Properties of the micelles of sulfonated methyl esters determined from the stepwise thinning of foam films and by rheological measurements

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ABSTRACT

Hypotheses
The micellar solutions of sulfonated methyl esters (SME) are expected to form stratifying foam films that exhibit stepwise thinning. From the height of the steps, which are engendered by micellar layers confined in the films, we could determine the micelle aggregation number, surface electric potential, and ionization degree. Moreover, addition of the zwitterionic surfactant cocamidopropyl betaine (CAPB) is expected to transform the small spherical micelles of SME into giant wormlike aggregates.

Experiments
Stratifying films from SME solutions are formed and the heights of the steps are recorded. The viscosity of mixed SME+CAPB solutions is measured at various concentrations and weight ratios of the two surfactants.

Findings
By theoretical analysis of the foam film data, we established that at 30–100 mM SME spherical micelles are formed and their aggregation number was determined. The addition of calcium ions, as in hard water, does not produce significant effect. However, SME and CAPB exhibit a strong synergism with respect to micelle growth as indicated by the high solution’s viscosity. For this reason, the SME+CAPB mixtures represent a promising system for formulations in personal-care and house-hold detergency, having in mind also other useful properties of SME, such as high hard water tolerance, biodegradability and skin compatibility.

Keywords: Sulfonated methyl esters; Micelle aggregation number; Stratifying foam films; Film thicknesses interpretation; Rheology of micellar solutions; Wormlike micelles.
1. Introduction

Here, on the basis of data for the stepwise thinning of foam films, we determine the aggregation number, $N_{\text{agg}}$, surface electrostatic potential, $\varphi$, and ionization degree, $\alpha$, of the spherical micelles formed in solutions of sulfonated methyl esters (SME). More precisely, we are dealing with $\alpha$-sulfo fatty acid methyl ester sulfonates, sodium salts, which are also known as methyl ester sulfonates (MES). We report also rheological data, which imply that the mixed solutions of SME and CAPB (cocamidopropyl betaine) undergo a transition from small spherical to giant wormlike micelles.

The sulfonated methyl esters (Fig. 1) are produced from renewable palm-oil based materials or as a by-product from bio-diesel synthesis [1–4]. They have been promoted as alternatives to the petroleum-based surfactants [5]. SMEs exhibit a series of useful properties such as excellent biodegradability and biocompatibility; excellent stability in hard water; good wetting and cleaning performance, and skin compatibility [2,6–11]. The SME surfactants are produced typically with even alkyl chainlengths, from $C_{12}$ to $C_{18}$. Here, they will be denoted $C_n$-SME, $n = 12, 14, 16, 18$.

![Cn-SME](image)

**Fig. 1.** Structural formula of $C_n$-SME.

In the early studies on the interfacial properties of SMEs, the critical micelle concentrations (CMC) of their solutions were determined from data for the surface tension and electric conductivity [12–19]. The CMC values obtained in these studies differ considerably because of the presence of small amounts of nonionic admixtures in the used SME samples. Recent neutron reflectivity measurements [20] and surface tension data processing [21] showed that the correct value of the saturation adsorption of the $C_n$-SME molecules at the air-water interface is $3.4 \pm 0.1 \, \mu\text{mol/m}^2$, the excluded area per molecule being $37 \, \text{Å}^2$. The effect of added NaCl on the CMC of SME solutions was quantified [21]. The binding energy of $\text{Ca}^{2+}$ ions to the headgroups of SME turned out to be considerably smaller than to the headgroups of linear alkylbenzene sulfonates (LAS) [22]. As a result, the SMEs possess a much higher hard water tolerance than LAS. The effect of multivalent counterions ($\text{Ca}^{2+}$ and $\text{Al}^{3+}$) on the surfactant adsorption was also studied by neutron
reflectivity [23,24]. The results for mixtures of SME with different chainlengths showed that the variations in the surface composition are described well by a pseudo phase approximation with repulsive interactions between C16-SME and C18-SME molecules [24].

The rheological studies with micellar solutions of SME [18] showed that the dependence of the zero-shear viscosity, $\eta_0$, on the NaCl concentration has a sharp maximum, which indicates the growth of wormlike micelles to the left of the peak, and transition to self-assemblies with another structure to the right of the peak.

In our previous study [21], we determined the dependence of CMC of C$_n$-SME on the number of carbon atoms in the alkyl chain, $n$, and on the NaCl concentration. Here, our goal is to extend this analysis to characterization of the C$_n$-SME micelles with respect to their aggregation number, surface electric charge and potential. For this goal, the method developed in Ref. [25], which is based on theoretical analysis of data for stratifying foam films containing layers of surfactant micelles, is applied; see also Refs. [26,27,28].

The stepwise thinning (stratification) of foam films is a manifestation of the action of the oscillatory structural force, which becomes significant if the effective volume fraction of surfactant micelles (or other colloidal particles) exceeds ca. 15 vol% [28,29]. It should be noted that premicellar aggregates could be present in the liquid films at concentrations below the CMC [30], but they do not form ordered layers and do not give rise to oscillatory forces. The first explanation of the stepwise transitions as a layer-by-layer thinning of an ordered structure of spherical micelles was given by Nikolov et al. [31,32,33]. Cryo-electron microscopy pictures of vitrified stratifying films at various stages of their evolution [34,35] directly proved that the stepwise transitions are due to the presence of ordered micellar layers inside the film and represent layer-by-layer drainage of the film.

It should be noted that stratifying films from SME solutions have not been investigated so far. To the best of our knowledge, systematic study on the properties of SME micelles, such as aggregation number, ionization degree and surface electric potential and their dependences on the surfactant chainlength and concentration is still missing. There is a single estimate based on static light scattering data that $N_{agg} \approx 50$ [36], but the dependence of $N_{agg}$ on chainlength and concentration has not been studied.

The paper is organized as follows. Section 2 presents the used materials and methods. Section 3 presents the experimental results for stratifying liquid films. In Section 4.1, the obtained data are analyzed theoretically and the values of micelle aggregation number, ionization degree and surface electric potential, as well as their dependences on the surfactant chainlength and concentration, are determined. In Section 4.2, we present an independent
verification of the used theoretical model against experimental data for the equilibrium film thickness. In Section 4.3, the packing parameter is estimated for different SME chainlengths in relation to the possibility for formation of micelles of different shapes. Finally, in Section 5 we examine the effect of added zwitterionic surfactant, CAPB, to check whether growth of giant wormlike micelles occurs with SME, as this happens with other anionic surfactants.

2. Materials and methods

2.1. Materials

Sulfonated methyl esters (SME) with three different alkyl chains, C12, C14, and C16, produced by the Malaysian Palm Oil Board (MPOB) and KLK OLEO, were used in our experiments. The molecular masses and the purities of the used samples are $M = 316$ g/mol and 97.4% for C12-SME; $M = 344$ g/mol and 97.9% for C14-SME; $M = 372$ g/mol and 96.0% for C16-SME [21,22]. The amount of water in the used samples was established by Karl Fisher analysis and taken into account when calculating the surfactant concentrations. In addition, by electric conductivity measurements we estimated the concentrations of NaCl admixture in the used samples relative to the surfactant: 16 mol% in C12-SME; 14 mol% in C14-SME, and 24 mol% in C16-SME. These samples were used in our experiments without further purification. The measured foam-film thicknesses and viscosities of micellar solutions are affected by the NaCl-admixture in Cn-SME. The effect of admixtures is taken into account in all theoretical calculations presented in this paper.

The experimental surface tension isotherms have well pronounced minima, which indicate the presence of small amounts of nonionic surface active admixtures, presumably unsulfonated methyl esters and fatty acids [21]. At concentrations above the CMC, these admixtures are solubilized in the micelles of SME and (as demonstrated below) their effect on the foam film thickness and micelle properties is negligible.

The zwitterionic surfactant cocamidopropyl betaine (CAPB), $M = 356$ g/mol, product of Evonik, commercial name Tego® Betain F50, was also used. The CMC of CAPB at 25 °C is 0.09 mM. By conductivity measurements, we established that 100 mM CAPB contains 120 mM NaCl in the used sample. Such high content of NaCl is typical for the commercially available CAPB samples [45,46]. The presence of NaCl admixtures in both Cn-SME and CAPB has been taken into account when interpreting theoretically the experimental data.

In some experiments, we used also calcium chloride, CaCl$_2$·6H$_2$O ($\geq$ 99 %), and sodium hydroxide, NaOH ($> 99$ %), both of them products of Sigma-Aldrich, as well as myristic (tetradecanoic) acid HC14 ($\geq$ 98 % from Fluka) and palmitic (hexadecanoic) acid HC16
The solutions were prepared with deionized water of specific resistivity 18.2 MΩ·cm purified by Elix 3 water purification system (Millipore). All experiments were carried out at a temperature of 25 °C.

2.2. Methods

Scheludko-Exerowa (SE) capillary cell [37,38] was used to study the drainage and evolution of foam films. Experiments with SE cell have been used to model the bubble-bubble interactions in foams [38] and the bubble-interface interactions [39], as well as to investigate dynamic phenomena in thin liquid films [40], including the phenomenon stratification [25,26,31,32]. The inner radius of the capillary cell was \( R_{in} = 1.5 \) mm and the applied capillary pressure was between 60 to 80 Pa. The SE cell is closed in a container, so that the water vapors are equilibrated with the studied solution and evaporation from the film is prevented. After a foam film is formed, its thickness decreases with time because of the drainage of liquid out of the film. The film thickness was determined interferometrically, from the measured intensity of light reflected from the film surfaces, which was registered by a photomultiplier and recorded by a computer in the course of the experiment. Monochromatic light of wavelength \( \lambda = 546 \) nm was used.

![Fig. 2. The model of foam film used to determine the actual film thickness \( h \); the length of the surfactant tail is denoted \( h_t \) and \( d \) is the diameter of the surfactant headgroup.](image)

The so-called equivalent water thickness of the film, \( h_w \), is determined assuming that the whole film consists of water of refractive index \( n_f = 1.333 \) [41,42]:

\[
h_w = \frac{\lambda}{2\pi n_f} \left[ k \pi + \arcsin(\Delta^{1/2}) \right]
\]

\[\Delta \equiv b[1 + \frac{4a(1-b)}{1-a^2}]^{-1}, \quad a \equiv \left( \frac{n_t-n_0}{n_t+n_0} \right)^2, \quad b \equiv \frac{I-I_{\min}}{I_{\max}-I_{\min}}\]

5
where \( I_{\text{max}} \) and \( I_{\text{min}} \) denote the maximum and minimum intensity of the reflected light; \( k = 0, 1, 2, \ldots \) is the order of the interference maxima; \( \lambda \) is the wavelength of the used monochromatic light; \( n_0 \) is the refractive index of the outer phase (in our case – air, \( n_0 = 1 \)). Note that for \( n_t = 1.333 \) and \( n_0 = 1 \), the approximation \( \Delta \approx b \) leads to a relative error that does not exceed 4%.

The equivalent water thickness of the film, \( h_w \), is slightly greater than the real film thickness, \( h \). In the case of dense surfactant adsorption layers, \( h \) can be estimated as follows (see Fig. 2):

\[
h = h_w - 2h_t \left( \frac{n_t^2 - n_0^2}{n_t^2 - n_0^2} \right) - 2d \frac{n_d^2 - n_t^2}{n_d^2 - n_0^2}
\]

(3)

where \( h_w \) is given by Eqs. (1) and (2); \( h_t \) and \( n_t \) are the thickness and refractive index of the dense layer of surfactant tails, whereas \( d \) and \( n_d \) are the thickness and the mean refractive index of the layer of surfactant headgroups. In the case of complete surface coverage, one could use the value \( n_t = 1.42 \). For sulfate or sulfonate headgroups immersed in water, one could use the value \( n_d = 1.394 \) for sodium sulfate decahydrate. The Tanford expression [43]

\[
h_t \equiv l = (0.154 + 0.1265n) \text{ nm}
\]

(4)

relates the extended length of the hydrocarbon tail, \( l \), with the number of the carbon atoms in the tail, \( n \). The diameter of the surfactant headgroup is \( d = 0.68 \text{ nm} \) [21]. Thus, from Eqs. (3) and (4) one obtains \( h = (h_w - 1.32) \text{ nm} \) for C12-SME; \( h = (h_w - 1.48) \text{ nm} \) for C14-SME, and \( h = (h_w - 1.68) \text{ nm} \) for C16-SME. The correction terms affect the values of the film thickness, \( h \), but they do not affect the heights of the stratification steps, \( \Delta h \) (see below).

**Rheological measurements** were carried out with mixed solutions of \( C_n \)-SME and CAPB. For this purpose, a rotational rheometer Bohlin Gemini (Malvern Instruments, UK) was used in steady-shear regime. The experiments were carried out with a cone-and-plate geometry. For viscosity lower than 40 \( \text{Pa} \cdot \text{s} \), the cone angle was 2° and the minimal gap distance was 70 μm; for higher viscosity, the angle and distance were, respectively, 4° and 150 μm. The temperature of 25 °C was controlled by a Peltier element and the evaporation was suppressed by a solvent trap. The shear stress, \( \tau \), was measured as a function of the applied shear rate, \( \dot{\gamma} \). Furthermore, the apparent viscosity, \( \eta(\dot{\gamma}) \), was calculated from the equation \( \eta = \tau / \dot{\gamma} \). The experimental shear rate varied from 0.01 to 100 s⁻¹. The zero-shear
viscosity, $\eta_0$, represents the limiting value of $\eta$ at $\dot{\gamma} \to 0$. This is a typical experimental protocol used to study the rheology of concentrated micellar solutions [44-47].

3. Experimental results

As an example of the observed processes, Fig. 3 shows photographs of consecutive stages of thinning of a foam film formed from 100 mM C16-SME solution in the SE cell. The stepwise decreasing of film thickness (stratification) takes place through the formation and expansion of spots of different thickness $h_j$, which corresponds to a film containing $j$ micellar layers ($j = 0, 1, 2, 3, \ldots$) [32,48]. With the decrease of film thickness, the spots look darker in reflected light. Thus, Fig. 3a shows the appearance of a spot of thickness $h_3$ that contains three micellar layers. This spot expands and covers the whole film area. Next, a spot of thicknesses $h_2$, which contains two micellar layers, appears and expands (Fig. 3b). Furthermore, a film with one micellar layer and thickness $h_1$ is formed (Fig. 3c), and finally a stable black film of thickness $h_0$ appears (Fig. 3d) and covers the whole film area. The Newton interference rings around the film are the most pronounced in Fig. 3d, which indicates a rise of the film contact angle with the decrease of film thickness [48].

![Fig. 3. Consecutive stages of stepwise thinning of a liquid film formed form 100 mM C16-SME solution: (a) appearance of film with three micelle layers and thickness $h_3$; (b) transition to film with two micelle layers and thickness $h_2$; (c) transition to film with one micelle layer and thickness $h_1$, and (d) transition to an electrostatically stabilized film of thickness $h_0$, which does not contain micellar layers. The scaling mark is 50 µm.](image)

The light reflected from the film is transmitted to a photomultiplier by an optical fiber. When the front of a darker expanding spot (Fig. 3) passes before the optical fiber, the photomultiplier registers a drop of intensity of the reflected light, $I$, which is converted into film thickness, $h$, by using Eqs. (1) – (3). As an example, Fig. 4 shows experimental dependencies of $h$ on time, $t$, obtained with foam films from C16-SME solutions in the SE cell. Similar experimental results for C12- and C14-SME are shown in Appendix A; see Figs. A1 and A2 therein.
Fig. 4a shows $h$-vs.-$t$ curves obtained at three different concentrations of C16-SME, viz. $C_S = 30, 50$ and 100 mM. One sees that the number of stepwise transitions increases and the height of the step, $\Delta h = h_j - h_{j-1}$, decreases with the rise of surfactant concentration. As known from previous experiments with ionic surfactant micelles [25,28], at a given surfactant concentration, $C_S$, $\Delta h$ is independent of the order of the step, $j$. Fig. 4b shows similar $h$-vs.-$t$ curves obtained in the presence of 10 mM NaOH, which was added to suppress the effect of fatty acid admixtures in the used SME sample. Fig. 4c presents similar curves, but obtained in the presence of 2.4 mM CaCl$_2$, which was added to investigate the effect of water hardness on the film stratification.

![Fig. 4a](image1)

![Fig. 4b](image2)

![Fig. 4c](image3)

![Fig. 4d](image4)

**Fig. 4.** Experimental dependencies of the film thickness, $h$, on time, $t$, for foam films formed in a SE cell from C16-SME solutions of concentrations denoted in the figure: (a) C16-SME alone; (b) with added 10 mM NaOH; (c) with added 2.4 mM CaCl$_2$; (d) comparison of the three drainage curves at 100 mM C16-SME.

The comparison of the drainage curves for films formed from 100 mM $C_n$-SME (see Figs. 4d, A1d, and A2d) shows that the drainage is the fastest for the films with NaOH, whereas the drainage is the slowest for the films with CaCl$_2$. In the latter case, the Ca$^{2+}$
counterions neutralize more efficiently the electrostatic repulsion between the headgroups of the adsorbed SME molecules, which leads to more densely packed adsorption layers [22] that become more rigid (almost tangentially immobile) and slow down the film drainage [49]. In contrast, the added NaOH ionizes the admixtures of fatty acids, which leads to lower surface dilatational elasticity and faster film drainage. The effect of NaOH is smaller than that of Ca$^{2+}$, because the amount of fatty acid admixtures in SME is relatively low [21].

![Fig. 5](image)

Fig. 5. Dependence of the experimental film thickness $h_j$ corresponding to $j = 0, 1, 2,$ and 3 layers of micelles in the film, on the SME concentration: (a) C12-SME; (b) C14-SME, and (c) C16-SME. For each $h_j$, the upper curves with empty symbols and the lower curves with full symbols correspond to solutions with 0 and 2.4 mM CaCl$_2$, respectively. The lines are guides to the eye.

Fig. 5 summarizes the results from all experiments with stratifying films from $Cn$-SME solutions without and with added CaCl$_2$. As seen in the figure, the effect of 2.4 mM CaCl$_2$ on the values of the film thickness is not so
significant. (The effect of CaCl₂ on the film drainage time in Fig 4d is more significant). The values of \( h_j \) for the solutions with added 10 mM NaOH turned out to be practically the same as those with 2.4 mM CaCl₂; see Fig A3 in Appendix A.

The data for \( h_j \) \((j = 0,1,2,3)\) shown in Fig. 5 serve as a basis for determining the micellar properties (see below). For this reason, the values of \( h_j \) were experimentally determined with a high precision. Each value of \( h_j \) in Figs. 5 and A3 represents the average from at least 30 measurements of \( h\)-vs.-\( t \) curves, like those in Fig. 4. As seen in Fig. 5, the error bars are relatively small.

As already mentioned, for a solution of given composition the heights of the steps are equal in the framework of the experimental error: \( h_3 - h_2 \approx h_2 - h_1 \approx h_1 - h_0 \approx \Delta h \). From the values of \( \Delta h \), the micelle aggregation number, \( N_{\text{agg}} \), surface electrostatic potential, \( \phi \), and ionization degree, \( \alpha \), have been determined. The obtained mean values of \( \Delta h \) and \( h_0 \) for \( Cn\)-SME without and with additives are listed in the second and third columns of Table 1. The values of \( h_0 \) serve for an independent verification of the model used to calculate \( N_{\text{agg}} \), \( \phi \), and \( \alpha \). The values of \( \Delta h \) in Table 1 are more than two times greater than the micelle hydrodynamic diameter that can be estimated as \( 2(h_1 + d) \); see Fig. 2 and the related text. This difference is due to the fact that the electric double-layer around the micelle contributes to \( \Delta h \) [28,32].

![Fig. 6](image.png)

**Fig. 6.** Plot of experimental data for the final equilibrium film thickness, \( h_0 \), vs. the C16-SME concentration, \( C_s \), at several different concentrations of added fatty acids denoted in the figure. The theoretical solid line is drawn without using any adjustable parameters; see the text.

To verify whether small amounts of nonionic surfactant admixtures can influence the thickness of the investigated films, we measured the final equilibrium film thickness, \( h_0 \), vs. the C16-SME concentration, \( C_s \), for several different concentrations of added fatty acids: 0, 4 and 8 mol% palmitic acid (HC16), and 8 mol% myristic acid (HC14) relative to the C16-SME.
Table 1. Measured step height, $\Delta h$, and final film thickness, $h_0$, and calculated concentration of surfactant monomers, $c_1$, micelle surface electrostatic potential, $\varphi$, degree of ionization, $\alpha$, and aggregation number, $N_{agg}$, for micellar solutions of Cn-SME.

| $C_S$ (mM) | $\Delta h$ (nm) | $h_0$ (nm) | $c_1$ (mM) | $-\varphi$ (mV) | $\alpha$ | $N_{agg}$ | $N_{max}$ |
|------------|-----------------|-------------|-------------|-----------------|---------|-----------|-----------|
| C12-SME    |                 |             |             |                 |         |           |           |
| 50         | 13.1±0.15       | 16.7±0.20   | 8.50        | 99.6            | 0.240   | 56±1.9    | 56        |
| 100        | 10.0±0.11       | 13.2±0.15   | 5.94        | 93.5            | 0.208   | 57±1.9    | 56        |
| C12-SME + 2.4 mM CaCl$_2$ | | | | | | |
| 50         | 13.1±0.16       | 15.7±0.19   | 7.33        | 96.8            | 0.228   | 58±2.1    | 56        |
| 100        | 10.1±0.12       | 12.6±0.14   | 5.37        | 91.5            | 0.201   | 59±2.1    | 56        |
| C12-SME + 10 mM NaOH | | | | | | |
| 50         | 13.0±0.15       | 15.3±0.15   | 6.92        | 95.7            | 0.224   | 57±2.0    | 56        |
| 100        | 10.0±0.12       | 12.4±0.14   | 5.16        | 90.7            | 0.198   | 57±2.1    | 56        |
| C14-SME    |                 |             |             |                 |         |           |           |
| 30         | 15.8±0.19       | 20.8±0.22   | 1.45        | 109             | 0.287   | 68±2.5    | 74        |
| 50         | 13.2±0.16       | 17.2±0.20   | 1.06        | 103             | 0.255   | 68±2.5    | 74        |
| 100        | 10.6±0.12       | 13.4±0.16   | 0.677       | 97.3            | 0.216   | 71±2.4    | 74        |
| C14-SME + 2.4 mM CaCl$_2$ | | | | | | |
| 30         | 15.9±0.19       | 18.9±0.20   | 1.10        | 104             | 0.262   | 70±2.5    | 74        |
| 50         | 13.4±0.16       | 16.1±0.20   | 0.869       | 99.4            | 0.239   | 71±2.5    | 74        |
| 100        | 10.7±0.13       | 12.8±0.15   | 0.602       | 93.1            | 0.207   | 73±2.7    | 74        |
| C14-SME + 10 mM NaOH | | | | | | |
| 30         | 15.6±0.18       | 18.2±0.19   | 0.996       | 102             | 0.254   | 66±2.3    | 74        |
| 50         | 13.1±0.15       | 15.7±0.18   | 0.808       | 98.0            | 0.234   | 67±2.3    | 74        |
| 100        | 10.5±0.12       | 12.6±0.14   | 0.575       | 92.1            | 0.204   | 69±2.4    | 74        |
| C16-SME    |                 |             |             |                 |         |           |           |
| 30         | 16.5±0.20       | 19.7±0.20   | 0.141       | 107             | 0.280   | 81±2.9    | 94        |
| 50         | 14.1±0.18       | 16.2±0.19   | 0.0996      | 101             | 0.246   | 84±3.2    | 94        |
| 100        | 11.3±0.15       | 12.4±0.13   | 0.0620      | 92.0            | 0.206   | 87±3.5    | 94        |
| C16-SME + 2.4 mM CaCl$_2$ | | | | | | |
| 30         | 16.7±0.20       | 18.0±0.20   | 0.109       | 102             | 0.257   | 84±3.0    | 94        |
| 50         | 14.2±0.18       | 15.3±0.18   | 0.0836      | 97.1            | 0.232   | 86±3.3    | 94        |
| 100        | 11.3±0.14       | 12.0±0.14   | 0.0561      | 90.0            | 0.199   | 87±3.2    | 94        |
| C16-SME + 10 mM NaOH | | | | | | |
| 30         | 16.3±0.20       | 17.4±0.18   | 0.0994      | 100             | 0.249   | 78±2.9    | 94        |
| 50         | 13.8±0.17       | 14.9±0.16   | 0.0783      | 95.8            | 0.227   | 79±2.9    | 94        |
| 100        | 11.0±0.13       | 11.8±0.12   | 0.0539      | 89.2            | 0.196   | 80±2.8    | 94        |
The pH of the studied solutions is \( \approx 5 \), so that a considerable part of the added fatty acid is present in protonated (nonionic) form. The experimental results, which are shown in Fig. 6, refer to concentrations above the CMC and indicate that the presence of small nonionic admixtures produces a negligible effect on the equilibrium film thickness, \( h_0 \).

It should be noted that the presence of NaCl as an admixture in Cn-SME contributes to the screening of electrostatic repulsion, which has affected the experimental values of \( \Delta h \) and \( h_0 \) in Table 1; they are lower than they would be in the absence of NaCl. (Note, however, that the predominant part of Na\(^+\) counterions in the studied solutions originates from the dissociation of Cn-SME molecules.) Hence the values of \( N_{agg} \) in Table 1, which are calculated from the measured \( \Delta h \) (see below), refer to the experimental Cn-SME samples, which contain NaCl admixtures. The presence of such admixtures is taken into account in our theoretical calculations of the surfactant monomer concentration, \( c_1 \); micelle surface potential, \( \varphi \), and ionization degree, \( \alpha \); see Table 1 and Section 4. The theoretically predicted dependence of \( h_0 \) on the SME concentration, \( C_S \), is in excellent agreement with the experimental \( h_0 \) vs. \( C_S \) dependence; see Section 4.2.

### 4. Theoretical section

#### 4.1. Estimation of \( N_{agg} \), \( \varphi \) and \( \alpha \)

For electrically charged spherical micelles (and more generally – colloidal particles), the height of the stratification steps, \( \Delta h \), is simply connected to the micelle bulk number concentration, \( c_{mic} \), viz. \( \Delta h = c_{mic}^{-1/3} \). This law has been experimentally established in a series of studies with thin foam films using the SE cell [31,32]; by CP-AFM measurements supported by SANS and SAXS experiments [50–54], as well as theoretically predicted by density functional calculations and MC simulations [50–55]. In the case of extended polyelectrolyte chains of concentration \( c_p \), another law, \( \Delta h \propto c_p^{-1/2} \), has been found experimentally [56,57].

The micelle concentration can be expressed as \( c_{mic} = (C_S - c_1)/N_{agg} \) where, as usual, \( C_S \) is the total input surfactant concentration and \( c_1 \) is the concentration of surfactant monomers in equilibrium with the micelles, both of them expressed as number of molecules per unit volume. Then, from the relation \( \Delta h = c_{mic}^{-1/3} \) one derives [25,28]:

\[
N_{agg} = (C_S - c_1)(\Delta h)^3
\] (5)
Eq. (5) enables one to determine the mean micelle aggregation number, \( N_{\text{agg}} \), from the experimental height of the step, \( \Delta h \). In Refs. [25,28], Eq. (5) with \( c_1 \approx \text{CMC} \) was used to estimate the aggregation number of several ionic surfactants from the measured \( \Delta h \). The relation \( c_1 \approx \text{CMC} \) is a good approximation for surfactants of low CMC, for which stratification is observed at \( C_S \gg \text{CMC} \). However, this is not a good approximation for surfactants with relatively high CMC, like C12-SME, for which CMC = 14.1 mM [21]. In addition, the relation \( c_1 = \text{CMC} \) is satisfied at the critical micellization concentration, where the first micelles appear. However, stratifying films are observed at surfactant concentrations, which are considerably higher than the CMC. At such concentrations, \( c_1 < \text{CMC} \), insofar as the concentration of surfactant monomers, \( c_1 \), decreases with the rise of \( C_S \) at \( C_S > \text{CMC} \) [58].

To achieve accurate determination of \( N_{\text{agg}} \) from Eq. (5) and to find out how significant is the decrease of \( c_1 \) at concentrations above the CMC, we applied the complete micellization theory from Ref. [58], as described in Appendix B. This task is facilitated by the fact that all necessary micellization parameters have been already determined in Ref. [21]; see Table B1 in Appendix B. The micellization theory from Ref. [58] yields also the other two parameters of interest: the micelle surface electric potential, \( \varphi \), and the micelle degree of ionization, \( \alpha \). Furthermore, one could find the micelle electric charge, \( q = \alpha N_{\text{agg}} e \), where \( e \) is the electronic charge.

The values of \( c_1 \), \( \varphi \) and \( \alpha \) for the investigated micellar solutions, determined as explained in Appendix B, are given in Table 1. Because of the lowering of \( c_1 \) at surfactant concentrations above the CMC, the values of \( c_1 \) in the investigated concentration range are markedly lower than the CMC values, which are 14.1, 4.0 and 1.1 mM, for C12-, C14- and C16-SME, respectively [21]. In view of Eq. (5), this effect is important for C12-SME, for which the calculated variation of \( c_1 \) as a function of \( C_S \) is shown in Fig. 7. Similar dependencies for C14- and C16-SME are shown in Fig. B1 in Appendix B. As seen in Fig. 7, \( c_1 \) decreases from 13.5 mM at \( C_S = 20 \) mM to 8 mM at \( C_S = 100 \) mM. In other words, even at 100 mM C12-SME, \( c_1 \) is 8% of \( C_S \), so that its effect on the calculated \( N_{\text{agg}} \) is not negligible; see Eq. (5). We calculated also plots of \( c_1 \) vs. \( C_S \) assuming the presence of nonionic admixtures in C12-SME. As seen in Fig. 7, the effect of these admixtures is rather small, practically negligible.
The calculated surfactant monomer concentration, $c_1$, as a function of the total C12-SME concentration, $C_S$, above the CMC for different mol% of nonionic admixture (C12 unsulfonated methyl ester) denoted in the figure.

Fig. 7. Calculated surfactant monomer concentration, $c_1$, as a function of the total C12-SME concentration, $C_S$, above the CMC for different mol% of nonionic admixture (C12 unsulfonated methyl ester) denoted in the figure.

The physical reason for the decrease of $c_1$ with the rise of total surfactant concentration (Fig. 7) is the fact that with the increase of $C_S$ the ionic strength of solution, $I$, also increases owing to the counterions dissociated from the newly formed micelles. The increased ionic strength provides better screening of the electrostatic repulsion between the surfactant molecules incorporated in the micelles, thus, decreasing their electrochemical potential. As a result, the micelle–monomer equilibrium is shifted toward the micelles, i.e. the concentration of surfactant in micellar form increases, whereas the concentration of monomers, $c_1$, decreases. These processes are described by the system of equations presented in Appendix B.

The solution of the aforementioned system of equations yields also the values of the micelle electrostatic potential $\phi$ and ionization degree $\alpha$; see Table 1. One sees that $\phi$ is in the range between 89 and 109 mV and decreases with the rise of total surfactant concentration $C_S$. $\phi$ decreases also with the addition of electrolytes, CaCl$_2$ and NaOH, the effect of NaOH being slightly stronger because of (i) the higher concentration of NaON and (ii) lower binding energy of Ca$^{2+}$ in the Stern layer (to the sulfonate headgroups of SME) as compared to Na$^+$; see Ref. [22]. In this respect, SME is unique among the anionic surfactants, and this fact correlates with its high hard-water tolerance.

The micelle ionization degree, $\alpha$, varies in the range between 0.19 and 0.29 (Table 1). This relatively low degree of ionization is due to the binding (adsorption) of Na$^+$ and Ca$^{2+}$ counterions on the surfactant headgroups expressed on the micelle surface. With the increase of the total surfactant concentration and the concentrations of added electrolytes (CaCl$_2$ and NaOH), $\alpha$ decreases, as it should be expected.
Next, with the values of $C_S$, $\Delta h$ and $c_1$ in Table 1 we calculated the micelle aggregation number, $N_{agg}$, using Eq. (5). $N_{agg}$ increases with the increase of surfactant chainlength and concentration (Table 1). Thus, $N_{agg}$ varies in the range 56 – 59 for C12-SME; 67 – 73 for C14-SME, and 78–87 for C16-SME. The concentrations of added electrolytes, CaCl$_2$ and NaOH, are relatively low as compared to the total solutions’ ionic strength, and their effect on the values of $N_{agg}$ is relatively weak.

Another way to estimate the micelle aggregation number is to assume that the radius of the micelle hydrocarbon core, $R$, is equal to the length of the extended surfactant tail, $l$, and to divide the volume of micelle hydrocarbon core to the volume of a single tail $[59]$:

$$N_{max} = \frac{4\pi l^3}{3v}, \quad v = (27.4 + 26.9n) \times 10^{-3} \text{ nm}^3$$

(6)

Here, the volume of the surfactant tail, $v$, and its extended tail, $l$, are estimated by using the Tanford formulas $[43,59]$: see Eq. (6) for $v$ and Eq. (4) for $l$. The aggregation number determined from Eq. (6) is denoted $N_{\text{max}}$. In reality $R \leq l$, so that $N_{agg} \leq N_{\text{max}}$ for a spherical micelle. (For elongated ellipsoidal micelles we could have $N_{agg} > N_{\text{max}}$.)

As seen in Table 1, for C12-SME we have $N_{agg} \approx N_{\text{max}}$ in the framework of the experimental accuracy. In other words, in the micelles of C12-SME a part of the surfactant tails are completely extended, so that $R \approx l$. In contrast, for C14- and C16-SME $N_{agg}$ is markedly smaller than $N_{\text{max}}$, i.e. the surfactant chains in the micelle are not completely extended. This could be due to a gain of chain-conformational free energy $[60,61]$.

It should be also noted that the obtained values of $N_{agg}$ for spherical micelles from $C_n$-SME (without additives; see Table 1) comply very well with a straight line:

$$N_{agg} = 7.75n - 3.72, \quad n = 12,14,16$$

(7)

The slope of this dependence, $7.75 \pm 0.14$, indicates that $N_{agg}$ increases with ca. eight molecules upon the addition of one CH$_2$ group to the hydrocarbon tail of $C_n$-SME. The values of aggregation number extrapolated from Eq. (7) for $n = 10$ and 18 are $N_{agg} = 40$ and 102, respectively.
4.2. Verification of the theoretical model

The experimental values of the final equilibrium thickness of the film $h_0$ in Table 1 give the possibility for an independent verification of the theoretical model, which has been already used to calculate $N_{agg}$, $\varphi$ and $\alpha$. Using the values of the latter three quantities, determined as explained in Appendix B, we can apply the thin-liquid-film theory from Refs. [25,28] (which accounts for the presence of ionic micelles in the bulk) to calculate $h_0$. If the theoretical values of $h_0$ obtained in this way coincide with the experimental values of $h_0$, this would confirm the correctness of the used theoretical model and the values of $N_{agg}$, $\varphi$ and $\alpha$ given in Table 1.

The theoretical calculation of $h_0$ is based on the force balance at the surfaces of the liquid film, which states that the disjoining pressure of the film should counterbalance the external capillary pressure (the sucking pressure applied in the SE cell), $P_c$:

$$\Pi_{el}(h_0) + \Pi_{vw}(h_0) = P_c$$

Here, $\Pi_{el}$ and $\Pi_{vw}$ are the electrostatic and van der Waals components of disjoining pressure. The capillary pressure can be easily estimated [32], $P_c \approx 2\sigma/R_{in}$, where $R_{in} = 1.5$ mm is the inner radius of the SE cell, and $\sigma$ is the surface tension of the solution; see Refs. [21,22]. The dependences of $\Pi_{el}$ and $\Pi_{vw}$ on $h_0$ can be described by formulas given in Ref. [25]. In particular, $\Pi_{el}$ depends on $c_1$, $c_{mic}$, $\alpha$, and $N_{agg}$, which have been determined in Appendix B; see also Appendix C. The reason for this dependence is the fact that the counterions, which are dissociated from the micelles of the ionic surfactant in the bulk, have to be taken into account when calculating the electrostatic component of disjoining pressure. As known, $\Pi_{el}$ equals the difference between the osmotic pressures of all ions in the midplane of the thin film and in the bulk; see Refs. [25,28] for details. We recall that the film of thickness $h_0$ does not contain surfactant micelles.

Substituting the theoretical expressions for $\Pi_{el}(h_0)$ and $\Pi_{vw}(h_0)$ in Eq. (8) and solving it numerically, we determine $h_0$ for each given $C_S$. The full system of equations and the principles of the computational procedure are described in Appendix C.
The lines in Fig. 8 present the theoretical dependencies of $h_0$ on $C_S$ for C12- and C14-SME with 0 and 10 mM NaOH, calculated without using any adjustable parameters. Similar results for C16-SME are shown in Fig. 6. In Fig. 8, the two curves for the case with 10 mM NaOH correspond to smaller $h_0$ because the ionic strength is higher in this case, which leads to a stronger suppression of the electrostatic repulsion between the two film surfaces. The symbols in Fig. 8 correspond to the values of $h_0$ in Table 1. The excellent agreement between the experimental points and the theoretical curves in Fig. 8 for C12- and C14-SME and in Fig. 6 for C16-SME confirms the validity of the used theoretical model and represents a strong argument in favor of the correctness of the calculated $N_{agg}$, $\varphi$, and $\alpha$ values in Table 1.

![Figure 8](image)

**Fig. 8.** Dependence of the final equilibrium thickness of the foam film on the total surfactant concentration, $C_S$. The symbols represent experimental values of $h_0$ from Table 1. The curves are the theoretical dependencies of $h_0$ on $C_S$, calculated without using any adjustable parameters.

The calculations of the dependencies of $h_0$ on $C_S$ in Appendix C include also calculation of the electric potential $\varphi_s$ of the film surfaces and the occupancy of the Stern layers at the film surfaces with bound counterions, $\theta$. (It should be noted that $\theta = 1 - \alpha_s$, where $\alpha_s$ is the ionization degree of the film surfaces.) As an example, the calculated dependencies of $\varphi_s$ and $\theta$ on the total surfactant concentration $C_S$ are shown in Fig. 9 for the case of C16-SME. As seen in the figure, the magnitude of the surface potential $\varphi_s$ markedly decreases from 172 mV at $C_S = 2$ mM (just above the CMC) to 93 mV at $C_S = 100$ mM (the latter value being close to the micelle potential $\varphi = 92$ mV at $C_S = 100$ mM; see Table 1). This decrease of $\varphi_s$ is accompanied with an increase of the occupancy of the Stern layer from $\theta = 0.50$ at $C_S = 2$ mM to $\theta = 0.79$ at $C_S = 100$ mM. Hence, the decrease of $h_0$ with the rise of $C_S$ (Figs. 6 and 8) is related not only to the increased Debye screening in the diffuse electric double layer inside the film, but also to the increase of counterion binding to the film surfaces.
4.3. Micellar packing parameter and area per headgroup

The formation of micellar aggregates of different shape is related to the geometrical packing parameter, which can be estimated as follows [59]:

\[
p = \frac{v}{al}
\]

where \( v \) is the volume of the hydrophobic chain of a surfactant molecule, \( l \) is its extended length and \( a \) is the area per headgroup at the surface of micelle hydrocarbon core. It should be noted that the exact definition of \( p \) contains the radius of micelle hydrocarbon core, \( R \), instead of the length of the extended chain, \( l \). Here, the assumption \( R \approx l \) was used as an approximation. In reality, \( R \leq l \) and the value of \( R \) can be determined by minimization of micelle free energy; see e.g. Ref. [61]. The values of \( l \) and \( v \) calculated from Tanford [43] formulas, Eqs. (4) and (6), are given in Table 2.

Table 2. Geometrical parameters of Cn-SME molecules and micellar packing parameter

| Surfactant | \( v \) (nm\(^3\)) | \( l \) (nm) | \( a_c \) (nm\(^2\)) | \( a \) (nm\(^3\)) (spherical micelle) | \( p_c \) |
|------------|------------------|-------------|----------------|----------------------------------|---------|
| C12-SME    | 0.350            | 1.672       | 0.37           | 0.628                            | 0.566   |
| C14-SME    | 0.404            | 1.925       | 0.37           | 0.629                            | 0.567   |
| C16-SME    | 0.458            | 2.178       | 0.37           | 0.630                            | 0.568   |

In Table 2, \( a_c 0.37 \) nm\(^2\) is the area per molecule in a closely packed adsorption layer, which was determined from the adsorption isotherms of Cn-SME at the air/water interface [22]. The values of the packing parameter, \( p_c \), are calculated from Eq. (9) with \( a = a_c \). We recall that
$p = \frac{1}{3}, 1/2$ and 1 for spherical, cylindrical and lamellar micelles, respectively. The values of $p_c$ correspond to the packing parameter of hypothetical $Cn$-SME micelles, for which the electrostatic repulsion between the headgroups is completely switched off. The obtained values of $p_c$, which are slightly above 0.5, indicate that $Cn$-SME could form wormlike micelles at sufficiently high concentrations of added electrolyte.

At not so high ionic strengths, the electrostatic repulsion between the surfactant headgroups is significant and promotes the formation of spherical micelles, as indicated by the film-stratification experiments described above. For spherical micelles $p = 1/3$ \[59,61\]. Then, using Eq. (9) and the values of $v$ and $l$ in Table 2 one can calculate the area per surfactant molecule, $a$, at the surface of a spherical micelle. As seen in Table 2, the values of $a$ estimated in this way are with more than 50% greater than the area $a_c$ per surfactant molecule in a closely packed monolayer.

5. Micelle growth in mixed solutions of $Cn$-SME and CAPB

In a previous study \[22\] it was shown that the CMC of mixed solutions of $Cn$-SME and CAPB obeys the law of ideal mixing. Here, we extend this analysis to concentrated solutions of $Cn$-SME and CAPB to investigate whether the mixing of these two surfactants gives rise to the growth of giant micelles, as this has been observed with mixed solutions of other anionic surfactants with CAPB \[45,46,47,62,63\]. The growth of such micelles is usually detected as a considerable increase of solution’s viscosity, from $10^2$ to $10^6$ times the viscosity of water. Most frequently, this rise of viscosity is due to the formation of long and entangled wormlike micelles that can be proved by cryogenic transmission electron microscopy (cryo-TEM) \[45,46\].

In our experiments, we mixed $Cn$-SME and CAPB ($n = 14, 16$) at different weight ratios. At sufficiently high concentrations, an increase of viscosity by orders of magnitude was detected by the rotational rheometer (see Section 2.2). As an illustration, Fig. 10 shows typical data from steady shear measurements of the apparent viscosity $\eta$ vs. the shear rate $\dot{\gamma}$. One sees that the solutions exhibit non-Newtonian behavior. At low values of $\dot{\gamma}$, a plateau is observed, which defines the zero-shear viscosity, $\eta_0$. At higher values of $\dot{\gamma}$, we observe shear thinning with linear dependence of $\eta$ on $\dot{\gamma}^{-1}$. Such rheological behavior is typical for wormlike micelles, but could be observed also with branched multi-connected micelles; see e.g. Ref. [45].
Fig. 10. Plots of experimental data for the apparent viscosity, $\eta$, vs. the shear rate $\dot{\gamma}$ for mixed micellar solutions of C$n$-SME and CAPB at different total surfactant concentrations and weight ratios of the two surfactants. The dashed line corresponds to $\eta \propto \dot{\gamma}^{-1}$.

Fig. 11 summarizes the results of our systematic rheological measurements with mixed solutions of C14- and C16-SME with CAPB. One sees that $\eta_0$ increases with the rise of the total surfactant concentration and of the fraction of CAPB in the mixture. Under the same conditions, the solutions with C16-SME are more viscous than those with C14-SME.

Fig. 11. Plots of experimental data for the zero-shear viscosity, $\eta_0$, vs. the total surfactant concentration for mixed solutions of C$n$-SME and CAPB at four different weight ratios of these two surfactants shown in the figure: (a) C14-SME + CAPB; (b) C16-SME + CAPB.

The solutions of C$n$-SME alone (denoted with 1:0 in Fig. 11) exhibit Newtonian behavior. At a concentration of 16 wt%, their viscosity is 2.0 mPa·s for C14-SME and 5.2 mPa·s for C16-SME.

In this series of experiments, the maximal viscosities have been measured at 1:1 C$n$-SME/CAPB (Fig. 11). At total surfactant concentration of 16 wt%, the zero-shear viscosity is $\eta_0 = 16$ Pa·s for C14-SME and $\eta_0 = 810$ Pa·s for C16-SME.
Note that the data in Fig. 11 refer to the viscosity of mixed solutions of Cn-SME and CAPB without any additives. In view of Refs. [18,45,46,47,63], one could expect that the addition of NaCl or cosurfactants (e.g. fatty acids and/or fragrances) one could additionally increase the viscosity of the mixed Cn-SME + CAPB solutions, and especially of those with lower content of CAPB. It should be noted that CAPB itself contains admixture of NaCl. Thus, 1 wt% CAPB contains 0.164 wt% NaCl, which is 28 mM NaCl. However, this amount of NaCl is relatively small. Typically, NaCl is used as thickening agent at concentrations in the range of 100 – 1000 mM [18]. Hence, the large values of $\eta_0$ in Fig. 11 are mostly due to the synergism of Cn-SME and CAPB with respect to the micelle growth, rather than to the presence of NaCl admixture in CAPB.

The typical viscosity of a shampoo formulation is of the order of 5 Pa⋅s. Hence, the data in Fig. 11 indicate that C14- and C16-SME in mixture with CAPB represent a promising system for formulations in personal-care and house-hold detergency. The structure of the formed micelles and the effect of various additives/cosurfactants could be a subject for subsequent studies.

6. Conclusions

The present paper is the first systematic study on stratifying films from solutions of sulfonated methyl esters, Cn-SME, $n = 12, 14, 16$, and on the properties of their micelles, such as aggregation number, $N_{agg}$, surface electric potential, $\phi$, and ionization degree, $\alpha$. The effects of surfactant concentration and chainlength, as well as of added CaCl$_2$ and NaOH on these micellar properties are investigated. Following the method developed in Refs. [25,28], we determined $N_{agg}$, $\phi$, and $\alpha$, by theoretical analysis of the data for stratifying films (Table 1). For the accurate determination of $N_{agg}$, we calculated the variation of the monomer concentration, $c_1$, using the detailed micellization model from Ref. [58]. The results show that in the concentration range between 30 and 100 mM Cn-SME, spherical micelles are formed with aggregation number increasing with the surfactant concentration and chainlength in the range of 56–59 for C12-SME; 66–73 for C14-SME, and 78–87 for C16-SME. The addition of 2.4 mM CaCl$_2$ (as in hard water) does not produce a significant effect on the micellar properties, in agreement with the fact that the SMEs are among the surfactants of the lowest hard-water sensitivity [7,64,65].
As an independent verification of the model used to interpret the thin-film data, we compared the theoretically calculated and experimentally measured equilibrium film thickness, \( h_0 \). The obtained excellent agreement between theory and experiment without using any adjustable parameters (Figs. 6 and 8) is a strong argument in favor of the correctness of the used model and the determined values of \( N_{\text{agg}}, \varphi \) and \( \alpha \).

Furthermore, in contrast with a previous finding [22] that the mixed solutions of SME and CAPB exhibit ideal mixing with respect to the CMC values, we established that these two surfactants exhibit a strong synergism with respect to the micelle growth at higher surfactant concentrations. The obtained high values of the zero-shear viscosity, up to 810 Pa\( \cdot \)s, indicate the growth of giant mixed micelles, most probably wormlike, like those observed in the mixed solutions of other anionic surfactants with CAPB [45,46]. To the best of our knowledge, this is the first study where synergistic rise of viscosity is reported for mixed solutions of \( C_n \)-SME with a zwitterionic surfactant. These results imply that the mixed solutions of SME and CAPB represent a promising system for formulations in personal-care and house-hold detergency, having in mind also the other useful properties of SME, such as high hard water tolerance, biodegradability and skin compatibility. For example, \( C_n \)-SMEs could serve as substituents of sodium laureth sulfates (SLES) in shampoo formulations.

An interesting continuation of this study would be to investigate both experimentally and theoretically the reasons for the strong synergism with respect to micelle growth in the mixed \( C_n \)-SME – CAPB solutions and to reveal which component of the micellar free energy is responsible for the observed effects.

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Appendices A, B, and C. Supplementary data

Supplementary data associated with this article can be found, in the online version, at  

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