

Cleaning Ability of Mixed Solutions of Sulfonated Fatty Acid Methyl Esters

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Abstract Here, we present results from a systematic study on cleaning of oily deposits from solid surfaces (porcelain and stainless steel) by solutions of fatty acid sulfonated methyl esters (SME), sodium salts. The zwitterionic dodecyltrimethylammonium oxide (DDAO) has been used as a cosurfactant. As representatives of the vegetable and mineral oils, sunflower seed oil and light mineral oil have been used. The process of oil drop detachment from the solid substrates (roll-up mechanism) has been monitored. In the case of porcelain, excellent cleaning of oil is achieved by mixed solutions of SME and DDAO. In the case of stainless steel, excellent cleaning (superior than that by linear alkylbenzene sulfonate and sodium lauryl ether sulfate) is provided by binary and ternary mixtures of SME, which may contain also DDAO. For the studied systems, the good cleaning correlates neither with the oil/water interfacial tension, nor with the surfactant chainlength and headgroup type. The data imply that governing factors might be the thickness and morphology of admicelle layers formed on the solid/water interface. The results indicate that the SME mixtures represent a promising system for formulations in house-hold detergency, having in mind also

other useful properties of SME, such as biodegradability, skin compatibility, and hard water tolerance.

Keywords Sulfonated methyl esters · Krafft point temperature · Dodecyltrimethylammonium oxide · Oily stain cleaning · Stainless steel · Porcelain

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Introduction

Sulfonated methyl esters (SME) of fatty acids are subject to increasing interest during the last two decades. SME are derived from renewable sources and are considered as a green alternative of petroleum-derived surfactants (Jin et al., 2016; Lim et al., 2016, 2019; Maurad et al., 2017; Siwayanan et al., 2014; Xu et al., 2018). SME are insensitive to the water hardness, unlike the linear alkylbenzene sulfonates (LAS), which are widely used in cleaning formulations (Cohen and Trujillo, 1999; Ivanova et al., 2017; Lim et al., 2016, 2019; Xu et al., 2018). Mixtures of SME and LAS have been shown to improve the LAS solubility in hard water and have been used to achieve significant builder's reduction in detergent formulations (Lim et al., 2019). Foaminess and foam stability are better with SME as compared to LAS (Lim et al., 2016; Tai et al., 2018). Detergency and cleaning by SME and SME + LAS formulations have been found comparable and even better than those with LAS alone (Lim et al., 2019; Maurad et al., 2017; Tai et al., 2018).

Along with the detergency characterization, there is a considerable advance in the physicochemical characterization and theoretical modeling of adsorption and micellization of

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the different SME and their mixtures with other ionic or non-ionic surfactants (Basheva et al., 2019; Danov et al., 2015; Ivanova et al., 2017; Patil et al., 2004; Wang et al., 2019; Wong et al., 2012; Xu et al., 2018).

Recent studies describe direct measurements of the cleaning performance of different SME in specialized tests evaluating the detergency power of powders (Lim et al., 2019; Siwayanan et al., 2014), laundry liquids (Maurad et al., 2017) or dishwashing liquids (Tai et al., 2018). These studies are helpful for industry to select the most suitable surfactants for commercial detergent products. However, the mechanism of soil removal processes has not been investigated using the available methods for characterizing the soil detachment at nano-, micro-, and macro-scales (Cuckston et al., 2019).

In the literature, there are few results about the factors that govern the cleaning performance. Indications that the soil detachment can depend on the surfactant alkyl chainlength (Gambogi et al., 2006; Lim et al., 2016; Siwayanan et al., 2014) and headgroup nature (Mahdi et al., 2015) have been found. The oil/water interfacial tension is also an important factor for oil drop detachment (Phaodee et al., 2018). Another governing factor is expected to be the surface energy of the solid substrate, which significantly depends on the surface type, treatment, aging, and so on. (Hedberg et al., 2014; Kim et al., 2016; Tsujii, 2017).

The detergency action of anionic surfactant solutions could be improved by the addition of zwitterionic cosurfactant, which has been used in various formulations such as shampoos, hand and body washes for foam boosting (Basheva et al., 2000), cleaning aids (Gambogi et al., 2006), and rheological thickeners (Christov et al., 2004). Zwitterionic surfactants have been found to improve also the solubilization capacity of the ionic surfactants (Golemanov et al., 2008). Interactions in mixed solutions of zwitterionic and anionic surfactants have been described by different approaches and synergistic effects have been found (Angarska et al., 2004; Basheva et al., 2019; Danov et al., 2004; Hines et al., 1998). Amine-oxide surfactants are among the most widely used zwitterionics and special attention has been paid to their salt and pH sensitivity (Maeda, 1996; Maeda et al., 1995; Schellmann et al., 2015; Singh et al., 2006). To the best of our knowledge, so far there is no study that relates the surface and bulk properties of SME solutions and of SME + zwitterionic mixtures to their action as detergents.

Our goal in the present article is to investigate the cleaning of oily deposits from solid surfaces by SME solutions and by SME + zwitterionic mixtures. As zwitterionic cosurfactant, dodecyldimethylamine oxide (DDAO) is used. The investigated solid substrates are porcelain and stainless steel, which are typical materials for kitchenware.

As representatives of the vegetable and mineral oils, sunflower seed oil (SFO) and light mineral oil (LMO) have been used. The cleaning efficacy is characterized by direct monitoring of the process of oil drop detachment from the substrates in the investigated surfactant solutions (Davis et al., 2006; Kolev et al., 2003; Kralchevsky et al., 2005; Rowe et al., 2002).

First, the used materials and methods are described. Next, the investigated systems are characterized by contact angles, interfacial tensions, and Krafft temperature of the surfactants. Furthermore, the results from the experiments on oil drop detachment are reported and discussed with respect to the factors, which govern the rather different cleaning performance of surfactants that have very similar chemical nature. We believe the results would be of interest to both industrial researchers developing new formulations and academic scientists investigating the physicochemical mechanisms of detergency.

Materials and Methods

Materials

The used SME (α -sulfo fatty acid methyl ester sulfonates, sodium salts, denoted also α -MES), are products of the Malaysian Palm Oil Board and KLK OLEO. In particular, C12-SME, C14-SME, and C16-SME are SME of the respective fatty acids: lauric, myristic, and palmitic. C1618-SME, represents a mixture of 85 wt% palmitic (C16-SME) and 15 wt% stearic (C18-SME) SME and has a mean molecular weight $M = 376.70 \text{ g mol}^{-1}$ and critical micellization concentration = 0.9 mM. C1618-SME is preferred in applications because of its lower Kraft temperature and better water solubility (Schambil and Schwuger, 1990). The surfactant samples were used as received.

We used also linear alkyl benzene sulfonate, sodium salt (LAS) product of Sigma Aldrich (St. Louis, Missouri, USA); sodium laurylethersulfate with two ethylene oxide groups (SLES) product of KLK OLEO, and N,N-Dimethyldodecylamine N-oxide (DDAO), product of Sigma Aldrich. The transition from the cationic to the zwitterionic form of DDAO occurs near pH = 6 (Maeda et al., 1995; Schellmann et al., 2015).

As inorganic salt additives, we used sodium chloride, NaCl (Honeywell, Offenbach, Germany), and calcium dichloride hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich). To adjust the desired pH of the solutions, HCl or NaOH were used. The solutions were prepared with deionized water from the Elix 3 (Millipore) water purification system.

All experiments were performed with solutions of 0.2 and 0.5 wt% total surfactant concentrations, which are

typical in cleaning applications (Jin et al., 2016; Lim et al., 2019). The solutions were prepared by intensive stirring for 1 to 24 h prior use. The solutions of C14-, C16-, and C1618-SME were heated to 40 °C for a better and faster dissolution. The pH was adjusted after the full surfactant dissolution.

Salt concentration is known to affect significantly the surface and interfacial tension of ionic surfactant solutions (Fainerman and Lucassen-Reynder, 2002; Gurkov et al., 2005; Kralchevsky et al., 1999, Kralchevsky and Danov, 2015). To fix the ionic strength of the studied solutions, NaCl was added at molar concentration that is *ca.* five times higher than the total molar surfactant concentration. Thus, all solutions with 0.5 wt% total surfactant concentration contain 0.365 wt% (≈ 62 mM) NaCl, whereas all solutions with 0.2 wt% total surfactant concentration proportionally contain 0.146 wt% (≈ 25 mM) NaCl.

As model liquid soils, we used SFO and LMO. Food grade sunflower oil was purchased from a local supplier and used after purification by passing through a column filled with the absorbents Silicagel 60 (Fluka, cat. # 60741) and Florisil[®] (60/100 mesh, Supelco, cat. # 20280-U). LMO product of Sigma-Aldrich (cat # 33,077–9) was used as received.

As solid substrates, we used glaze porcelain and stainless steel. Rectangular porcelain plates of size $3 \times 3 \times 0.5$ cm were cut from a white feldspar porcelain dinnerware plates. The plates were cleaned by soaking in ethanol, abundant rinsing with deionized water, and drying at ambient temperature. Stainless steel AISI 304 (Cold rolled, bright annealed, average roughness 0.05–0.1 μm) was used as rectangular flat plates of size $2 \times 2 \times 0.1$ cm. The stainless steel sample plates were cleaned by consecutive soaking in ethanol and in Decon 90TM liquid detergent, abundant rinsing with deionized water, and drying at ambient temperature for several hours.

Experimental Methods

The solutions' surface and interfacial tensions, σ_{AW} and σ_{OW} , were determined by using the "pendant/buoyant drop" method. For this goal, a buoyant bubble or drop was formed on the tip of a J-shaped hollow needle dipped in the aqueous solution. The surface tension was determined by drop shape analysis (Hoorfar and Neumann, 2006; Rotenberg et al., 1983) with the software DSA1 on the instrument DSA10 (Krüss GmbH, Hamburg, Germany).

To determine precisely the Krafft temperature for 0.5 wt% surfactant solutions, we measured the solutions' turbidity using a ultraviolet/visible spectrophotometer Jasco V-700 at wavelength 500 nm. The temperature was decreased by 0.5° steps starting from 30 °C. The samples were tempered for 10 min at each temperature and the measurements were

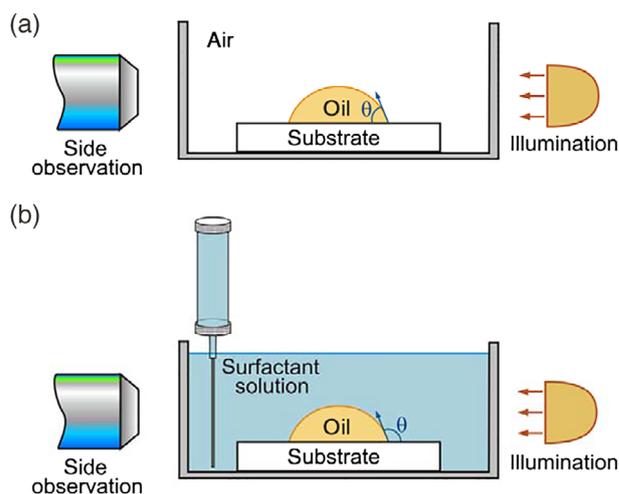


Fig. 1 Schematic presentation of the setup used to measure contact angles. (a) Drop on a solid substrate in air; the contact angle θ is measured across the *liquid* phase. (b) Drop on a solid substrate in aqueous solution; the contact angle θ is measured across the *water* phase

performed afterward. The Krafft temperature was determined from the onset of rise of turbidity (Heckmann et al., 1987; Tzocheva et al., 2012).

Contact angles of water and oil drops on the used solid surfaces were determined by side observations using the instrument DSA10 and DSA1 software (Krüss GmbH, Hamburg, Germany).

Monitoring the Oil Drop Detachment in Surfactant Solutions

The systematic observation of soil removal has been realized by using a glass cuvette mounted on the instrument DSA10. The procedure is as follows. First, we put a dry substrate on the bottom of the 50 mL rectangular glass cuvette. Next, 3 μL oil drop is placed on the substrate and its three-phase contact angle, θ , is measured (Fig. 1a). The drop is left at rest for 10 min. Afterward, 20 mL surfactant solution is gently poured in the cuvette. The shrinking of the oil-drop/substrate contact area (with possible drop detachment) has been observed for 15 min (Fig. 1b), and the contact angle variation has been recorded. All experiments have been performed at least twice using at least two separate substrates of each type for each solution and oil.

After the aqueous phase is poured in the experimental cell (Fig. 1b), the contact area oil/substrate begins to shrink. At that, we distinguish three scenarios of oil drop evolution (Fig. 2a).

1. *No detachment*: The shrinkage of the three-phase contact line (and the decrease of contact angle θ)

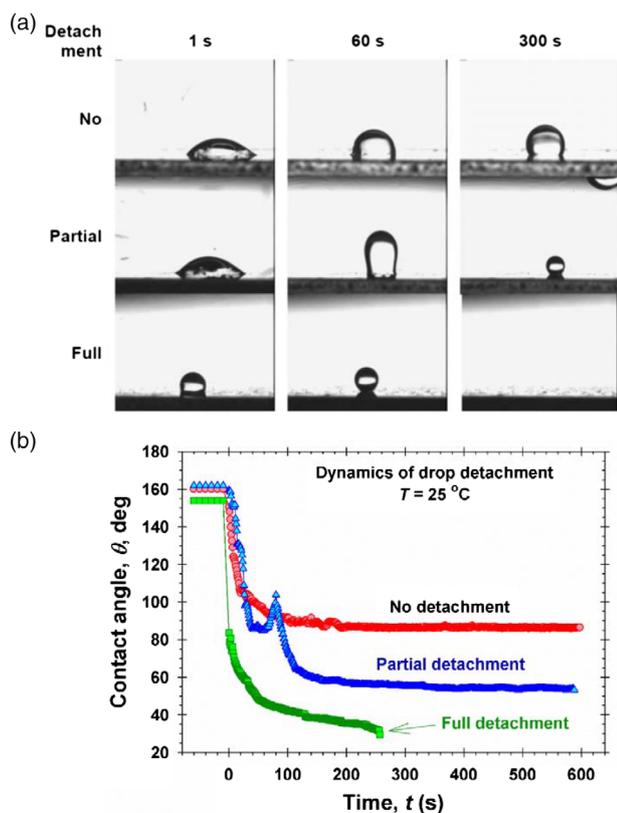


Fig. 2 (a) Photographs illustrating the three scenarios of evolution of oil drops in surfactant solutions: (i) no detachment; (ii) partial detachment and (iii) full detachment. (b) The respective typical variations of contact angle θ . The moment $t = 0$ corresponds to pouring the surfactant solution in the experimental cell

decelerates and stops at a relatively large contact angle, for example, $\theta > 80^\circ$ (Fig. 2b). The drop remains attached to the substrate.

2. *Partial detachment*: At a certain stage of the contact-line shrinkage, necking instability appears and the drop breaks to two parts at the neck. The upper (larger) part is detached, whereas the lower part remains fixed to the substrate as a residual drop. In Fig. 2b, the moment of drop breakage corresponds to the local maximum of θ .
3. *Full detachment*: In this case, the necking instability occurs within few seconds after pouring the surfactant solution. After that, the contact angle of the residual droplet gradually decreases up to its full detachment (Fig. 2). Such behavior corresponds to the roll-up mechanism of cleaning (Shi et al., 2006; Smulders, 2002; Tsujii, 1998).

In some experiments, a residual droplet remains attached to the substrate with a small contact angle (across water), but this drop detaches if it is subjected to a minor external force (which is present in real cleaning experiments). Such a case will be referred as *almost full detachment*.

Experimental Characterization of the Studied Systems

Contact Angle Measurements

The cleaned dry porcelain and stainless steel substrates were characterized by measuring the drop contact angle θ of 3 μL drops of water, SFO, and LMO; the upper phase is air (Fig. 1a). The results are shown in Table 1, where the values of θ are average over at least six different drops on more than three different plates of the same material. The standard deviation is $\pm 5^\circ$.

The data for water drops show that porcelain is markedly more hydrophilic than stainless steel. This leads to much easier cleaning of oily soils from porcelain than from stainless steel (see below).

The comparison of the data for SFO and LMO indicates that the mineral oil wets the solid substrate much better than the vegetable oil. This fact is related to the use of mineral oils as lubricants. However, both oils wet the solid surfaces better than water, which can be explained with the greater contribution of dispersion interaction to the surface free energy in the case of oils (Israelachvili, 2011).

Solutions' Surface Tension and Turbidity

We performed measurements of the surface tension of 0.2 wt% solutions of the used SME surfactants in the absence and presence of DDAO. In the solutions with DDAO, the weight fractions of SME and DDAO are, respectively, 0.8 and 0.2, the total surfactant concentration being the same, *viz.* 0.2 wt%. The pH was varied in the range between 4 and 8. It should be noted that the dishwashing liquids in the market have pH in the range from 6 to 10 (Shi et al., 2006) but the requirement for skin mildness gives preference to formulations with pH close to 6. The range $4 < \text{pH} < 8$ is used also in skin cleansing formulations (Gambogi et al., 2006; Harmalker and Lai, 2006).

Fig. 3 shows data for the pH dependence of the surface tension, σ_{AW} , of the studied solutions. The most significant effect in this figure is the lowering with 8–10 mN m^{-1} of σ_{AW} for C14-SME and C16-SME solutions upon the replacement of a part (20%) of SME with DDAO. This

Table 1 Solid/liquid/air contact angle, θ , for drops of deionized water, sunflower oil (SFO), and light mineral oil (LMO); $T = 25^\circ\text{C}$

Substrate	Solid/liquid/air contact angle, θ		
	Water	SFO	LMO
Porcelain	38°	23°	<10°
Stainless steel	53°	18°	<10°

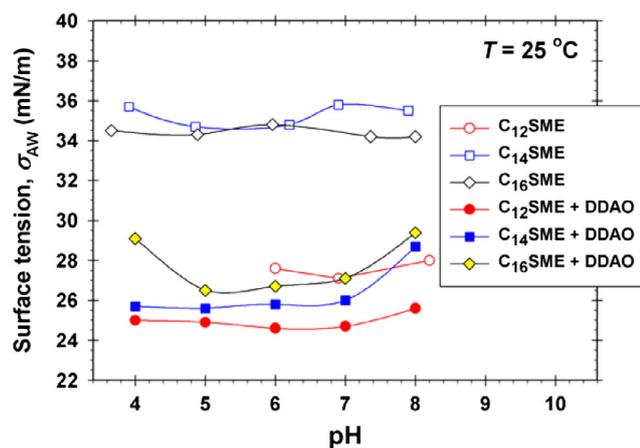


Fig. 3 Effect of DDAO on the surface tension of SME solutions, σ_{AW} , at various pH. For all solutions, the total surfactant concentration is 0.2 wt% and they contain also 0.146 wt% NaCl. The weight fractions of SME and DDAO in the mixed solutions (full symbols) are, respectively, 0.8 and 0.2

effect is expected to favor the cleaning of oils from solid surfaces. Similar surface tension drop has been observed for mixtures of sodium dodecyl sulfate-DDAO mixtures (Angarska et al., 2004) and has been practically applied for optimization of dishwashing formulations (Shi et al., 2006).

For C12-SME (without DDAO) σ_{AW} is markedly lower as compared to C14- and C16-SME. This can be explained with the presence of admixture of unsulfonated lauric-acid methyl ester (a residual component from the synthesis) in the used surfactant sample. The replacement of a part of C12-SME with DDAO further lowers σ_{AW} , which takes the lowest values among the solutions characterized in Fig. 3.

The data in Fig. 3 do not show any strong effect of pH on σ_{AW} in the investigated concentration range. A shallow minimum of σ_{AW} is observed only for C16-SME + DDAO. In our subsequent experiments, pH = 6 is fixed, which is close to the aforementioned minimum.

Table 2 Surface tension, σ_{AW} , of solutions at total surfactant concentration 0.5 wt% with 0.365 wt% added NaCl, in the presence or absence of DDAO and CaCl_2 ; pH = 6 and $T = 25^\circ\text{C}$

Surfactant	Ca^{2+} (mM)	σ_{AW} (mN m^{-1})
SLES	0	31.7
SLES	5	29.4
4:1 SLES/DDAO (w/w)	5	24.5
C16-SME	0	34.6
C16-SME	5	31.2
4:1 C16-SME/DDAO (w/w)	0	26.7
4:1 C16-SME/DDAO (w/w)	5	25.8

In relation to the influence of water hardness, we studied the effect of added CaCl_2 on σ_{AW} (Table 2). The concentration of added Ca^{2+} was 5 mM, which corresponds to very hard water. The addition of 5 mM Ca^{2+} decreases σ_{AW} with 1–2 mN m^{-1} . The effect is stronger for SLES as compared to C16-SME, in agreement with the finding for relatively low binding energy of the Ca^{2+} ions to the sulfonate groups of SME (Ivanova et al., 2017). The lowering of σ_{AW} with 7–9 mN m^{-1} due to DDAO is a much stronger effect than that of 5 mM Ca^{2+} .

Unlike the clear solutions of SLES and C16-SME with Ca^{2+} presented in Table 2, the solutions of 0.5 wt% LAS + 5 mM Ca^{2+} were very turbid. This is related to the high sensitivity of LAS to hard water. However, if the concentrations of surfactant and calcium are decreased to 0.2 wt% and 0.9 mM, respectively, all studied solutions become clear (Fig. 4a).

Furthermore, to visualize the sensitivity of LAS to Ca^{2+} we increased the surfactant and calcium concentrations to 0.5 wt% and 2.25 mM, respectively (Fig. 4b). As expected, the solution of LAS is the most turbid. The 4:1 LAS/DDAO solution is less turbid, which is due to the replacement of a part of LAS with DDAO. The solutions of SLES and C16-SME are completely clear. However, the presence of DDAO in the solutions of SLES and C16-SME slightly increases the turbidity (Fig. 4b). We could hypothesize that Ca^{2+} is able to bridge between the zwitterionic form of DDAO and two anionic surfactant molecules, which leads to precipitation of the formed hydrophobic complex with three alkyl chains.

By turbidimetry, we measured the Krafft temperature, T_K , of some of the studied solutions, which are clear at 25°C . Among the systems in Table 3, C14-SME has the lowest $T_K = 10.1^\circ\text{C}$, because of its shortest alkyl chain. In contrast, C16-SME has the highest T_K , which is slightly below 25°C . In agreement with literature evidence (Schambil and Schwuger, 1990), C1618-SME has a significantly lower Krafft temperature, $T_K = 18.0^\circ\text{C}$. Another binary surfactant mixture, 4:1 C16-SME/C12-SME, has $T_K = 22.0^\circ\text{C}$, which is lower than that of C16-SME alone,

Table 3 Krafft temperature of unary, binary, and ternary surfactant solutions at a total surfactant concentration of 0.5 wt% containing also 0.365 wt% NaCl at pH = 6

Surfactant	Krafft temperature
C14-SME	10.1 $^\circ\text{C}$
C16-SME	24.8 $^\circ\text{C}$
C1618-SME	18.0 $^\circ\text{C}$
4:1 C16-SME/C12-SME	22.0 $^\circ\text{C}$
3:1:1 C16-SME/C12-SME/DDAO	17.9 $^\circ\text{C}$

The mix ratios are by weight.

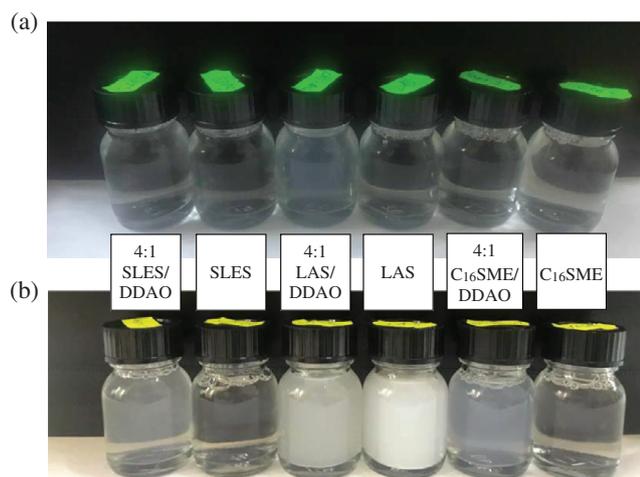


Fig. 4 Photos of glass vials containing (a) 0.2 wt% total surfactant concentration + 0.9 mM Ca^{2+} ; (b) 0.5 wt% total surfactant concentration + 2.25 mM Ca^{2+} (hard water). In both cases pH = 6 and $T = 25^\circ\text{C}$. The mix ratios are by weight (w/w)

but higher than that of C1618-SME, despite the shorter chain of C12-SME. Finally, a ternary surfactant mixture, 3:1:1 C16-SME/C12-SME/DDAO, has Krafft temperature $T_K = 17.9^\circ\text{C}$, which is close to that of C1618-SME.

Results from the Cleaning Experiments and Discussion

Cleaning of Oils by Solutions of Single Surfactant

Systematic study on oily soil removal with drops from SFO and LMO deposited on porcelain and stainless steel was carried out with six ionic surfactants: LAS, SLES, C12-, C14-, C16-, and C1618-SME (Fig. 5). All cleaning aqueous solutions contained 0.5 wt% surfactant and 0.365 wt% NaCl at pH = 6.

In the case of *porcelain* substrate, the results are as follows. For the vegetable oil (SFO), with all six studied surfactants we observed *full detachment* of the drops within less than a minute. In contrast, for the mineral oil (LMO) with all six surfactants we observed *no detachment* of the drops—both cases are illustrated in Fig. 2. This difference correlates with the fact that LMO wets better porcelain than SFO (Table 1).

In the case of *stainless steel* substrate, the results are presented in Fig. 5a. These results are rather surprising. With LAS, SLES, C14-SME, and C16-SME *no detachment* of oil drops is observed. In contrast, *full detachment* of both SFO and LMO drops is observed with C1618-SME. With C12-SME, we observed full detachment of the SFO drops and partial detachment of the LMO drops.

The comparison of Fig. 5a, b indicates that there is no correlation between low interfacial tension and good cleaning performance. Indeed, the LAS solution has the lowest σ_{OW} , whereas the C12-SME solution—the highest one. However, the cleaning performance of C12-SME is much better than that of LAS.

Likewise, the comparison of Fig. 5a with the data in Table 3 shows that there is no correlation between low Krafft temperature and good cleaning. Indeed, C14-SME has lower Krafft temperature than C1618-SME. However, the cleaning performance of C1618-SME is much better than that of C14-SME.

There is no correlation also between the surfactant chainlength and the cleaning performance. Indeed, C12-SME and C1618-SME have different chainlengths, but similar cleaning performance (Fig. 5a). Moreover, the

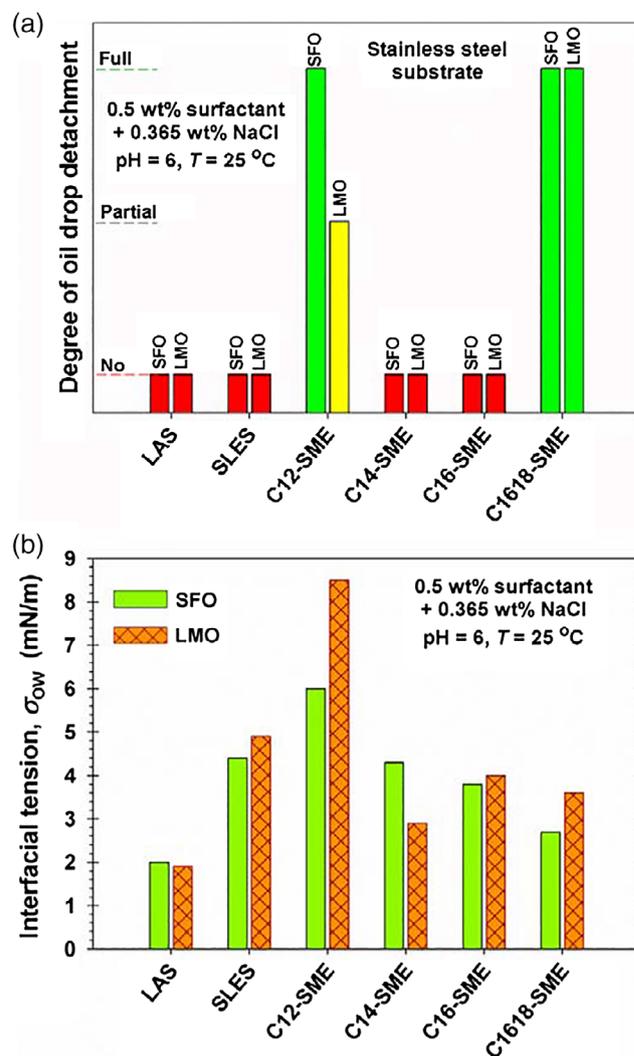


Fig. 5 (a) Results from the drop detachment experiments with SFO and LMO on stainless steel in solutions of anionic surfactants. (b) The respective values of oil/water interfacial tension, σ_{OW}

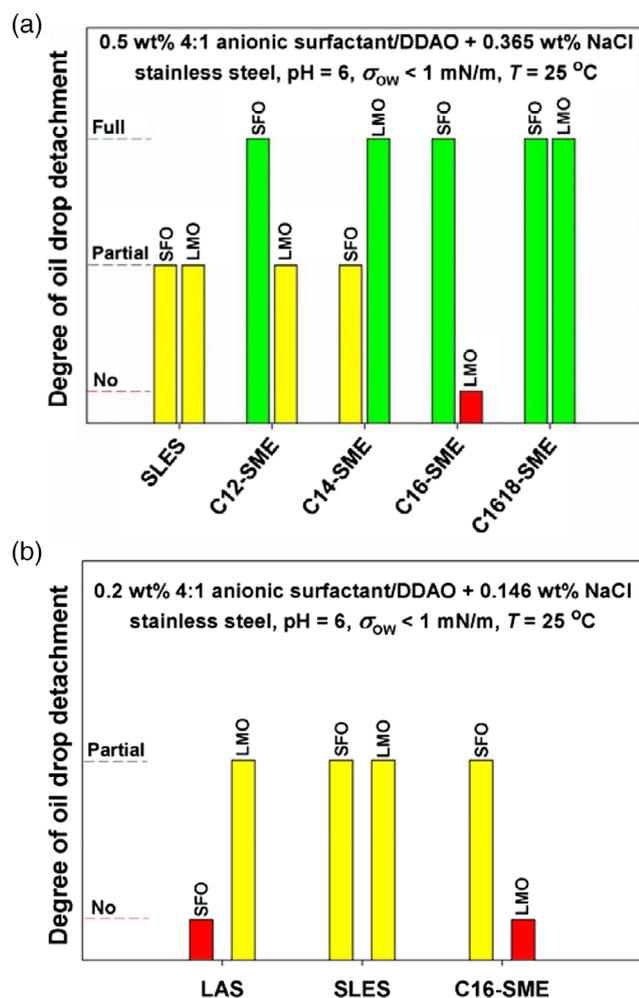


Fig. 6 (a) Results from the drop detachment experiments with SFO and LMO on stainless steel in 4:1 solutions of anionic surfactant and DDAO. (a) 0.5 wt% total surfactant concentration + 0.365 wt% NaCl; (b) 0.2 wt% total surfactant concentration + 0.146 wt% NaCl. The mix ratios are by weight

chainlengths of LAS, SLES, and C12-SME are similar, but their cleaning performance is rather different.

In addition, surfactants with identical headgroups, C12-, C14-, C16-, and C1618-SME exhibit very different cleaning performance (Fig. 5a). This means that both the headgroups and hydrocarbon chains of surfactant molecules matter for the cleaning process. This fact implies that the formation of surfactant adsorption bilayers or admicelles on the solid surface affect the detachment of oil drops. The morphology of the admicellar layer seems to be very specific and dependent on the kind of solid surface and surfactant type (Atkin et al., 2001; De Oliveira Wanderley Neto et al., 2014; Wangchareansak et al., 2013; Zhang and Somasundaran, 2006). We could hypothesize that admicelles of appropriate morphology can penetrate in the wedge-shaped region near the three-phase contact line

and can act as “molecular jacks” that promote the full detachment of the oil drops from the substrate.

Mixed Solutions of Anionic Surfactant and DDAO

To improve the cleaning action of the surfactant solutions, we added the zwitterionic surfactant DDAO to the solutions of SLES, C12-, C14-, C16-, and C1618-SME. In this series of experiments, the ratio anionic/zwitterionic surfactant was 4:1 (w/w) and the total surfactant concentration was 0.5 wt%. For both SFO and LMO, the presence of DDAO lowered the oil/water interfacial tension σ_{ow} below 1 mN m^{-1} (the used DSA method does not allow one to measure precisely interfacial tensions lower than *ca.* 1 mN m^{-1} ; Hoorfar and Neumann, 2006). Despite the fact that the interfacial tension was $< 1 \text{ mN m}^{-1}$, it was not low enough to cause spontaneous emulsification, so that the mechanism of drop removal was roll-up again.

In the case of *porcelain* substrate, the treatment with the aforementioned 4:1 anionic/DDAO surfactant solutions leads to *full detachment* of the drops from both SFO and LMO (Fig. 2). In other words, the presence of DDAO very essentially improves the cleaning of LMO from porcelain.

In the case of *stainless steel* substrate, the results are presented in Fig. 6a. The SLES+DDAO solution provides partial detachment of both SFO and LMO drops. The treatment with C12-SME + DDAO solution leads to full detachment of SFO drops, but partial detachment of LMO drops. For C14-SME + DDAO solutions, the roles are exchanged—partial detachment of SFO, but full detachment of LMO. The treatment with C16-SME + DDAO solution leads to full detachment of SFO drops, but no detachment of LMO drops. Finally, with and without DDAO the solutions of C1618-SME provide full detachment of both SFO and LMO drops (Figs. 5a and 6a).

The solutions with 0.5 wt% 4:1 LAS/DDAO are turbid. To avoid the precipitation, we decreased the total surfactant concentration to 0.2 wt%. In Fig. 6b, we compare the cleaning performance of 0.2 wt% 4:1 LAS/DDAO solutions with the performance of 0.2 wt% 4:1 SLES/DDAO solutions and 0.2 wt% 4:1 C16-SME/DDAO solutions for oil drops on stainless steel. The lowering of the total surfactant concentration from 0.5 to 0.2 wt% does not affect the cleaning performance of SLES solutions—at both concentrations, we observe partial detachment of the oil drops (Fig. 6a, b). However, the lowering of the total surfactant concentration worsens the cleaning of SFO by C16-SME solutions—from full detachment to partial detachment. Finally, the treatment with LAS + DDAO solution leads to full detachment of LMO drops, but no detachment of SFO drops.

In summary, the presence of DDAO in the surfactant solutions markedly improves the cleaning of oily deposits

from stainless steel (Figs. 5a and 6a). In general, the decrease of the total surfactant concentration from 0.5 to 0.2 wt% worsens the cleaning performance, compare Fig. 6a, b. This is not surprising, because the average thickness and morphology of the adsorbed surfactant (admicelles) on the solid surface are expected to essentially depend on surfactant concentration (De Oliveira Wanderley Neto et al., 2014; Zhang and Somasundaran, 2006).

Mixing of amine-oxide surfactants with anionic surfactants is known to boost the growth of wormlike micelles in the bulk of solution (Hoffmann et al., 1992). In particular, the mixing of SME with the zwitterionic surfactant cocamidopropyl betaine (with or without added electrolyte) produces a strong synergistic effect on the micelle growth in the bulk (Yavrukova et al., 2020). The present results on cleaning indicate that the mixing of SME with the zwitterionic DDAO could promote also the formation of admicelles on the surface of stainless steel.

Cleaning of Oils by Binary SME Solutions

Because all studied 0.5 wt% solutions of anionic surfactants + DDAO lead to full detachment of SFO and LMO drops from porcelain, our investigations have been continued with stainless steel substrates, which are more difficult to clean. We recall that no detachment of oil drops has been observed in solutions of C14-SME and C16-SME (Fig. 5a).

Here, we investigate whether the mixing of C14-SME and C16-SME with shorter chain SME could improve the cleaning of oily stains. For this goal, we monitored the detachment of SFO and LMO drops from stainless steel substrates in mixed solutions of 0.5 wt% total surfactant concentration and composition 4:1 C14-SME/C12-SME, 4:1 C16-SME/C12-SME, and 4:1 C16-SME/C14-SME.

The results are presented in Fig. 7a. The best results (full detachment of both SFO and LMO drops) were obtained with the 4:1 C16-SME/C14-SME solutions, which perform similarly to C1618-SME—compare the rightmost columns in Figs. 5a and 7a. The treatment with the other two mixed solutions, 4:1 C14-SME/C12-SME and 4:1 C16-SME/C12-SME, leads to full detachment of LMO drops (which is a considerable improvement), but no detachment of SFO drops was observed.

The comparison of the drop detachment data in Fig. 7a with the respective data for the interfacial tension σ_{OW} in Fig. 7b shows the absence of any correlation again. In such a case, the different behaviors of the studied surfactant solutions should be related to the three-phase contact angle θ (Fig. 1b) that, in turns, depends on the solid/water interfacial tension, σ_{SW} (Tsuji, 2017). As already mentioned, the values of σ_{SW} are affected by the structure and morphology of the surfactant adsorption layers on the

solid/water interface, which may include formation of admicelles.

Cleaning of Oils by Ternary Surfactant Solutions with DDAO

Finally, we added the zwitterionic surfactant DDAO to the double mixtures from Fig. 7a to verify whether further improvement of oil cleaning from stainless steel could be achieved. The results are shown in Fig. 8. In the presence of DDAO, the excellent cleaning performance of the C16-SME + C14-SME mixture is preserved. Moreover, the presence of DDAO improves the cleaning performance of the C14-SME + C12-SME and C16-SME + C12-SME mixtures—for both SFO and LMO we observe almost full detachment of the oil drops. This means that the main mass of the oil drop has been detached and only a small (nanoliter) drop has remained on the substrate. Such small drop

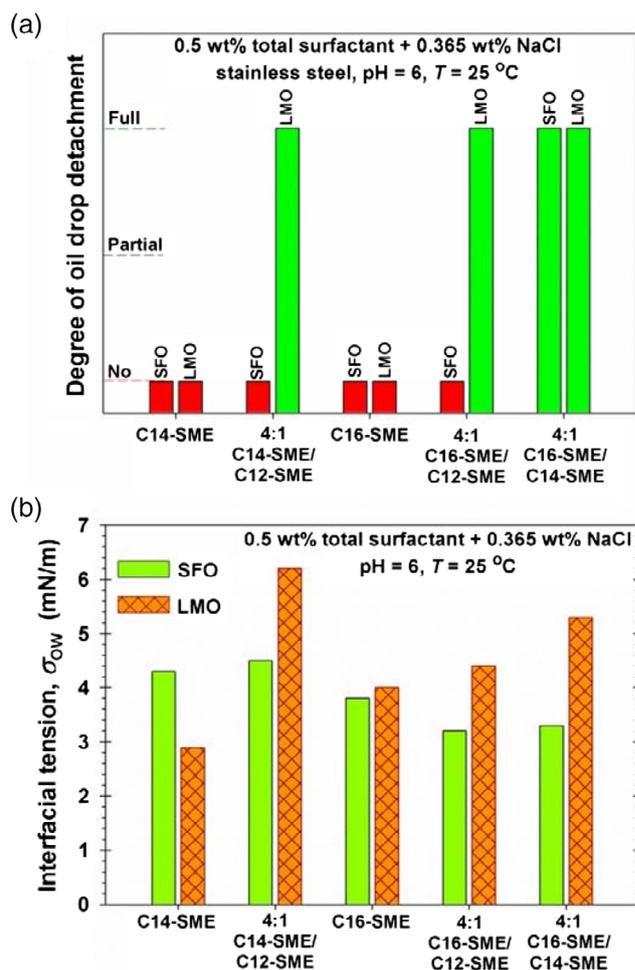


Fig. 7 Comparison of data for unary and binary SME solutions. (a) Results from the drop detachment experiments with SFO and LMO on stainless steel. (b) the respective values of oil/water interfacial tension, σ_{OW} . The mix ratios are by weight (w/w)

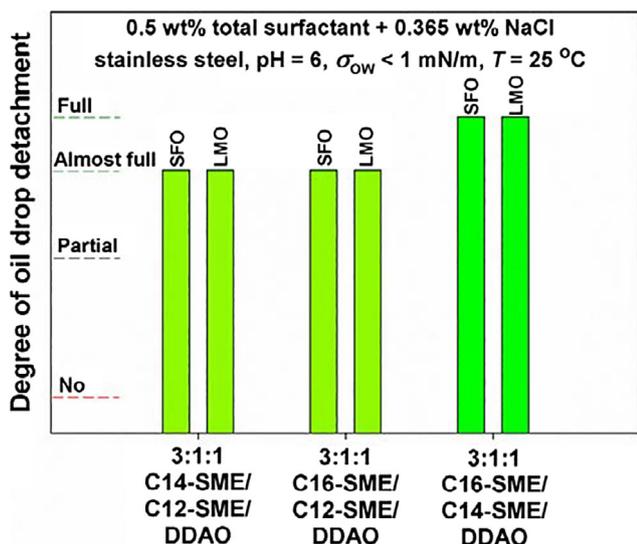


Fig. 8 Results from the drop detachment experiments with SFO and LMO on stainless steel in ternary mixed solutions of SME and DDAO. The mix ratios are by weight

can be easily detached under the action of a minor mechanical force.

The mixing of anionic SME with a zwitterionic surfactant gives rise to the growth of giant wormlike micelles in the bulk of surfactant solution (Basheva et al., 2019; Yavrukova et al., 2020). The results in Fig. 8 could be an indication that the mixing of SME with DDAO promotes the formation of mixed surfactant layers, possibly—admicelles, on the surface of stainless steel. Mixed solutions of amine oxide with alkyl sulfates or alkyl ethoxy sulfates find wide applications in grease cleaning (Lant and Keuleers, 2016). The results in Figs. 7 and 8 show that superior cleaning could be obtained by combinations of SME surfactants, with or without amine oxide, thus, avoiding the use of LAS (hard-water sensitive) as in other studies (Lim et al., 2019; Maurad et al., 2017; Tai et al., 2018).

Conclusions

The present article reports results from a systematic study on the cleaning of oily deposits from porcelain and stainless steel by solutions of SME of fatty acids, sodium salts. As a cosurfactant, dodecyltrimethylamine oxide (DDAO) has been used. Comparative experiments with LAS and SLES have been also performed. As representatives of the vegetable and mineral oils, SFO and LMO have been used. The process of oil drop detachment from the solid substrates (roll-up mechanism) was studied by direct observations (Figs. 1 and 2). In general, the surfactants are

expected to promote the detachment of oil drops from the substrate by lowering the oil/water and solid/water interfacial tensions, σ_{ow} and σ_{sw} (Tsujii, 2017). In view of potential applications in house-hold detergency, all experiments have been carried out at pH = 6 (mild to skin).

The experiments showed that excellent cleaning of oil from porcelain can be achieved by the mixed solutions of SME and DDAO. For this reason, all subsequent experiments were focused on cleaning of oil from stainless steel.

In the case of single-surfactant solutions, full oil drop detachment from stainless steel was observed with C1618-SME and C12-SME, whereas no drop detachment was observed for C14-SME, C16-SME, LAS, and SLES (Fig. 5a). The addition of DDAO improves the cleaning by C14-SME and C16-SME, but only with respect to one of the two types of oil (Fig. 6a). The mixing of C14-SME and C16-SME leads to excellent cleaning performance (Fig. 7a), which is similar to that of C1618-SME. Finally, excellent cleaning was obtained also with ternary surfactant solutions, composed of two SME and DDAO (Fig. 8).

The results for the investigated systems indicate that the good cleaning of oils from stainless steel correlates neither with the oil/water interfacial tension, nor with the surfactant chainlength, headgroup type, or Krafft point (Figs. 5 and 7). The only possible explanation remains the lowering of σ_{sw} that could be caused by formation of admicelles on the solid surface (De Oliveira Wanderley Neto et al., 2014; Zhang and Somasundaran, 2006). The cleaning action seems to be influenced by the morphology of the admicellar layer, which is very specific and depends on the kind of solid surface and surfactant mixture (Atkin et al., 2001; Wangchareansak et al., 2013). This issue could be a subject of subsequent studies, where the formation of admicelles could be confirmed by appropriate experimental methods, for example, atomic force microscopy or appropriate spectroscopy methods.

The results show that binary and ternary mixtures of SME, which may contain also DDAO, exhibit excellent cleaning performance (superior than that of LAS and SLES) for the two types of oils and two types of substrates. For this reason, the SME mixtures represent a promising system for formulations in house-hold detergency, having in mind also other useful properties of SME, such as biodegradability, skin compatibility, and high hard water tolerance.

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Conflict of interest The authors declare that they have no conflict of interest.

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