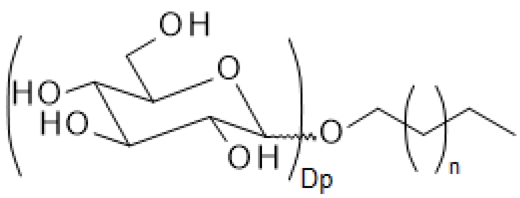


Figure 1. Protocol summary

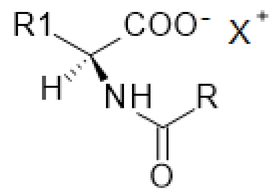
To get comparable results, ingredients were evaluated at the same concentration (%AM diluted in demineralized water) alone or in combination. Micellar waters benchmark were tested as such, in a similar manner to their condition of use.

Results.

Among the parameters studied during the development of the method (such as nature of the foundation to be removed, film carrier etc), pH of the surfactant solutions (4 to 11) showed no significant effect on performance and it was therefore decided to evaluate the solutions in their spontaneous state. On the contrary, the concentration of the materials proved to be critical. This highlighted the value of evaluating the performance of ingredients at low concentrations, representative of the use in micellar waters. A first evaluation of the performance of mild surfactants with different chemical structures at 10% Active Matter (AM) to compare the results with a previous publication [2], led to the selection of the most effective materials, in particular alkyl polyglucoside with short-chain structure and amino acid derivatives (Figure 2), without however allowing to differentiate them (data not shown).



Alkyl PolyGlucoside



LipoAminoAcid

Figure 2. Chemical structure of the selected surfactants

On the contrary, Sodium Cocoyl Glutamate, Sodium Lauroyl Sarcosinate, Cocamidopropyl Betaine, Poloxamer 184, PEG-40 Hydrogenated Castor Oil and Polysorbate-20 have proven to be ineffective compared to water alone. A second, more realistic evaluation at 1% AM revealed significant differences between the surfactants tested and made it possible to compare their performances.

Tested alone (Figure 3), humectant & moisturizing essential additives such as glycerin and Xylitylglucoside complex had no impact on cleansing performance compared to water alone. The absence of effect of Polysorbate-20 and Poloxamer 184 was also confirmed. Looking at the results of the other surfactants, some of them demonstrated good cleansing properties on both films of foundation: PEG-6 Caprylic Capric Triglyceride, Sodium Cocoyl Apple Amino Acids, Sodium Lauroyl OAT Amino Acids, Coco and Decyl Glucoside while others showed lower performance on the Water-in-Silicone foundation: Disodium Cocoamphodiacetate, Lauryl Glucoside & Myristyl Glucoside & Polyglyceryl-6 Laurate, Caprylyl/ Capryl Glucoside. The influence of the fatty chain length in the Glucoside surfactant family was highlighted with the most versatile efficiency for C10 and C12 materials. Heptyl Glucoside, used in formulation as a non-foaming bio-based solubilizer, demonstrated lower performance than the glucosides with longer fatty chain length, but its performance far exceeds that of Polysorbate-20, used for a similar purpose as it can be also seen on the photos of the film after cleansing in figure 4.

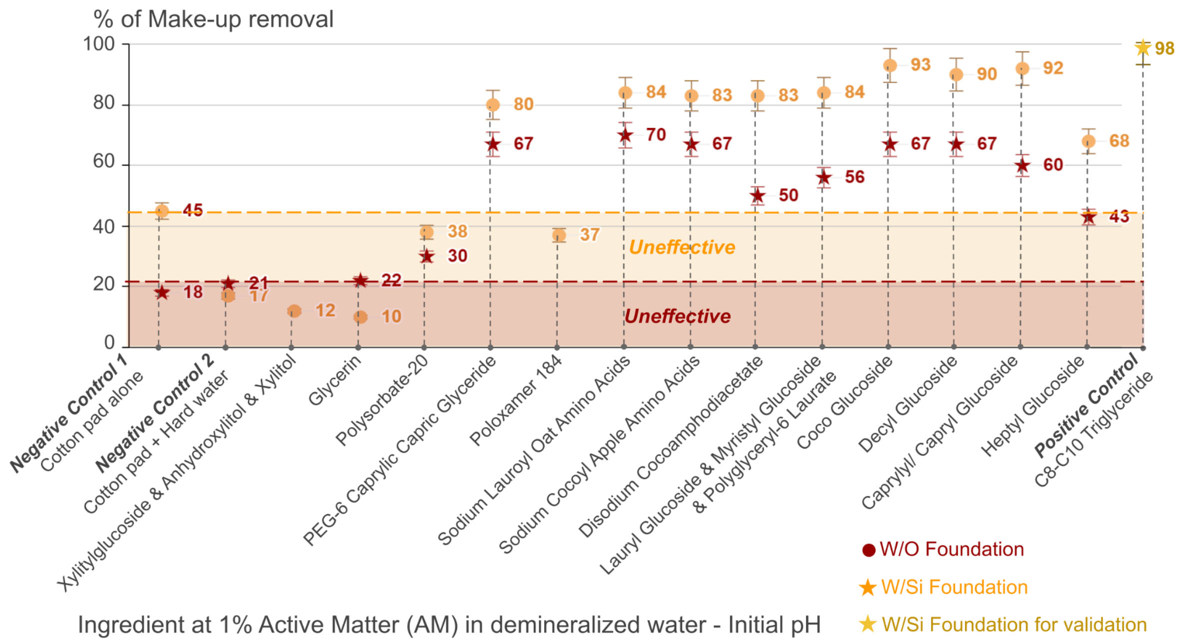


Figure 3. Cleansing performance of Ingredients tested alone

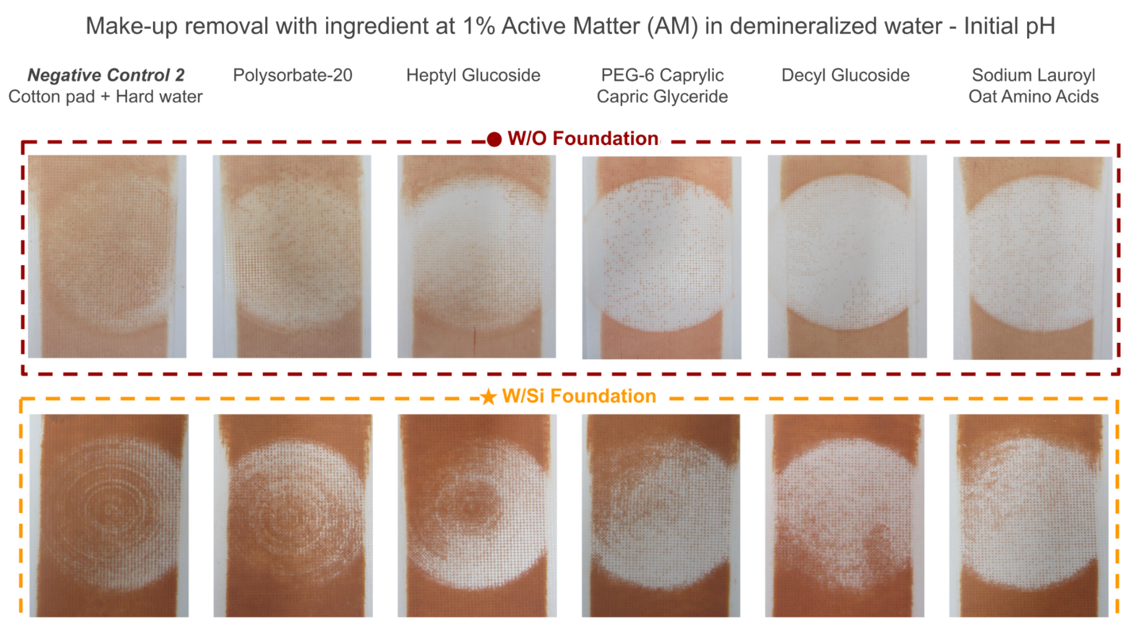


Figure 4. Photos of films after cleansing with ingredients tested alone

Results obtained on micellar water benchmarks (Figure 5), based on a previously evaluated surfactant, confirmed the consistency of the responses and the ability of the method to evaluate finished formulations. Micellar benchmarks had the same reaction pattern than their respective surfactants: good performance on both foundations for benchmark 1, as it was the case for PEG-6 Caprylic Capric Triglyceride and lower efficiency on W/Si foundation for benchmark 2, as it was the case for Disodium Cocoamphodiacetate. At the same time, other ingredients seemed to impact the results in a positive or a negative manner, even if it was not possible to compare results coming from different concentrations.

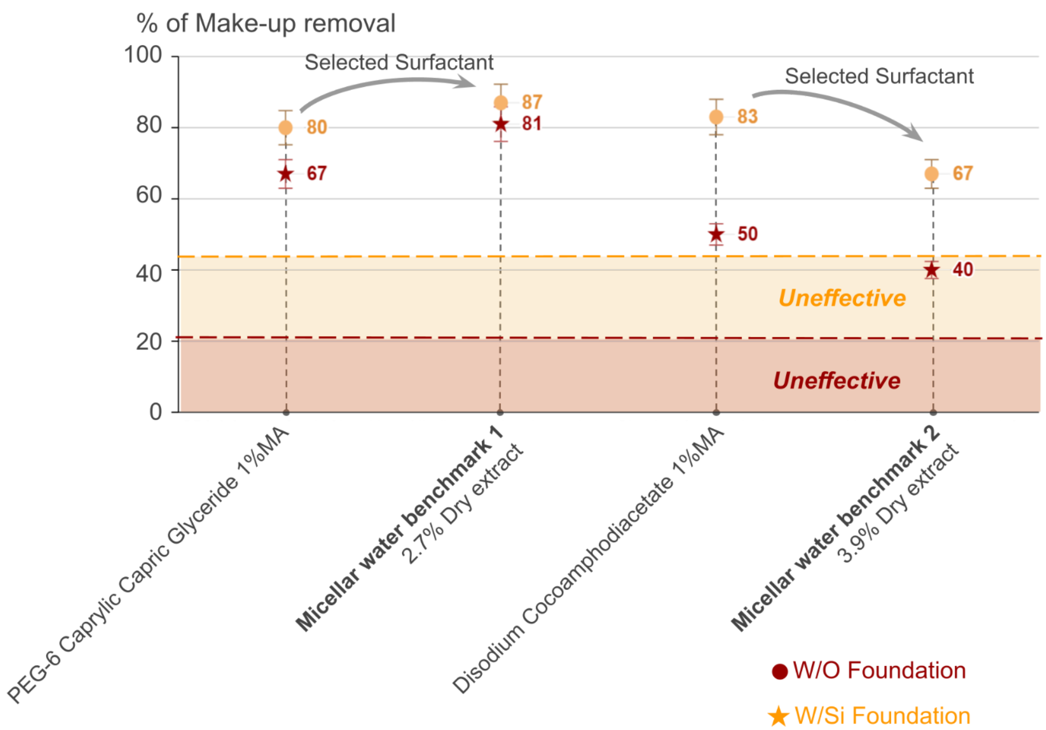


Figure 5. Cleansing performance of micellar water benchmarks

When combining some ingredients, previously tested alone (Figure 6), the influence of an optimized combination of ingredients was emphasized. Glycerin added to a surfactant with good and versatile cleansing performance, Decyl Glucoside or Sodium Lauroyl OAT Amino Acids, had no decisive impact. However, it significantly decreased make-up removal in combination with Heptyl Glucoside. These observations are consistent with a previous publication showing the effect of glycerol on the increase in CMC of sodium dodecyl sulfate as a function of its concentration, attributed to a reduction in solvent polarity that counteracts micellization [3].

Looking at the ternary combinations, both containing Sodium Lauroyl OAT Amino Acids and glycerin, the result of the association with Heptyl Glucoside could have been expected in comparison with the results of Heptyl Glucoside alone. However, the reduction in performance in combination with Decyl Glucoside was completely unpredictable. These results did not demonstrate the interest of combination of surfactants to increase cleansing efficiency, despite double active matter content.

Taken altogether, the trials demonstrated that the Water-in-Silicone foundation was the hardest to remove, irrespective of the cleanser's composition.

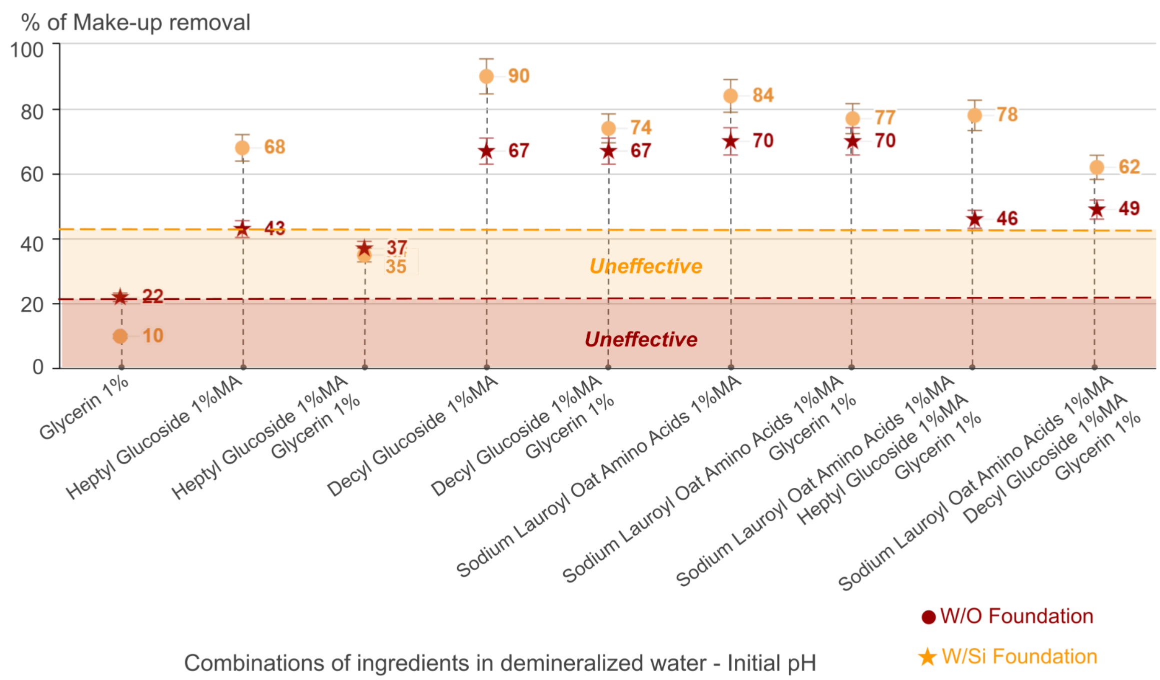


Figure 6. Cleansing performance of Ingredient combinations

Discussion.

The method developed benefits from conditions close to the actual routine of micellar waters: evaluation of the ability to eliminate different make-up formulations, according to the targeted claims, and ability to distinguish materials at concentrations similar to those typically used in micellar waters. If the habits refer to the CMC value of the surfactant to select effective cleaning materials at low dose, some differences could be highlighted in the ranking of performance compared to the practical evaluation on makeup removal. As a first example, looking at their respective CMC values [4], Cocamidopropyl betaine (CAPB; CMC = 23.7 mg/L) should have a better performance than Disodium Cocoamphodiacetate (CMC =36.5 mg/L AM), while CAPB has not been more effective than water alone in removing foundations. Another example was seen in the amino acids surfactant family: Sodium lauroyl sarcosinate (CMC =2.9 g of commercial product/L evaluated in house using Wilhelmy plate method; 30% AM) should have similar performance than Sodium Lauroyl Oat Amino Acids (CMC =2.2 g of commercial product/L evaluated in house using Wilhelmy plate method; 30 % AM) while Sodium lauroyl sarcosinate was ineffective to remove foundation. One explanation for this discrepancy may lie in the fact that CMC mainly addresses lipid soiling (sebum, skin debris) while the film of foundation contains components of other natures such as pigments layers [5] or anti-transfer polymeric film, that are not all hydrophobic materials and represent an additional difficulty for cleaning. Wetting capacity was also widely cited as a critical parameter, additional to CMC, for surfactant cleaning performance [6]. Again, some differences could be highlighted in the ranking of performance compared to the practical evaluation on makeup removal. As a counter-example, in addition to discrepancy with CMC values, Sodium lauroyl sarcosinate has stronger wetting properties than Lauroyl Oat Amino Acids: wetting time of 25 seconds compared to 46 seconds for Lauroyl Oat Amino Acids (measure of the time when standard cotton discs dropped onto a surfactant solution at 0.1% AM are fully wetted and start to skink; ISO 8022). Taken together, these examples highlighted the interest of a global test, close to conditions of use.

Moreover, this work highlighted the interest not only to select an efficient cleansing surfactant but to study carefully the combinations with other ingredients to optimize the make-up removal performance. Considering all the results, the method reproducibility was good with a maximum standard deviation of 6 %.

Conclusion.

The *in vitro* test based on colorimetric measurements after mechanical cleansing was revealed as a simple and reproducible tool to evaluate the effectiveness of the removal of makeup from surfactant solutions, at a concentration level similar to those used in micellar waters. It was also demonstrated that the method was suitable for studying the influence of ingredient combinations to optimize micellar water formulations. To date, only the clear solution form has been evaluated and an interesting prospect will be to question the suitability of the method for screening other water-based formulations: cream-gel and emulsions.

Conflict of Interest Statement.

Authors are Seppic employees. Authors have no other conflict of interest to declare.

References.

1. Rolls, E. (2020). Clean Chemistry–The Science Behind Cleansing Products. Discovering Cosmetic Science, 19.
2. Qu D (2004) Quantifying Cleansing Efficacy of Facial Cleansers Using Objective Measurements. Poster presented at 23 RD IFSCC, Orlando, USA.
3. Khan H, Seddon, JM, Lawa RV, Brooks N, Robles E, Cabral JT, Ces O (2019) Effect of glycerol with sodium chloride on the Krafft point of sodium dodecyl sulfate using surface tension. Journal of Colloid and Interface Science 538; 7: 75-82.
4. Shoaib A, Fuller J (2002) Household & Personal Products Industry.
5. Free, M. L., & Zhu, Y. (2022). The Use of Surfactants in Enhanced Particle Removal During Cleaning. In Surfactants in Precision Cleaning: 125-159. Elsevier..
6. Noh H, Kang T, Ryu JS, Kim SY. Oh S-G (20169) Synergy effect for performance of anionic SDS/ADS mixtures with amphoteric and nonionic surfactants.J. of Korean Oil Chemists' Soc. 33; 3: 449~45.