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# SUSTAINABILITY

# Sulphonated Methyl Ester a promising surfactant for detergency in hard water conditions

KEYWORDS: Surfactants, detergency, Krafft temperature, foam, surfactant mixtures.

ABSTRACT: We report results on the physical phase behavior of sulphonated methyl esters in different water hardness conditions. We also compare its foam performance against a number of other surfactants in correlation with their Krafft points at different levels of water hardness. Whilst SME is slightly behind in terms of solubility in deionized water it gains ground as the level of water hardness goes up and is significantly better when certain mixtures are used. The best results are observed at 1:1 ratio for Krafft point as well as for foam performance. The results suggests potential applications for this relatively new palm oil derived surfactants, namely in regions with high levels of water hardness.

## INTRODUCTION

Sulphonated methyl esters (SME) have been identified quite some years back as a green alternative to the current surfactant leader of the Home Care market - the linear sodium alkyl benzene sulphonate (LAS), as well as alpha olefin sulphonates (AOS), primary alcohol sulphate (PAS) and alcohol ethoxylated sulphate (AES) which are predominantly petrol derived (1, 6). With the increased awareness of leading Fast Moving Consumer Goods (FMCG) companies with regard to preserving the scarce planet resources for the future generations, i.e. doing business in a sustainable manner, the demand for renewable and highly performing substitutions of the current petrol based surfactants has never been stronger. The sulphonated methyl esters are also non-toxic, very mild and easily bio-degradable (7, 10). One drawback in the last couple of years has been the drop in the crude oil price, due to a complex set of reasons, which had a negative impact on the penetration of SME in the Home Care market. Irrespective of the cost advantage the LAS might have at the moment, the surfactants for detergency are also selected and graded on their performance in, sometimes, challenging conditions (11, 12). In some parts of the world, for example India or China, it is not unheard of water hardness to gravitate towards 1500 ppm Ca/Mg ions (North India regions) (13). The challenge for most surfactants in such conditions is to stay "alive"/functional, i.e. not to get precipitated at

which point they lose their surface activity and no longer provide detergency benefits (14, 16). In the current article we will demonstrate the superiority of SME with regard to its functionality in hard water conditions over LAS. Kraft point measurements as well as foam formation and foam stability will be reported in order to estimate the robustness of its performance. Standard, widely accepted, methods have been utilised in order to make it easier for anyone to check what we state here.

The SME used in this study was produced in our plant (KLK Oleomas Sdn Bhd) in Westport and comprises a mixture of SME molecules with chain lengths of 12, 14, 16 and 18 carbon atoms. The composition of C16/C18 seriously favours the performance of the surfactant when it comes to oily soil removal. In this respect even at mild conditions the SME demonstrates superiority to LAS.

## Materials and methods
### Materials
The $\alpha$-SME used for the study were commercial mixtures of $C_{12}$ to $C_{14}$ and $C_{16}$ to $C_{18}$ surfactants, where $C_{12}/C_{14}$ was abbreviated as C1214 SME and $C_{16}/C_{18}$ mixture was abbreviated as C1618 SME. The $\alpha$-SME are products of KLK Oleomas (Malaysia). The non-ionic fatty alcohol ethoxylate, $AEO_7$ ($C_{12}$-$C_{14}$,7 EO) was produced by KOLB (Switzerland), part of KLK Oleo Group of Companies. Linear alkylbenzene sulfonate (LAS) and sodium laureth sulfate (SLES) were purchased from KLK Tensachem S.A. (Belgium) also part of KLK Oleo Group of Companies also. These samples were used in all experiments without any further purification. Milli-Q water was used for the preparation of aqueous solutions. Calcium chloride, $CaCl_2$ and magnesium chloride, $MgCl_2$ used to prepare hard water solutions were purchased from Fisher Scientific and used as is.

### Determination of Krafft Temperature, $T_k$
In this study visual observation was used to determine the $T_k$ of surfactants (17, 18). Stock sample solution with a concentration of 0.2 wt % active was prepared by dissolving the respective surfactant in distilled water or water at the desired water hardness, followed by gentle agitation and mild heating until complete dissolution was achieved. The solutions were cooled overnight to induce precipitation, and reach equilibrium prior the $T_k$ determination. The $T_k$ was determined by heating 10 ml of surfactant solution in a sealed tube until a clear solution

was obtained and the reproducibility of temperature reading of three measurement was ± 0.5 °C. $T_k$ of SME-based binary surfactants at various ratio were determined.

### Foaming Measurements

Bartsch method (hand shaking) was used to determine the foaming performance and foam stability of SME surfactants. The experiments were conducted at 20 °C and 30 °C, respectively, at 0 ppm, 100 ppm and 400 ppm water hardness and the active content for all surfactants was fixed at 0.2 wt %. A fixed amount (40 ml) of surfactant solution was poured into a graduated cylinder. A stopper was placed onto the cylinder and it was shaken for a fixed number of times. The foam height was then measured. The foam stability was measured 5 minutes after the initial foam height. The foam stability is calculated using equation 1

$$Foam\ Stability\ (\%) = \frac{Initial\ Foam\ Height,\ t=0}{Foam\ Height\ at\ t=5\ mins} \times 100$$

All the binary surfactant mixtures were prepared at 1:1 ratio.

## RESULTS AND DISCUSSIONS

### Krafft point measurement

The Krafft point, $T_k$, is an important characteristics of any ionic surfactant as it is a measure for its ability to form micelles at certain temperature [19]. Should this temperature is too high that makes the surfactant difficult to work with as its basic surface active properties would be compromised due to its precipitation state below this temperature [20]. The main source of inconvenience comes from the ions responsible for the hard water conditions, namely $Ca^{2+}$ and $Mg^{2+}$. Upon interaction with negatively charged surface active ions they could form insoluble doublets that no longer could effectively participate in either the process of detergency or foaming. Therefore any surfactant that manifests tolerance and robustness towards hard water conditions would be highly preferable.

| Surfactant | DI water (°C) | 100 ppm (°C) | 400 ppm (°C) |
|---|---|---|---|
| SME C1214 | 0.0 | 11.0 | 12.5 |
| SME C1618 | 18.5 | 25.5 | 35.5 |
| LAS | 0.0 | 68.0 | ND |
| SLES | 0.0 | 0.0 | 0.0 |
| AGS 124 | 0.0 | 0.0 | 0.0 |

*ND – Not dissolvable at 100 °C

**Table 1.** $T_k$ of surfactants.

For homologue surfactants it is the hydrophobic chain length that strongly influences the $T_k$ of surfactants. The shorter chain length of α-SME (SME 1214) leads to lower $T_k$ values in all water hardness conditions compared to that of the longer chain homologue (SME C1618). An increase in the chain length of the hydrophobic portion reduces its water solubility thus giving rise to an aggregation trend and unwillingness to dissolve unless a specific temperature threshold has been achieved. The reduced solubility of surfactants with chain length C16 and above is well known in the literature and SME is not exception in this [21].

Despite the fact that α-SME is less soluble in water compared with other surfactants, it manifests better water hardness tolerance compared to an anionic surfactant such as



**Figure 1.** A simplified molecular structure of α-SME, R stand for the alkyl chain.
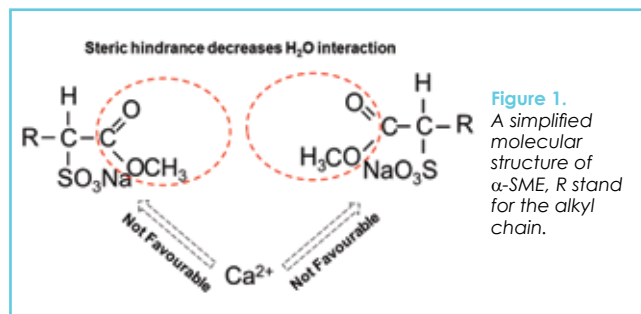
LAS [15]. The $T_k$ of LAS increases steeply and LAS forms insoluble precipitate at high water hardness, above 200 ppm (20 French Hardness), which is impossible to dissolve even in boiling water conditions. In general the majority of anionic surfactants are very sensitive to the presence of hard water ions, $Ca^{2+}$ and $Mg^{2+}$ respectively. The almost irreversible binding of the aforementioned ions render the surfactant doublets highly hydrophobic leading to significant precipitation. Unless some modification to the surfactant molecules have been done, e.g. ethoxylation of primary sulphate alcohols (AES) both, their hard water tolerance and effectiveness in detergency, would be challenged. The SME has some specific structure characteristic that allows for the molecule to be relatively insensitive towards the presence of such multivalent ions. The presence of ester group near the sulphonic group that is linked to the alpha carbon atom, probably sterically hinders the ability of $Ca^{2+}$ and $Mg^{2+}$ to electrostatically bind to the surfactant anion, see Figure 1. In Figure 2, data on $T_k$ for different mixtures of surfactants are presented. The first thing worthwhile noting is the low hard water tolerance of LAS (Figure 2a). Even at 100 ppm levels the LAS molecules would need temperatures of about 70 °C in order to perform in a solution. At 200 ppm however even boiling water would not dissolve the formed precipitate. The SME behaviour is rather unusual for anionic surfactant as its response to the increase of hard water levels is pretty flat, going from 18 up to 30 for the pure SME C1618 surfactant. Even at 500 ppm the surfactant is usable as long as the temperature is above 30 °C. Things get better should we consider mixtures of SME C1618 and LAS. It is a remarkable synergistic effect that is being observed at the 1:1 ratio where the Tk drops to 12 °C at 0 ppm and goes as high as 26 °C at 500 ppm. This is very encouraging as the mixtures can be used even at ambient conditions without reduction in their performance irrespective of the water hardness conditions.

Not surprisingly in Figures 2b and 2d the AES and the non-ionic surfactants did not encounter any negative impact from the hard water conditions. This can be explained with the ethoxylation for the AES as this would affect the manner AES interacts with the multivalent counterions resulting in high tolerance [22]. The non-ionic by their nature are not expected to be affected [23]. The interesting data for the reader is the observed further reduction for the 1:1 mixture between SME and SLES, which is significantly better than the mixture between LAS and SME, cf. Figure 2a. The non-ionic is doing similar job giving the SME extra space for detergency, i.e. lower temperature at high water hardness. Even the shorter chain homologue of SME, cf. Figure 2c boosts its water hardness tolerance although it is not as efficient as the SLES and non-ionics at 1:1 ratio. A schematic presentation of the hypothetical configuration for the surfactant mixtures can
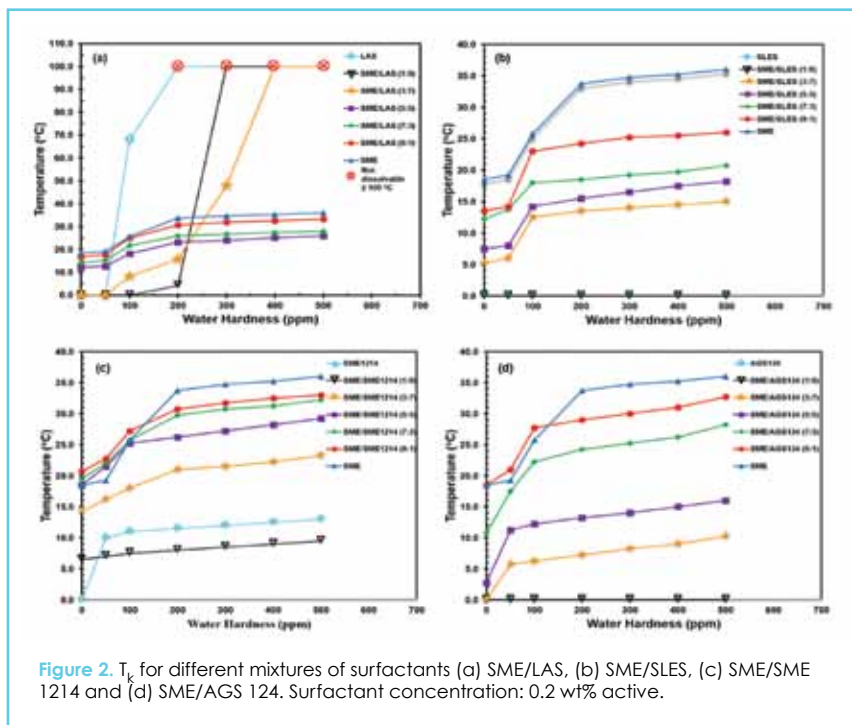
**Figure 2.** $T_k$ for different mixtures of surfactants (a) SME/LAS, (b) SME/SLES, (c) SME/SME 1214 and (d) SME/AGS 124. Surfactant concentration: 0.2 wt% active.

α-SME (SME C1618) is greater than its shorter chain counterpart (SME C1214). This is due to the longer chain length in the same homologue series, which results in lower cmc (8) and more rapid lowering of surface tension as a result of the micelles excess, leading to better foaming performance for SME C1618. The difference in the cmc between SME C1618 SME and its shorter chain counterparts SME C12C14 could reach orders of magnitude, e.g. C12 CMC is 14.1 mM whilst C18 CMC is 0.32 mM (25). As discussed before (see the Krafft point results and discussion) the increase of water hardness and temperature (Figure 4b) has less effect on α-SME, showing its excellent water hardness tolerance.

The foam stability of surfactants as a function of water hardness is shown in Figures 4c-d. All surfactants, except SME C1214 show very good foam stability for 5 minutes after the initial foam height had been recorded. Foam stability for SME C1214 in deionized water is poorer due to its higher CMC as a result of its shorter hydrocarbon chain. Longer chain length surfactants (C16/C18) usually manifest higher interfacial elasticity thus contributing to slower film drainage and improved mechanical strength of the liquid lamellae formed between air bubbles on top of their lower CMC. The stability of SME C1214 however, significantly improves at high water hardness condition. In general, addition of electrolyte enhances adsorption of surfactants and reduces their CMC. Hence, at higher electrolyte level (water hardness) both the surfactant adsorption and the number of micelles as a result of the reduction on CMC are increased. Both effects would lead to improved foam stability. This agrees with reports in the literature [8] that in hard water shorter anionic compounds manifest improved foaming.

be seen in Figure 3. The efficacy of the $T_k$ lowering by the co-surfactant is a function of several parameters, e.g. length of the hydrocarbon chain, the bulkiness and charge of the polar co-surfactant head, the relative ratio, etc. The ability of the co-surfactant molecules to accommodate themselves in between the SME molecules loosens the packing density thus reducing the ability of divalent metal counter-ions to strongly interact with the surfactants. In absence of co-surfactants that would lead to the formation of crystalline phases and is one of the reasons for its poorer water solubility at low temperatures. This behaviour is also behind the difficulties for dissolving SME in water above 30 wt% as above this concentration the system probably undergoes a hexagonal – to – cubic phase transition. All in all, SME has manifested a flat response to the water hardness conditions whence its ability to handle challenging water hardness conditions.
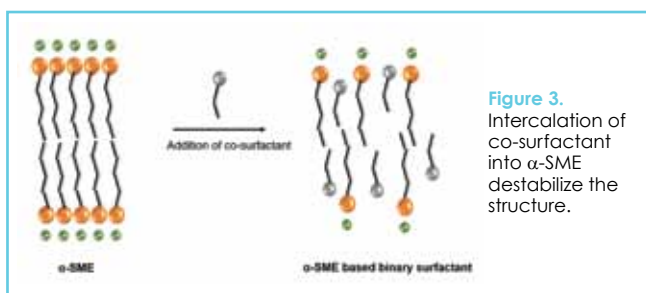


**Figure 3.** Intercalation of co-surfactant into α-SME destabilize the structure.

### Foaming performance of single surfactants
The initial foam height of surfactants as a function of water hardness is shown in Figure 4, the foam tests were conducted at two temperatures, 20 °C and 30 °C to ensure that we have captured the performance on both sides of the Krafft point of the respective mixture. Not surprisingly, *cf*. Figure 4a, SLES gives best foamability while α-SME shows foamability comparable to LAS. AGS 124 being a non-ionic surfactant, is a poor foamer, which is typical for this type of surfactants (24). Foamability of longer chain length

### Foaming performance for mixtures of surfactants
A single surfactant, however efficient, could hardly ensure the desired characteristics, especially when challenging conditions are considered. Most often than not, the applications require a mixture of surfactants that would possess synergistic behaviour aimed at tackling challenging conditions. In what follows we have tried to explore the effect of mixtures of SME with different widely used surfactants at the same hardness water levels as for the pure surfactants. Similar to the Krafft point determination both mixtures of LAS and SME C1618 and SLES and SME C1618 show good synergism, see Figures 5a-b. The foamability of LAS on its own suffers when the water hardness reaches 400 ppm. The combination however, shows good performance even at these hard water conditions. This is re-iterating the positive correlation between the Krafft point reduction and the foamability for the mixture.

In Figures 5c and 5d results on foamability of mixtures of SME C1618 and SLES are shown as well as the individual surfactant's performance. The results clearly demonstrate the foamability of SLES even in the presence of high level
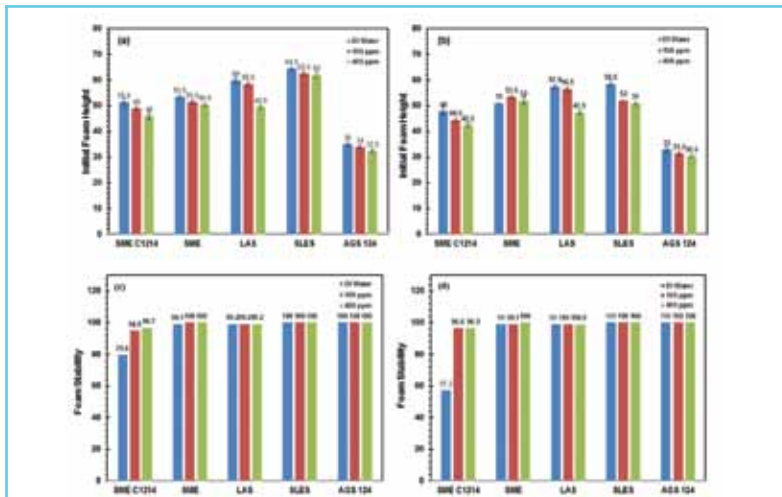
**Figure 4.** Variation of the initial foam height as function of the water hardness (a) 20 °C and (b) 30 °C. Foam stability as function of the water hardness (c) 20 °C and (d) 30 °C Surfactant concentration: 0.2 wt% active.
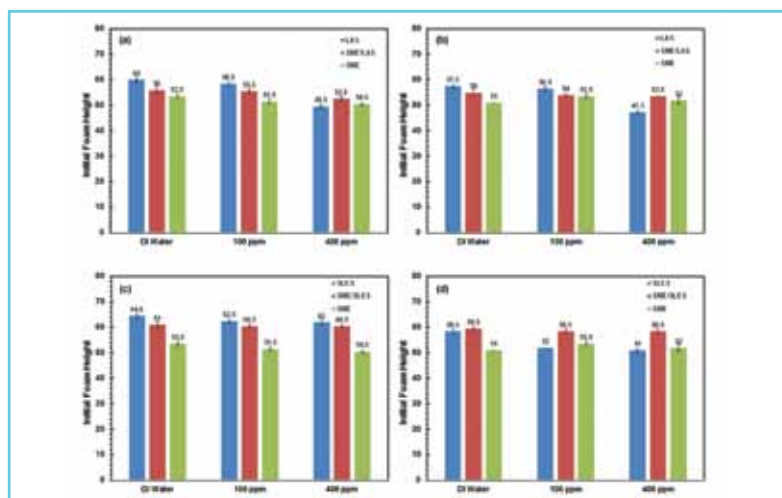


**Figure 5.** Variation of the initial foam height as function of the water hardness for LAS, SME C1618 and LAS/SME C1618 (a) 20 °C, (b) 30 °C and variation of the initial foam height as function of the water hardness for SLES, SME C1618 and SLES/SME C1618 (c) 20 °C, (d) 30 °C. Surfactant concentration: 0.2 wt% active.
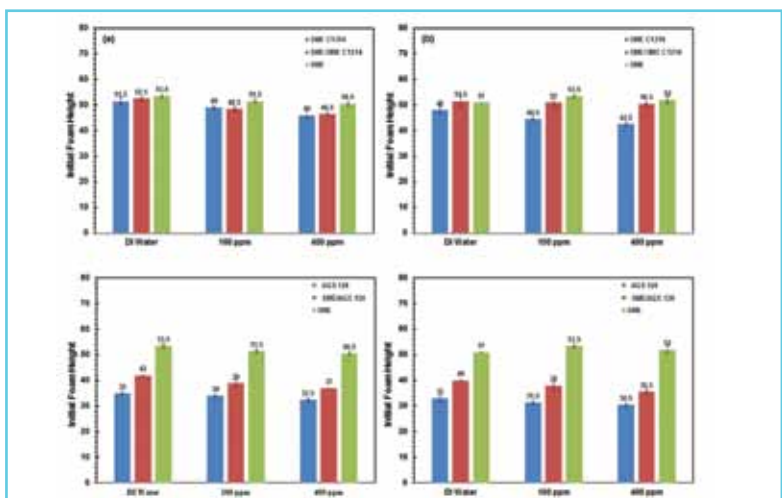


**Figure 6.** Variation of the initial foam height as function of the water hardness for SME C1214, SME C1618 and SME C1214/SME C1618 (a) 20 °C, (b) 30 °C and variation of the initial foam height as function of water hardness for AGS 124, SME C1618 and AGS 124/SME C1618 (c) 20 °C, (d) 30 °C. Surfactant concentration: 0.2 wt% active.

of hard water ions, due to the presence of ethoxylated part, but more importantly they demonstrate the significant improvement in foamability of the mixture compared to the SME on its own. This effect is important as the foam is a strong cue for surfactants' performance when it comes to fabric cleaning irrespective of the lack of evidence that proves this point (26). Given that SME is a strong performer on a broad range of oily stains compared with SLES on its own, the improved foamability would benefit end consumers for whom the foam is of paramount importance.

The shorter chain version of SME, namely C1214 comes short to produce the same foam level as SME C1618 but as it has been discussed this is mainly due to the higher CMC of the former mix. The blending of C1214 and C1618 results in a better performing surfactant mix with regard to foam compared with C1214 on its own. This is especially true at higher temperature, see Figures 6 a,b.

As it was discussed before non-ionic surfactants on their own do not make good foaming agents. This is mainly stemming from the way they come to stabilise the bubbles and their kinetics. The combination of SME C1618 with non-ionic surfactant AGS 124 improves the foamability of the mixture. This could be used in formulations in which the non-ionic surfactant is the main cleaning agent (e.g. hard surface cleaning) and a foam boost is required without compromising the cleaning performance.

**CONCLUSION**

SME C1618 is a relatively new anionic surfactant based on renewable palm oil stock that manifests excellent tolerance towards hard water conditions. This unusual feature makes it preferred surfactant in regions where the level of Ca and Mg ions exceeds 200 ppm. The presence of SME in a mixture with other surfactants has a positive effect on both the foamability of SME and the robustness of the other surfactants with regard to hard water conditions, e.g. LAS. The performance of SME is subject to more studies and in a following manuscript we are going to report on its detergency performance in hard water conditions as well as its mildness with regard to enzymes, second most expensive ingredients (with perfume) in a fabric cleaning formulation (27). The foamability of SME seems also to sustain even at high level of hard water conditions compared with LAS, which is a very important feature for foam-centred end users. More fundamental work is needed to identify the applications where SME would outperform LAS, the main surfactant currently in use for detergency.

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