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## Advances in shampoo formulation: synergism of anionic/cationic/zwitterionic surfactant ternary system

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### Article info.

### ABSTRACT

#### Key Words:

Synergy, Anionic, Cationic, Zwitterionic, Surfactant, Mixed micelle



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*There is a rule among cosmetic formulators of not mixing an anionic surfactant with a cationic surfactant in the same formulation, especially if it's a clear product, since this interaction will result in the appearance of turbidity (precipitation). Nevertheless, vast reports show not only the possible but also synergistic combination of surfactants with opposed charge, conferring unique properties to the final product. The aim of this study is to evaluate the use of a co-surfactant as a novel tool for maintaining high levels of both cationic and anionic surfactants mixed in the same product, without precipitation. Not only we found this possible at certain rates, but also attributes of the system such as viscosity, detergency and foam stability, were improved.*

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## I. Introduction

The formulation of a 2-in-1 shampoo that efficiently works as a cleaner as well as a conditioner has been one of the holy grails in the cosmetic industry. Initially, conditioning agents in shampoos were oils that deposited randomly over the hair surface, in order to reduce the system entropy. Cationic polymers were introduced later to aid in the deposition of oils, through several mechanisms, like coacervation and ionic interactions with hydrophilic groups present in hair proteins. In the general practice, the

introduction of a cationic surfactant in a shampoo is thermodynamically restricted due to the formation of neutral complexes with anionic surfactants in the form of precipitates. Kume et al. (2008) reviewed the extensive scientific literature that exists about the interaction of oppositely charged surfactants. In one of the reports reviewed, Sun et al. (2011) showed that equimolar mixtures of sodium dodecyl sulfate (SDS) and dodecylammonium chloride (DDAC) form stoichiometric complexes that may or not coprecipitate, while the excess of one or the other component may lead to the formation of mixed micelles. It has been shown that the phase behaviors of cationic/anionic surfactant mixtures strongly depend on the molar ratio, the actual concentrations of the individual surfactants, the relative number of alkyl chains per surfactant, and the temperature, resulting in a rich array of aggregates (Sohrabi et al., 2008). While most of the studies focus only in a cationic/anionic binary system, Shiau et al. (1994) studied the influence of the addition of a nonionic surfactant to this system. The addition of a nonionic surfactant affects the precipitation behavior of the mixture, by lowering its critical micelle concentration, enhancing mixed micellization. Moreover, the presence of both cationic and anionic surfactants is of great interest in the cosmetic field (like in 2-in-1 shampoos) to produce a product that efficiently cleans and conditions. Recent attempts include the inclusion of a quaternized polymer (Chan et al., 2017), the use of long chain esters of fatty acids (Dierker et al., 2014), and the in-situ production of a gel network (Simone et al., 2015). Our study aims to investigate the effect of the addition of a zwitterionic surfactant to the cationic/anionic surfactant binary system, which at the isoelectric point bares both a positive and a negative charge simultaneously.

## II. Materials and Methods

**Chemicals:** The following surfactants were obtained from a local distributor of Galaxy Surfactants: Cetrimonium chloride (Quartamin 60W30, 30% active matter), Cocamidopropyl betaine (Betadet HR, 30% active matter) and Sodium laureth sulfate (Emal 227E, 27% active matter). The surfactants were used without further purification.

**Preparation of mixed surfactant solutions:** Tested samples were prepared by combining variable amounts of Sodium laureth sulfate (SLES), Cocamidopropyl betaine (CAPB) and Cetrimonium chloride (CTC). All samples were prepared in deionized double distilled water, and equilibrated at 25°C in a water thermostat. Recordings were performed within the first day of sample preparation.

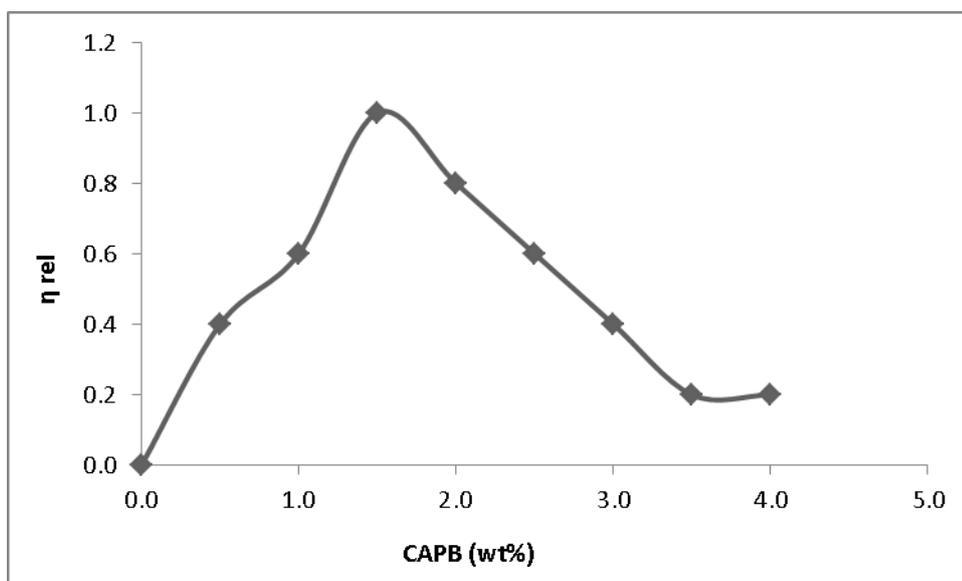
**Methods:** Viscosity measurements were carried out on an Ubbelohde suspended level capillary viscometer with appropriate thermostating ( $\pm 0.1^\circ\text{C}$ ). The cloud point is determined visually by noting the temperature at which the continuously heated solution suddenly became turbid. Heating was regulated to about 1 °C per min around the cloud point. Oil solubilization capacity was determined by a turbidimetric method in which samples of hexane plus surfactant solution were tumbled for 72 hours at 21°C, and then measured visually with a Brinkmann PC 800 probe colorimeter. Foam height was evaluated by the Ross-Miles method at 50 °C, by measuring foam volumes at 30 s and 10 min. Foam stability was determined by comparing the foam volumes after 10 min and 30 s in the Ross-Miles apparatus.

## III. Results and Discussion

### Viscosity

When SLES and CTC are mixed at a similar concentration (1 wt%), precipitation occurs as a result of the formation of a SLES-CTC complex, due to the attraction between oppositely charged head groups and the hydrophobic tails of the two surfactants. The interaction between both ionic groups starts as a binding process, followed by a charge neutralization which usually leads to the formation of a highly hydrophobic mixed surfactant, that behaves as a non-ionic surfactant. The viscosity of this solution is similar to that of water, correlating with the loss of interfacial activity of the mixture. On the contrary, when CAPB is introduced in the mixture before the CTC, instead of precipitation, there is an increase in

viscosity which continues as the level of CAPB increases, while maintaining a 1 wt% fixed concentration of SLES and CTC (Figure 01).

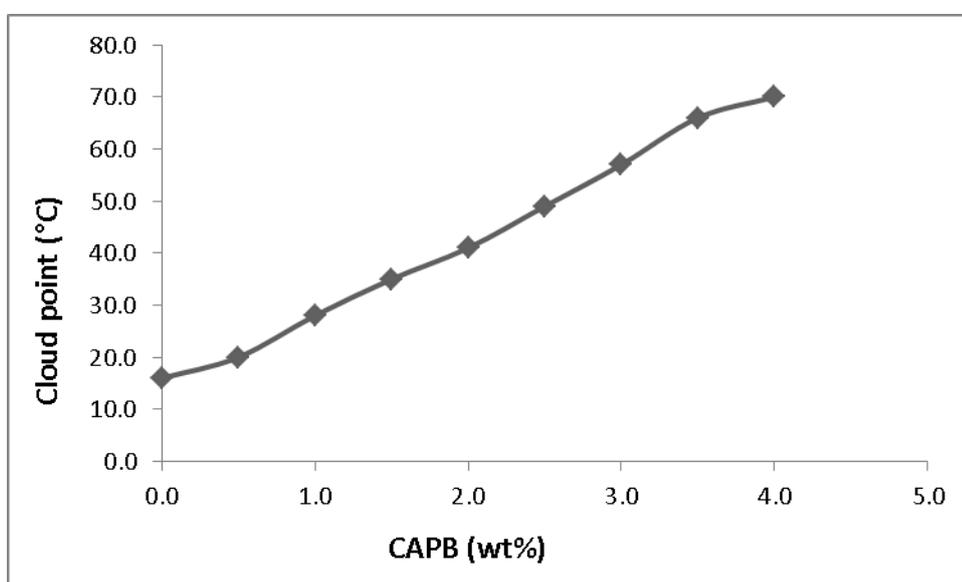


**Figure 01.** Plot of relative viscosity of the mixture SLES-CTC (1:1 wt%) as a function of CAPB added (wt%) at 25°C.

This increase is explained by the expansion of micelles due to partial neutralization of the micelle charge by the added surfactant (Koehler et al., 2000). But after a peak in viscosity at 1.5 wt% of CAPB, a gradual descent is followed with every new addition of surfactant. At this point, micelles become less polar with every CAPB increase, resulting in chain contraction and relative viscosity decrease.

### Cloud point

The solution of SLES-CTC was turbid when both surfactants were mixed at a 1:1 ratio, but became clear after additions of CAPB (Figure 02).

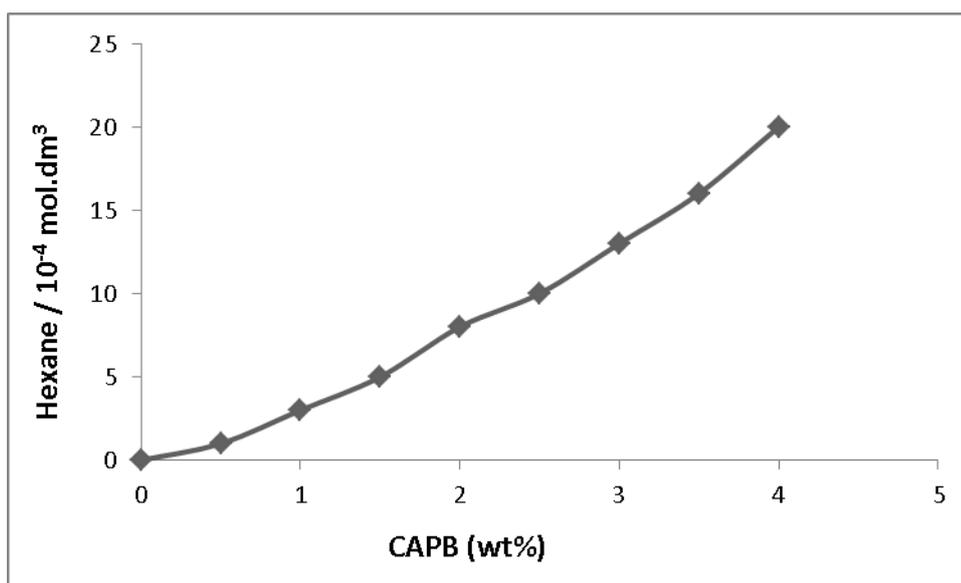


**Figure 02.** Cloud point of the mixture SLES-CTC (1:1wt%) as a function of CAPB added (wt%).

In general, it is easy for the SLES-CTC ion pairs to be precipitated from solution. However, the ion pairs have been "solubilized" by forming mixed micelles with CAPB in the present case, resulting in an increase of the cloud point, similarly to the observed linear increase in the clouding temperature of Triton X-100 on addition of small amounts of Sodium dodecyl sulfate (Valaulikar, 1985).

### Oil solubilization

When mixing SLES with CAPB prior to the addition of CTC, intramolecular complexes are formed in the mixed micelles by the electrostatic interaction of oppositely charged head groups of CAPB and SLES, allowing for a significant micellar growth and sphere-rod transition, resulting in the appearance of viscoelastic behavior (Iwasaki et al., 1990). When CTC is added to the mixture, the systems show a linear increase in their capacity to solubilize hexane (increased clarity) regardless of their viscosity.



**Figure 03.** Solubilized amount of hexane against CAPB added (wt%) to the SLES-CTC (1:1 wt%) system.

This has been attributed to more stable micelles solutions which have a lower concentration of sub-micellar aggregates, which are usually present in the mixed micelles of only SLES and CAPB.

**Table 01.** Foaming properties for surfactant mixtures of SLES-CTC (1:1 wt%) at different additions of CAPB (wt%).

CAPB	SLES	CTC	Volume of foam (mL)		$V_{10 \text{ min}} / V_{30 \text{ s}}$
			After 30 s	After 10 min	
0.5	1.0	1.0	440	415	0.94
1.0	1.0	1.0	450	430	0.96
1.5	1.0	1.0	530	515	0.97
2.0	1.0	1.0	475	450	0.95
2.5	1.0	1.0	460	445	0.97
3.0	1.0	1.0	450	430	0.96
3.5	1.0	1.0	440	425	0.97
4.0	1.0	1.0	430	410	0.95

## Foaming

The foaming ability is defined as the foam volume at 30 s and the foam stability is expressed by the ratio of the foam volumes after 10 min and 30 s (Wang et al., 2009). From the results presented in Table 01, three points can be underlined in the weight ratio range studied. First, all the mixed surfactants where CAPB was added have greater foaming abilities and foam stabilities than that of only SLES and CTC. Second, the increase in foaming ability with the addition of CAPB has a peak (at 1.5 wt% addition), after which a decrease in foaming ability is noted. It has been also shown that foaming stability follows a similar pattern as foaming ability.

## IV. Conclusion

A zwitterionic surfactant can make possible to combine a cationic and an anionic surfactant without precipitation. This ternary mixture also showed many unique properties like favoring the formation of larger mixed micelles that can enhance detergency, improving viscoelastic behavior of films which produce more stable foam, and are also more tightly packed with a more hydrophobic interior, reflected in the more rapid partitioning or solubilization of oily soils. This properties can be very useful when used properly, such as in the formulation of a 2-in-1 shampoo.

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## VI. Glossary

### Cetrimonium chloride

Chemical name : hexadecyl-trimethylammonium chloride  
Commercial name : Quartamin 60W30  
Chemical formula : C<sub>19</sub>H<sub>42</sub>ClN

### Cocamidopropyl betaine

Chemical name : {[3-(Dodecanoylamino)propyl](dimethyl)ammonio}acetate  
Commercial name : Betadet HR  
Chemical formula : C<sub>19</sub>H<sub>38</sub>N<sub>2</sub>O<sub>3</sub>

### Sodium laureth sulfate

Chemical name : α-sulfo-ω-(dodecyloxy)-poly(oxyethane-1,2-diyl), sodium salt  
Commercial name : Emal 227E  
Chemical formula : CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>OSO<sub>3</sub>Na

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### APA (American Psychological Association)

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### MLA (Modern Language Association)

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### Chicago and or Turabian

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