Hill, C., Umetsu, Y., Fujita, K., Endo, T., Sato, K., Yoshizawa, A., Rogers, S. E., Eastoe, J., & Sagisaka, M. (2020). Design of Surfactant Tails for Effective Surface Tension Reduction and Micellization in Water and/or Supercritical CO₂. *Langmuir*, 36(48), 14829-14840. [48]. <https://doi.org/10.1021/acs.langmuir.0c02835>

Peer reviewed version

Link to published version (if available):
[10.1021/acs.langmuir.0c02835](https://doi.org/10.1021/acs.langmuir.0c02835)

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Design of surfactant tails for effective surface tension reduction and micellization in water and/or supercritical CO₂

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Abstract

Interfacial properties and water-in-CO₂ (W/CO₂) microemulsion (μ E) formation with double and novel triple tail surfactants bearing trimethylsilyl (TMS) groups in the tails are investigated. Comparisons of these properties are made with those for analogous hydrocarbon (HC) and fluorocarbon (FC) tail surfactants. Surface tension measurements allowed for critical micelle concentrations (CMC) and surface tensions at the CMC (γ_{CMC}) to be determined, resulting in the following trend in surface activity FC > TMS > HC. Addition of a third surfactant tail gave rise to increased surface activity, and very low γ_{CMC} values were recorded for the double/ triple tail TMS and HC surfactants. Comparing effective tail group densities (ρ_{layer}) of the respective surfactants allowed for understanding of how γ_{CMC} is affected by both the number of surfactant tails and the chemistry of the tails. These results highlight the important role of tail group chemical structure on ρ_{layer} for double tail surfactants. For triple tail surfactants, however, the degree to which ρ_{layer} is affected by tail group architecture is harder to discern, due to the formation of highly dense layers. Stable W/CO₂ μ Es were formed by both the double and triple tail TMS surfactants. High pressure small-angle neutron scattering (HP-SANS) has been used to characterize the nanostructures of W/CO₂ μ Es formed by the double and triple tail surfactants, and at constant pressure and temperature, the aqueous cores of the microemulsions were found to swell with increasing water-to-surfactant ratio (W_0). A maximum W_0 value of 25 was recorded for the triple tail TMS surfactant, which is very rare for non-fluorinated surfactants. These data therefore highlight important parameters required to design fluorine-free environmentally responsible surfactants for stabilizing W/CO₂ μ Es formation.

Keywords: Double tail surfactants, triple tail surfactants, trimethylsilyl surfactants, supercritical CO₂, solubilizing power, Small-Angle Neutron Scattering

Introduction

The emission of volatile organic compounds (VOCs) is known to be detrimental to the environment. As such, investigations into the development of novel greener solvent media have been of great interest.¹⁻⁴ From these investigations, supercritical CO₂ (scCO₂) has emerged as a promising substitute for VOCs, offering both green and energy saving properties, as well as being cheap, non-toxic and non-flammable.⁵ As scCO₂ can dissolve certain low molecular weight and non-polar materials, it is routinely employed as a solvent for various commercial processes, such as coffee decaffeination, chromatography, extraction, organic synthesis and nanomaterials processing.⁵ However, developing scCO₂ as a “universal solvent” is hindered due to its non-polar nature, in which polar and or high molecular weight compounds are only sparingly soluble or insoluble in the solvent.^{5,6} Hence, one of the important issues for scCO₂ applications is to improve the solubility of polar materials in scCO₂ solvency. By achieving this, improvements will enable broadening of scCO₂-based technologies for industries to substitute volatile organic compounds (VOCs).

The solvent properties of scCO₂ can be improved through incorporation of self-assembling surfactants or amphiphilic polymers in a CO₂ continuous phase to form water-in-scCO₂ (W/CO₂) microemulsions.^{3,7-11} This provides enhanced flexibility for modification of CO₂ properties such as wettability, viscosity and interfacial tension. As such, significant efforts have been devoted to designing these CO₂-philic materials which are effective W/CO₂ microemulsion stabilizers.^{3,7,12-17} New advances in surfactant molecular design have found low surface energy (LSE) surfactants to be efficient stabilizers for W/ CO₂ microemulsions, transforming it from a very weak solvent medium into a universal environmentally benign fluid, capable of carrying numerous CO₂-phobic materials.¹⁸

Several models are used to quantify the solubility of surfactants in scCO₂, the most popular being fractional free volume (FFV).¹⁹ FFV is calculated directly from surfactant tail geometry and surface coverage, with low FFV values generally being found to be a necessary condition for W/CO₂ microemulsion formation, due to decreased interfacial tension, reduced overlap between tails and increased interfacial curvature.¹⁹ In addition to this, potential surfactants for W/CO₂ microemulsion

stabilisation are generally investigated in terms of surface tension reduction at the air/water interface, due to the experimental difficulty in determining the effect on W/ CO₂ interfacial tensions under high pressure conditions.²⁰ Although the air/ water interface is not a perfect model for the W/CO₂ interface, it is an easy to access and study environment that allows comparison of adsorption and surface-packing properties of known CO₂-philic materials.²⁰

In earlier studies, several surfactants with high levels of fluorination were found to be compatible with CO₂ and have a high interfacial activity at the W/ CO₂ interface, leading to the formation of stable W/ CO₂ μ Es.^{3,12,21} However, it is well known that FC surfactants are both very expensive and have a negative impact on the environmental issues due to persistence, bioaccumulation and toxicity.²² As a way of reducing the level of fluorination in these environmentally burdensome surfactants, approaches have been made to design so-called hybrid surfactants consisting of both FC and hydrocarbon (HC) tails featuring the same headgroup.^{23,24} For example, sodium 4H,4H,5H,5H, 5H-pentafluoropentyl-3,5,5-trimethyl-1-hexyl)-2-sulfosuccinate (Hybrid CF₂/AOT4), contains a low amount of fluorine (18.8 wt%) and can stabilize W/CO₂ microemulsions up to water-to-surfactant molar ratio $W_0 = 10$ ([surfactant] = 0.05 mol dm⁻³). In addition to these low fluorine-containing hybrid surfactants, low surface energy hydrocarbon (HC) surfactants bearing highly methylated double or triple tails, and no fluorine, have been shown to effectively stabilize W/ CO₂ μ Es.^{3,12,25}

Highly branched HC surfactants, termed “*hedgehog*” surfactants have been reported to achieve aqueous surface tensions at the CMC (γ_{CMC}) of 24.6 mN m⁻¹,²⁶ which is lower than some surfactants (di-HCF₄ $\gamma_{\text{CMC}} = 26.8$ mN m⁻¹, di-CF₁ $\gamma_{\text{CMC}} = 27.0$ mN m⁻¹) commonly used to stabilize W/ CO₂ μ Es.²⁷ Some of these hedgehog-type surfactants have been successful for formation of W/ CO₂ μ Es. Early studies with commercially available AOT (sodium bis (2-ethyl- 1-hexyl) sulfosuccinate) in scCO₂ indicated lack of aggregation without co-surfactants.²⁸ However, methylation of the AOT surfactant tails (with 3,5,5-trimethylhexyl) to yield AOT4 (sodium bis (3,5,5-trimethyl-1-hexyl)-2-sulfosuccinate) enhanced solubility in scCO₂ ($P_{\text{trans}} = 500$ bar at 33 °C ; $W_0 = 0$;

[surfactant] = 0.10 mol dm⁻³).²⁸ Further developments of CO₂-phillic HC surfactants were found to be achieved through increasing the number of tails.²⁰ The triple-tail anionic surfactant TC14 (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate) showed aggregation in scCO₂ under mild conditions ($P_{\text{trans}} = 160$ bar, $W_0 = 0$, [surfactant] = 0.04 mol dm⁻³ at 25 °C). Additional success in this area was achieved through the use of single tail isostearyl surfactants bearing hedgehog-type tails.²⁵ The custom-synthesised surfactant SIS1 (sodium 2- (4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl sulfate) and was found to have excellent aqueous surface tension reduction ($\gamma_{\text{CMC}} = 25$ mN m⁻¹). Furthermore, SIS1 was found to show transparent phases identified as W/CO₂ μ Es (Winsor II or IV) up to $W_0 = \sim 50$, however relatively high temperature (>55 °C) and pressure (>210 bar) were still required.

A new group of surfactants showing promise for W/CO₂ microemulsion formation have trimethylsilyl (TMS)-terminated alkyl tails. Czajka *et al.* synthesised a series of sodium bis(trimethylsilyl-alkyl)sulfosuccinate based HC surfactants with short branched tail structures (TMS-methyl, TMS-ethyl and TMS-propyl) incorporating the TMS groups directly into the tails.²⁹ Each of the TMS surfactants were found to perform well in reducing aqueous surface tensions, the lowest value of $\gamma_{\text{CMC}} = 22.8$ mN m⁻¹ being achieved by the surfactant with the longest tail length (AOTSiC). The reason for the strong performance of these surfactants in terms of surface tension reduction is due to an increased surfactant tail volume and improvement in surfactant packing efficiency in the surface film. The aggregation behaviour of these TMS surfactants has been investigated in water through the use of Small-angle Neutron Scattering (SANS), and it was found that growth/elongation of the aggregate structures occurred with increasing tail length.²⁹

This study focuses on developing non-fluorinated (or low F-content) surfactants that are effective and efficient at both lowering aqueous surface tensions and stabilising W/CO₂ μ Es. The detailed investigations highlight the effects of tail structure, namely double vs triple-tail bearing branched HC-tail, branched TMS-tail and short FC-tail have on the interfacial properties in water, *n*-hexane and

CO₂ (surfactant structures shown in **Table 1**). These results will therefore aid in the design of novel surfactants for W/CO₂ μ Es with no (or minimal) environmentally hazardous fluorine.

Materials and methods

Materials

The synthesis and purification of double and triple tail hedgehog surfactants were all conducted as previously reported.^{20,24,29} For completeness the detail is given in the Supporting Information. Ultrapure water with a resistivity of 18.2 MΩ cm was generated from a Millipore Milli-Q Plus system. CO₂ (Ekika Carbon Dioxide Co., Ltd, 99.99%) and D₂O (Aldrich, 99.9 %) were used as received.

Table 1. Structure of the surfactants used in this study

Double Chain Surfactant	General Structure	R Group
AOTtBE		(CH ₃) ₃ C-CH ₂ CH ₂ -
AOTSiC		(CH ₃) ₃ Si-CH ₂ CH ₂ CH ₂ -
4FS(EO) ₂		F(CF ₂) ₄ CH ₂ CH ₂ -
Triple Chain Surfactant		
TCtBE		(CH ₃) ₃ C-CH ₂ CH ₂ -
TCSiC		(CH ₃) ₃ Si-CH ₂ CH ₂ CH ₂ -
4FT(EO) ₃		F(CF ₂) ₄ CH ₂ CH ₂ -

Methods

Surface tension

Surface tension measurements were carried out on a Krüss K100 force tensiometer using the Wilhelmy plate method at 35 °C. Glassware was washed thoroughly with a dilute Decon solution and then with wash cycles of methanol and ultra pure water. The cleaning cycles were repeated until the surface tension of water at 25°C was returned as 72 ± 0.2 mN m⁻¹. Stock surfactant solutions were prepared and aliquots were added to pure water to give desired concentrations. Each concentration measurement was repeated over a period of up to 30 min to ensure equilibration. Attempts were made to model the data using the Gibbs adsorption isotherm, which relates the surface excess to changes in the surface tension with concentration:

Equation 1:
$$\Gamma = - \frac{1}{2.303mRT} \frac{d\gamma}{d\log C}$$

Equation 2:
$$A_{\text{cmc}} = \frac{1}{\Gamma_{\text{cmc}} N_A}$$

where Γ is the surface excess, Γ_{cmc} is the surface excess at the critical micelle concentration (CMC), A_{cmc} is the area per molecule at the CMC, R is the gas constant, T is temperature, γ is surface tension C is concentration and N_A is the Avogadro number. The prefactor, m , is dependent on the surfactant type and structure, as well as the presence of extra electrolyte in the aqueous phase.^{30–32} For non-ionic and zwitterionic surfactants, a value of 1 for the pre-factor has been confirmed,^{31,32} and for 1:1 ionic surfactants, in the absence of extra electrolyte, $m = 2$ has been confirmed.³⁰ It has been shown that traces of multivalent ionic impurities can lead to changes in this prefactor, therefore leading to problems employing the Gibbs adsorption isotherm.³³ In this study, only anionic surfactants are being studied and therefore a prefactor of 2 has been used in all calculations as indicated in the literature.^{30–}

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High-Pressure Small-Angle Neutron Scattering (HP-SANS) Measurements and Data Analysis

Due to the range of neutron wavelengths available, time-of-flight SANS is suitable for studying the shapes and sizes of colloidal systems. HP-SANS is a particularly important technique for determining surfactant aggregation structures in scCO₂ and formation of W/CO₂ microemulsions. All HP-SANS measurements in this study were performed at 45 °C and 350 bar. The SANS 2D time-of-flight instrument, at the Rutherford Appleton Laboratory at ISIS UK, was used in conjunction with a stirred high- pressure cell (Thar). The path length was 10 mm, and the neutron beam diameter was 10 mm. The accessible Q range was 0.005–0.2 Å⁻¹, arising from an incident neutron wavelength of 2.2–14 Å. Measurements gave the absolute scattering cross section $I(Q)$ (cm⁻¹) as a function of momentum transfer Q (Å⁻¹), which is defined as $Q = (4\pi/\lambda)\sin \theta$. Absolute intensities were determined by calibrating the received signal from a partially deuterated polymer standard, which was corrected

for sample transmission as well as cell and solvent backgrounds. All data were normalized for transmission, empty cell, solvent background, and pressure induced changes in cell volume as previously reported.²³

Pre-weighed amounts of water (D₂O for 4FS(EO)₂, 4FS(EO)₃, 4FT(EO)₃ and TCtBE, and H₂O for AOTSiC and TCSiC) and surfactant were loaded into the Thar cell. CO₂ (11.3 g) was then introduced into the cell by high pressure pump, and the surfactant/ water/CO₂ mixture was pressurized up to 350 bar at 45 °C by decreasing the inner volume of the pressure cell. The surfactant concentrations were 16.7 mM for fluorinated surfactants and 50.0 mM for non-fluorinated surfactants in the scCO₂ condition. The higher concentrations for non-fluorinated surfactants were to ensure sufficient signal. With vigorous stirring of the cell contents, visual observations were carried out to identify whether the mixture was a transparent single IV μ E or turbid phase, and then HP- SANS measurements were conducted for both phases. CO₂ densities were calculated using the Span–Wagner equation of state (EOS).³⁴

During a SANS experiment, neutrons are scattered by short-range interactions with sample nuclei, with the “scattering power” of different components being defined by a scattering-length density (SLD), ρ (cm⁻²). For aqueous micellar systems, deuterated water, D₂O ($\rho_{D2O} = 6.32 \times 10^{10}$ cm⁻²) was used to provide the necessary contrast. For CO₂, $\rho_{CO2} = \text{mass density} \times (2.50 \times 10^{10} \text{ cm}^{-2})$.³⁵ At the experimental pressure and temperature of 350 bar and 45 °C, the mass density of CO₂ is 0.917 g cm⁻³. Therefore, ρ_{CO2} can be calculated as: $0.917 \times (2.50 \times 10^{10} \text{ cm}^{-2}) = 2.29 \times 10^{10} \text{ cm}^{-2}$. The scattering length densities of surfactant (ρ_{surf}) and D₂O (ρ_{D2O}) were obtained using:

Equation 3:
$$\rho = \sum_i \frac{b_i}{V_m}$$

where b_i are neutron scattering lengths and V_m is molecular volume as obtained from the mass density. Scattering length densities of all surfactants are shown in the Supporting Information.

W/CO₂ microemulsions were modelled as spherical core-shell particles with a Schultz distribution in the core radius (R_c).³⁶ For polydisperse spherical droplets at volume fraction ϕ , radius

R_i , volume V_i , and coherent scattering length density ρ_p dispersed in a medium of ρ_m , the normalized SANS intensity $I(Q)$ (cm^{-1}) may be written as:

Equation 4: $I(Q) = \phi(\rho_p - \rho_m)^2 [\sum_i V_i P(Q, R_i) X(R_i)] S(Q, R_{hs}, \phi_{hs}, \tau, \varepsilon)$

where $P(Q, R_i)$ is the single particle form factor, $X(R_i)$ is the Schultz distribution which describes the polydispersity using an average radius, R^{av} , and a root-mean-squared deviation, $\sigma = R^{av}/(Z + 1)^{0.5}$, Z being a width parameter and $S(Q, R_{hs}, \phi_{hs}, \tau, \varepsilon)$ is the sticky hard sphere structure factor with Percus-Yevick closure,³⁷ and a hard-sphere model modified for polydispersity was used as previously reported.³⁸ The perturbation parameter is $\varepsilon = \Delta/(\sigma + \Delta)$, where Δ and σ are the width of the attractive square well pair potential and the hard core diameter ($\sigma = 2R_c$), respectively. The attractive stickiness, τ , is defined as:

Equation 5: $\tau = \frac{1}{12\varepsilon} \exp(U_0/kT)$

τ is a function of both the perturbation parameter and the interaction strength in terms of the depth of the well, U_0 . From the definition, that smaller τ means stronger attraction.

All SANS data were fit using the analysis package SASView. In the analysis, values of volume fraction ϕ_{hs} were calculated using the known sample compositions based on added amounts of surfactant and water. Reverse micelle shells were estimated to be surfactant tails + linking groups, and values of shell thickness t_s were identified to be distances between C-atom connecting to the sulfonate group and the furthest H- or F-atom at the tail tips, which were estimated from individual and isolated 3D surfactant structures (Supporting Information) modelled by MM2 (Molecular Mechanics program 2) calculations (Chem 3D; CambridgeSoft Corp., Cambridge, MA). Those are about 11 Å for all surfactant molecules used here, so that t_s was fixed at this value in the fit analysis.

Therefore, the fitted parameters are core radius R_c , polydispersity index σ/R_c , stickiness τ , and perturbation parameter, ε . These structural parameters were initially set at physically reasonable values, guided by those obtained from preliminary Guinier analyses (R_{sph}) and σ/R_c^{av} (0.20) which reported for many common W/O μE systems.^{24,39,40} The sequence of fitting parameters was as

follows; firstly, at constant σ/R_c and ε values, the other two parameters were adjusted to the experimental data, and then suitable σ/R_c and τ were obtained by floating for the best fit (minimize sum of weighted squared residuals). As noted above, the σ/R_c value mostly gave the best fits at 0.2.

Results and discussions

Surface Tension Lowering Ability of Double Tail and Triple Tail Surfactants

Equilibrium surface tension (γ) measurements for the double and triple tail surfactants were made in aqueous solutions as a function of concentration (C) at 35 °C, allowing determination of the critical micelle concentration (CMC) and limiting surface tension at the CMC (γ_{CMC}). In addition to this, calculations of the surfactant tail densities (ρ_{layer}) as well as the minimum areas per molecule (A_{min}) were used to identify the relationship between γ_{CMC} , ρ_{layer} and intermolecular arrangement. As previously discussed, γ_{CMC} is a useful parameter for predicting the solubilizing ability surfactants in scCO_2 and hence formation of W/ CO_2 microemulsions.^{25–27} The reason for this is because the air/water and water CO_2 interfacial properties are correlated, and microemulsions generally form at interfacial tensions below 1 mN m^{-1} .^{24,41}

Equilibrium γ vs. $\log(C)$ plots for the double and triple tail surfactants at 35 °C are shown in **Figure 1**. All surfactants show a reduction in γ with increasing concentration, displaying clear break points at their respective CMCs. In the case of 4FS(EO)₂ there is an apparent break point below CMC, consistent with premicellisation. Values of A_{min} were calculated for each surfactant by taking local tangents of the γ - $\log C$ plot below the CMC and employing the Gibbs adsorption isotherm (Equations 1 and 2). The calculated interfacial parameters CMC, γ_{CMC} and A_{min} are displayed below in **Table 2**, with both low CMC and γ_{CMC} values being observed for all studied surfactants.

Figure 1. Change in surface tension as a function of Log (surfactant concentration) for aqueous solutions at 35 °C. Solid lines are fits using the Gibbs equation.

Table 2. Interfacial properties of double and triple tail surfactants studied in this work at 35 °C. ^a Critical micelle concentration, ^b Surface tension at the CMC, ^c Minimum effective molecular area obtained through the use of the Gibbs adsorption equation. Data for AOT14 and TC14 have been reported by Mohamed *et al.*²⁰

Surfactant	Hydrophobic tail, R	CMC ^a / M	γ_{CMC} ^b / (mN m ⁻¹)	A_{min} ^c / Å ²
AOTSiC	(CH ₃) ₃ SiCH ₂ CH ₂ CH ₂ -	2.3 x 10 ⁻³	23.9	87
TCSiC		3.6 x 10 ⁻⁵	23.5	115
AOTtBE	(CH ₃) ₃ CCH ₂ CH ₂ -	7.2 x 10 ⁻²	26	95
TCtBE		4.6 x 10 ⁻³	24.6	138
4FS(EO) ₂	F(CF ₂) ₄ CH ₂ CH ₂ -	4.1 x 10 ⁻⁴	18	94
4FT(EO) ₃		3.6 x 10 ⁻⁶	18.3	130
AOT14	(CH ₃) ₃ CCH ₂ -	2.4 x 10 ⁻³	28.6	100
TC14		2.2 x 10 ⁻²	27.0	144

As all surfactants in this series bear the same headgroup, the results therefore suggest that the limiting values of the γ_{CMC} and CMC are closely related to both the chemical architecture and number of surfactant tails. It has been previously reported that the progressive lowering of these limiting interfacial properties is observed up to a maximum of three surfactant tails, whereas addition of a fourth tail provides no additional benefits.⁴² Considering the different tail groups in the series of surfactants, another trend of increasing surface activity is observed in the following way: FC > TMS > HC. Undoubtedly, the reasons for this trend are due to differences in effective surfactant tail densities, and hence the ability to pack effectively and efficiently at the air/water interface, parameters which will be discussed below.^{29,43,44}

Of the surfactants examined in this study, the FC surfactants exhibit the lowest and most effective capacity to reduce the aqueous γ (lowest value = 18.0 mN m⁻¹ for 4FS(EO)₂). This is typical for FC surfactants, which are widely recognised for their ability to reduce aqueous surface tensions to low levels, due to large cross sectional areas, lower packing density per unit area and therefore weaker intermolecular interactions per unit area.^{44,45} Although the FC surfactants from this series

display the lower values of aqueous surface tension, it is important to note that the double and triple tail HC surfactants show comparable γ_{CMC} values to previously reported double tail FC surfactants, DiHCF4 (26.8 mN m⁻¹) shown in Table S1 (supporting information).¹² Mohamed *et al.*^{20,46} have also reported similar surface tensions for highly-methylated double and triple tail HC surfactants AOT14 and TC14 (data and structures given in Table 2 and Table S1, respectively). It is important to note that the addition of one CH₂ group, i.e. AOTtBE/ TCtBE compared to AOT14/ TC14, leads to a marked difference in γ_{CMC} , a point that will be examined in the next section.

Trimethylsilyl (TMS) tail surfactants contain Silicon atoms in the tips of the surfactant tail groups. This substitution leads to the surfactant tail groups having an increased volume due to the larger atomic radius of Si compared to C.²⁹ The effectiveness in reduction of γ for these TMS surfactants can be seen in Table 2. Both the double and triple tail TMS surfactants exhibit γ_{CMC} values below 24 mN m⁻¹ and in the case of the triple tail surfactant, this is reached at a very low concentration of 36 μM . Czajka *et al.*²⁹ previously carried out a systematic study on a range of related TMS surfactants with increasing numbers of CH₂ groups in the hydrophobic tails group. Results showed that there is roughly a linear decrease in both CMC and γ_{CMC} with increasing number of CH₂ groups, as well as an additional decrease in these values compared to HC analogues.²⁹

The increase in surface activity from FC to TMS to HC is evident from the data presented here, but it is also important to appreciate the structure property relationship that leads to this observed behavior. One of the clearest ways of characterizing an adsorbed layer is in terms of its limiting area per molecule A_{min} , or area per molecule at the CMC, as this provides an indication about how the molecular structure controls packing at the interface.²⁹ As has been previously reported,⁴³ it is instructive to both compare and investigate how the tail branching, and hence surfactant tail density, leads to the observed interfacial properties.

Links between lowering surface tension and surfactant tail density

The general structure-property relationship for γ reduction indicates that low surface tensions

(energies) are achieved through efficient packing of surfactant molecules at the air/ water interface, and the effective surfactant tail volume is known to have a large impact on this.^{26,43–45} One of the reasons that FC surfactants display the most efficient reduction in γ is due to the larger occupied volumes of fluoroalkyl moieties. According to Krafft *et al.*, the mean volumes of CF₂ and CF₃ groups can be estimated as 38 and 92 Å³, whereas those of CH₂ and CH₃ are around 27 and 54 Å³, respectively.⁴⁴ This leads to an order of increasing surface energy as follows: CF₃ < CF₂ < CH₃ < CH₂.⁴⁷

However, as previously discussed, through design of surfactants with highly methylated tails that increase the –CH₃ to –CH₂– ratio per headgroup, it is possible to achieve highly dense surfactant layers with low values of γ_{CMC} .^{26,43} Tail branching drives A_{min} higher because of the increased bulkiness of the tails, which in turn causes a decrease in the number of surfactant molecules per unit area, hence fewer tail–tail interactions occur.

As shown above in **Figure 1** and **Table 2**, further enhancements of the aqueous interfacial properties can be introduced by replacing *t*-butyl groups with a TMS group. The reason for this being due to the larger atomic radius of Si compared to C which allows for a lowering of the packing density per unit area.²⁹ The A_{min} values for the range of TMS surfactants studied by Czajka *et al.* were found to decrease with increasing number of CH₂ groups, therefore showing that the molecules are able to pack more efficiently at the air/water interface.²⁹ This behaviour has been previously understood due to a decrease in the rigidity of the surfactant tail as the length is increased; a behaviour that is also observed when comparing AOT14 to AOTtBE in **Table 2**. Compared to a *t*-butyl group, incorporation of a TMS moiety into a surfactant tail leads to an overall increase in molecular volume. With this in mind, it is interesting to note the similarities in A_{min} values between TMS and HC surfactants for both the double and triple tail analogues. Similarly, here the relationship between the density of the surfactant tail layer and the observed interfacial properties will be considered for the double and triple tail surfactant.

For the range of surfactants studied here, A_{min} values are shown to increase through addition

of a third surfactant tail group, but the increment for the third tail is reduced. This suggests that triple tail surfactants are able to improve the space-filling efficiency of the surfactant tails at the air/ water interface as compared the double tail surfactant counterparts.²⁰ Previous work has also shown that $A_{\min}$ is directly affected by the density of the surfactant film, a parameter which is associated with the branching position of the tail groups.²⁶ The branching factor accounts for the contributions from both the extent and position of a surfactant tail relative to the headgroup. Increasing the branch length and/or branching closer to the headgroup increases $A_{\min}$, due to geometrical constraints.⁴³ The structure and degree of branching of the surfactant tails in this study are very similar (see **Table 1**), therefore similar branching factors within this series of surfactants are observed (see **Supporting Information**). Unlike previous studies,^{25,26,43} the branching factor is therefore unlikely to have a key role in affecting $A_{\min}$ values and will not be discussed further.

To confirm the relationship between γ_{CMC} and the density of the surfactant tail layer at the air/water interface (ρ_{layer}), the apparent mass densities of the surfactant films were estimated using:

Equation 6:

$$\rho_{\text{layer}} = \frac{m_{\text{tail}}}{A_{\min} \cdot L}$$

where m_{tail} is the tail molecular weight (g) and L is the tail length (cm), therefore giving ρ_{layer} with units of g/cm^3 . To allow for direct comparisons between ρ_{layer} values and to remove the effect of heavy elements within a tail structure, m_{tail} values for the TMS and FC have been calculated with atomic weights of C and H instead of Si and F, respectively. For consistency, all surfactant tail lengths were calculated from 3D structure estimations (see **Supporting information**).

Figure 2 shows the relationship between γ_{CMC} and ρ_{layer} for the surfactants in this study as well as for AOT14/ TC14 and a series of straight chain double-tail surfactants (di- $C_n\text{SS}$). For all surfactants, addition of a third surfactant tail leads to an increase in ρ_{layer} and the density of the layers increase in the following way $\text{HC} > \text{TMS} > \text{FC}$. This series of surfactants therefore show that the lower γ_{CMC} values obtained for the FC and TMS surfactants are not a result of ρ_{layer} , instead are a

result of the incorporation of moieties within the tail group that have lower individual surface energies.

Figure 2. Relationship between γ_{CMC} and density of surfactant tail layer using A_{min} at 35 °C. Tail lengths for all surfactants were calculated from 3D molecular structure estimations shown in supporting information. The data for AOT14 and TC14 were taken from data reported by Mohamed *et al.*²⁰ and data for di- C_n SS were reported by Eastoe *et al.*⁴³

As previously mentioned, the effects of heavy elements on ρ_{layer} have been removed and the data can therefore be compared directly. The relatively low ρ_{layer} values for the FC surfactants can be understood by (1) the weaker intra and intermolecular FC-FC interaction and (2) the larger volumes occupied by the fluoroalkyl groups and hence larger A_{min} values.⁴⁴ When considering the HC surfactants, it is important to note the similarities between the structures, i.e. addition of one CH_2 group in the tail group in AOTtBE/ TCtBE compared to AOT14/ TC14. It was shown above in **Table 2** that this difference in structure fed through to a decrease in both A_{min} and γ_{CMC} , which has been previously understood as being due to a reduction in the rigidity of the surfactant tails.²⁹ Furthermore, the data here show that ρ_{layer} also increases with addition of the extra CH_2 group, therefore demonstrating that this addition leads to more efficient packing of the surfactants at the air/water interface, an effect that is enhanced further through increasing the number of surfactant tails. It has

been previously shown that for a range of straight chain double tail surfactants such as di- C_n SS (where n is the chain carbon number), a longer tail length (from $n = 4 - 8$) drives $A_{\min}$ lower, resulting in a more densely packed layers and thus higher ρ_{layer} (data reproduced in **Figure 2**).⁴³ However, despite the increase in ρ_{layer} with increasing n , γ_{CMC} values do not follow the same trend, instead γ_{CMC} decreases up to $n = 6$ and increases for $n > 6$. A tail length of $n = 6$ is therefore optimal for straight chain double tail surfactants to obtain low γ_{CMC} values.⁴³ It is interesting to note that although surfactant tails bearing *t*-butyl groups have lower ρ_{layer} values than some straight chain di- C_n SS, much lower γ_{CMC} values are produced by surfactants with this *t*-butyl branching. This indicates further that it is the incorporation of lower surface energy groups (CH_3 instead of CH_2 in this case) that leads to the significant reductions in γ_{CMC} .^{45,47}

Due to similarities in the tail structure between the TMS and HC surfactants in this study, the extent to which the ρ_{layer} is affected by the change from Si to C in the tail group is reflected in the data. The larger atomic radius of Si feeds through to decrease from 0.62 to 0.58 g cm⁻³ when comparing the double tail HC to TMS surfactant, and 0.64 to 0.63 g/cm⁻³ when comparing the triple tail HC to TMS surfactant. A larger increase in ρ_{layer} in going from double to triple tail surfactant is therefore observed for the TMS surfactant compared to the HC surfactant, 0.05 and 0.02 g/cm⁻³, respectively. Calculations of the surface coverage (Φ_{cmc}) have been previously carried out on TMS and HC surfactants to estimate the packing efficiency.^{29,45} For TMS surfactants high Φ_{cmc} values were reported compared to HC analogues. The improved packing efficiency was attributed to the larger size of Si compared to C, which is consistent with the concept of efficient space filling between the surfactant tails due to the increased molecular volume of the tail tips.

Overall, these data show that the interfacial properties of surfactants can be significantly enhanced by increasing the number of surfactant tails. For all surfactants, both the tail length and chemical structure of the surfactant tails play important roles in influencing the interfacial properties. It has been shown that γ_{CMC} values are more affected by the individual surface energies of the chemical moieties within tail structures instead of increased packing density.

Nanostructures of double and triple-tail surfactants stabilized microemulsions

Small-angle neutron scattering (SANS) is a powerful technique for obtaining structural information about self-assembling systems in different media. Here, the series of double and triple-tail surfactants have been subject to investigation as aqueous systems, D₂O/heptane microemulsions and W/ CO₂ μ Es. SANS profiles and analysis of the TMS surfactants in D₂O are shown in the **Supporting Information**. The aim with these analyses is to determine the suitability of these triple tail surfactants for use as effective stabilizers for W/CO₂ μ Es.

The SANS profiles, along with fitted $I(Q)$ functions, for the series of double and triple-tail surfactant as surfactant/W/CO₂ mixtures are shown below in **Figures 3 and 4**, and the structural parameters from data modelling in **Figure 5** and **Table S4 S5** in **Supporting Information**. All stable W/CO₂ microemulsion systems were studied at 50 mM, 45 °C and 350 bar, apart from 4FT(EO)₃ which was measured at 16.7 mM. It should be noted that 4FS(EO)₂ along with additional FC surfactants used for comparisons have already been studied in terms of W/CO₂ microemulsion formation,²⁴ but the triple tail analogue has not. Raw SANS profiles of the additional FC surfactants are shown in **Figure S3** in the Supporting Information. The sizes of the W/CO₂ microemulsion droplet domains have been initially approximated using Guinier and Porod approximations (see **Supporting Information**).

Stable W/CO₂ and W/heptane microemulsions were not formed with the double tail HC surfactant AOTtBE (see **Figure S6** in Supporting Information). In the W/CO₂ mixtures, AOTtBE are almost insoluble in the CO₂ phase, lacking sufficient CO₂-philicity for microemulsion formation. However, the triple tail HC surfactant TCtBE, has sufficient solubility in both heptane and the CO₂, to form stable microemulsions in the organic solvent, suggesting that the triple tail structure is a key feature. Interestingly, Bragg peaks are observed in the SANS data for TCtBE/D₂O/CO₂ mixtures as shown in **Figure 3**, consistent with aggregates comprised of repeating units, whereby the layer

spacing (d) can be estimated using $Q_{\max}$ and $d = 2\pi / Q_{\max}$. The Bragg peak shifts to lower $Q_{\max}$ values as W_0 ($W_0 = [\text{water}]/[\text{surfactant}]$) is increased from 5 to 10, corresponding to a change in d from ~ 28 to $38 \text{ \AA}$, respectively. This increase in layer spacing therefore suggests swelling of the W/CO₂ phase due to the increase in water concentration. In the case of double and triple-tail HC surfactants, AOT14 and TC14, the double tail surfactant does not form stable W/ CO₂ microemulsions, whereas the triple tail surfactant does.^{20,46} The underlying factors that lead to this observed behaviour may be linked to a reduction in the surface energy and increase in surfactant tail group density in films through addition of the third surfactant tail.²⁰

Figure 3. SANS profiles for W/CO₂ mixtures with 50 mM TCtBE at different W_0 values, 45 °C and 350 bar.

Significantly, it was shown that the triple tail surfactant vastly improved the space-filling efficiency of the surfactant tails (reduction in the FFV), therefore favouring the formation of reversed micelles through better separation of water molecules and the CO₂-phobic headgroups from CO₂ phase.¹⁹ This same space-filling efficiency was observed here for all triple tail surfactants, as shown by the increases in ρ_{layer} compared to double tail analogues. With an extra CO₂-philic ester group,

this, therefore, demonstrates how triple tail HC surfactants offer improvements in CO₂ compatibility over the more common double-tail analogues.

Both the double and triple-tail TMS surfactants formed stable W/CO₂ and W/heptane microemulsions as shown by clear SANS profiles in **Figure 4** and **Figure S7**, respectively. For the W/CO₂ μ E systems, AOTSiC and TCSiC are stable up to $W_0 = 5$ and 25, respectively. It should be noted that a water solubilisation capacity of 20 or over is quite rare for non-fluorinated surfactants systems. In the low Q region of SANS data, the scattering is known to scale as $I(Q) \sim Q^{-D}$, where D is the characteristic “fractal” for the colloids, hence, the gradient of a log-log plot will be a $-D$.^{48,49} In the case of non-interacting spheres, D should be zero in this low Q region, whereas $D = 1$ for rods and 2 for disks. For both TMS surfactants at all values of W_0 , the gradients in the low Q region of the log-log plots were found to be ~ 0 , suggesting the presence of globular or spherical aggregates.

By modelling of the data using a Schultz distribution of polydispersed core/shell spherical particles, subtle changes in the size of the D₂O microemulsion core (radii, R_c) can be resolved. **Figure 5** shows the changes in the radii obtained by the model fitting as a function of W_0 for FC and TMS surfactants. Both TMS surfactants have similar R_c values at $W_0 = 1.7$ and 5, i.e. the maximum solubilization capacity for AOTSiC. The radius R_c of TCSiC continues to increase linearly up to a value of ~ 11.5 Å at $W_0 = 20$. The observation of a linear function below the solubilizing capacity has been previously used to provide an estimate for the effective headgroup area:²⁴

Equation 7: $\alpha(p) R_c = (v_{\text{head}}/A_{C/W}) + (v_w/A_{C/W}) W_0$

where v_w is volume of D₂O molecule, v_{head} is volume of surfactant headgroup, $A_{C/W}$ is area per

Figure 4. SANS profiles for W/CO₂ μ Es with 16.7mM fluorinated surfactants or 50 mM TMS surfactants at different W_0 values, 45 °C and 350 bar.

surfactant molecule at W/CO₂ interface and p is the polydispersity index (called σ/R_c in this article),

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intercept yielding the average headgroup volume (v_{head}) via the headgroup radius.²⁴ Using this linear region below the solubilization capacity (i.e. between $W_0 = 5-15$) gives $A_{C/W}$ value of $600 \text{ Å}^2 \pm 69$.

This considerably large value of $A_{C/W}$ are likely due to the bulky triple-tail stretching over the headgroup area. It is interesting to note the difference between the area per surfactant molecule at the W/CO_2 interface compared to that of the air/ water (A/W) interface (115 Å^2 , **Table 2**), it was almost five times larger than at A/W interface. Such a large $A_{C/W}$ suggests that the triple tails are widely opened and expanded by solvation with many CO_2 molecules as shown in the graphical TOC, in contrast with closed and shrunk by no solvation at A/W interface. This is also true for the A/W interface, whereby it has been shown that the area per surfactant molecule is on average 60% larger at the W/CO_2 compared to the A/W interface.²⁰ Furthermore, TCSiC has two structural (and 2x optical) isomers having different C-sulfonate bond positions caused by sulfonation of the aconate intermediate. The disordering in the 3D structures may not allow close packing of surfactant molecules at water surface. The effect of structural disordering could be amplified by the tails opening with CO_2 solvation, resulting in the considerably large $A_{C/W}$ value.

Comparisons between the area per surfactant molecule can also be made between W/CO₂ and W/O interfaces. Here, stable W/CO₂ and W/O μ Es were formed by AOTSiC at $W_0=5$, and the area per surfactant molecule were calculated by using **Equation 10** (described later) as 281 ± 64 and 54 ± 4 Å², respectively. The significant difference observed between the area per surfactant molecule at the interfaces have been previously investigated by thermodynamic interfacial tension measurements.^{50–52} Two reasons were reported as the key drivers for these differences, the first being as a result of the difference in interfacial tension at the pure W/CO₂ interface (typically 20 - 30 mN m⁻¹) compared to a much larger value of 50 mN m⁻¹ at the W/O interface.^{51,52} This leads to a smaller driving force required for surfactant adsorption at the W/ CO₂ interface compared to the W/O. Less surfactant molecules will therefore be required to lower the interfacial tension to the required value for μ E formation, implying that aggregation numbers (N_{agg}) will be lower and area per molecule values will be higher for W/CO₂ systems compared to W/O.⁵¹ Aggregation number (N_{agg}) values calculated by using **Equation 8** (described later) for AOTSiC in W/CO₂ and W/O μ Es are 5 and 282, respectively, hence further emphasize this key driver. The second reason for these observed differences were as a result of the greater penetration of the smaller CO₂ molecules into the surfactant tail region (entropic effect), compared to typically larger organic solvents. Those differences in

solvent properties between scCO₂ and a conventional oil likely resulted in the larger effective packing parameter (EPP) of AOTSiC in W/CO₂ μ E than in the W/O μ E, that is EPP = 2.4 for W/CO₂ and 1.63 for W/O at $W_0=5$ calculated using **Equation 13** described later.

Considering AOTSiC and 4FT(EO)₃ in this study, clear linear droplet swelling functions in the R_{core} vs. W_0 data (see **Figure 5**) were not obtained below the solubilization capacity (maximum W_0 of 4FT(EO)₃ < 30). Using these data above the solubilization limit of the surfactants to calculate $A_{C/W}$ will therefore lead to large uncertainties as a result of water molecules separating from the reverse micelles. Therefore, in order to investigate $A_{C/W}$ values, the following calculations were carried out making use of calculated reverse micelle aggregation numbers (N_{agg}):

Equation 8: $N_{\text{agg}} = C_{\text{surf}}/C_{\text{micelle}}$

Equation 9: $C_{\text{micelle}} = (V_{\text{water}} C_{\text{water}} + V_{\text{head}} C_{\text{surf}})/(V_{\text{core}}) = C_{\text{surf}} (V_{\text{water}} W_0 + v_{\text{head}} N_A)/(v_{\text{water}} N_A)$

Equation 10: $A_{C/W} = s_{\text{core}}/N_{\text{agg}}$

where N_A is Avogadro's number, C_{surf} and C_{water} , C_{micelle} are molar concentrations of surfactant, water and reverse micelle, v_{core} is volume per aqueous core, V_{water} , V_{head} , and V_{core} are molar volumes of water, surfactant headgroups and aqueous cores containing headgroups ($V_{\text{head}} = v_{\text{head}} N_A$, $V_{\text{core}} = v_{\text{core}} N_A$), respectively. For the calculation of $A_{C/W}$, s_{core} is the surface area per aqueous core, being calculated using the sphere radius (R_c) as well as the calculation of v_{core} for C_{micelle} .

According to theory,^{53–55} the spontaneous packing parameter (SPP) can be obtained by:

Equation 11: $\text{SPP} = v_{\text{tail}}/(A_0 l_{\text{tail}})$

where v_{tail} and l_{tail} are hydrophobic tail volume and length, respectively. These symbols have the same meanings as in the expression of the effective packing parameter (EPP).⁵⁵ Entropy is taken into account by the fact that the area per molecule minimizes the free energy of the surfactant film (A_0 is the area that minimizes the free energy). According to this approach reverse micelles would be obtained with $\text{SPP} > 1$ (reversed cores form if the surfactant tails orient upward) to ~ 1 (cylindrical). In the case of W/CO₂ μ Es, EPP values should be calculated by taking account of solvation of the head

and tail groups with water and CO₂ into the A_0 and v_{tail} values. If the hydrophobic part is assumed to be a truncated cone, the volume should be: ^{23,24}

Equation 12: $v_{\text{tail}} = l_{\text{tail}}(A_{\text{C/W}} + A_{\text{tail}} + (A_{\text{C/W}} A_{\text{tail}})^{0.5})/3$

where A_{tail} is area per hydrophobic tail terminus, respectively. When A_0 is replaced by $A_{\text{C/W}}$ for the calculation of EPP in W/CO₂ μ Es, **Equation 11** can be simply expressed as:

Equation 13: $\text{EPP} = \{s_{\text{micelle}} + s_{\text{core}} + (s_{\text{micelle}} s_{\text{core}})^{0.5}\}/(3s_{\text{core}})$

where s_{micelle} is surface area per reverse micelle. In this study, the values of s_{micelle} were calculated from the spherical core radius (R_c), with surfactant tail length l_{tail} assumed to be 11 Å (between the tail terminal F- or H-atom and the C-atom bearing the sulfonate group). All the values of $A_{\text{C/W}}$, N_{agg} and EPP obtained by **Equations 8-13** are calculated based on the assumption that all surfactant molecules are adsorbed at the W/CO₂ interface. Calculated $A_{\text{C/W}}$ values for this series of surfactants along with a series of previously reported FC surfactants²⁴ are reported in **Table 3**, and N_{agg} / EPP vs. W_0 data are shown in **Figure 6** and listed in **Tables S7-8 S8-9** in the Supporting Information.

Table 3. Area per surfactant molecule at W/CO₂ interface ($A_{\text{C/W}}$) in Å² calculated by dividing core surface area by aggregation number N_{agg} for W/CO₂ microemulsions with different W_0 values at 45 °C and 350 bar. Data for 4FG(EO)₂, 8FS(EO)₂ and 8FG(EO)₂ from Sagisaka *et al.*²⁴

W_0	Area per surfactant molecule at W/CO ₂ interface, $A_{\text{C/W}}$ / Å ²						
	4FS(EO) ₂	4FT(EO) ₃	AOTSiC	TCSiC	4FG(EO) ₂	8FS(EO) ₂	8FG(EO) ₂
1.7			285 ± 21	529 ± 52			
5			281 ± 64	414 ± 46			
10	389 ± 336			421 ± 36	79 ± 1	142 ± 30	
15		378 ± 4		436 ± 30			
20	176 ± 1			465 ± 31	118 ± 2		
22						99 ± 1	99 ± 1
25				503 ± 32			
30		516 ± 4			125 ± 1		
40	224 ± 1	620 ± 8			157 ± 1	122 ± 1	
44							134 ± 1
50		652 ± 5					
60	259 ± 1				193 ± 1	147 ± 1	134 ± 1
80					227 ± 1	190 ± 1	178 ± 3

Data in **Table 3** show marked increases in $A_{C/W}$ values for triple-tail surfactants compared to the double tail analogues. This is shown by increases of $\sim 140 \text{ \AA}^2$ (at $W_0 = 5$) and $\sim 280 \text{ \AA}^2$ (at $W_0 = 40$) for addition of a third tail to TMS and FC surfactants, respectively. As this same analysis has not been possible for the HC surfactants in this study, it is important that comparisons are made to previously reported triple tail HC surfactants which are known to stabilize W/CO₂ microemulsions. The triple tail HC surfactant TC14 stabilizes W/ CO₂ microemulsions up to $W_0 = 5$, and calculations show that TC14 has $A_{C/W} = 128 \text{ \AA}^2$.^{20,46} For this range of surfactants the trend in $A_{C/W}$ values is therefore as follows: FC > TMS > HC, the same trend observed for water solubilizing ability. This could result from differences in the CO₂-philicity of the tails (or number of CO₂ molecules solvated with the tails).

The large values of $A_{C/W}$ associated with the triple tail surfactants feed through to low observed N_{agg} values. Disregarding the $W_0 = 1.7$ point for TCSiC due to the apparent N_{agg} value of < 1, the triple tail surfactants display relatively stable N_{agg} numbers, both being between 3 and 4. The EPP is an indicator of the bulkiness of a given hydrophobic group compared to the headgroup, and guides interfacial curvature of any surfactant assembly structure.²⁴ Surfactants with small relatively small headgroups compared to tail volume will display EPP values of > 2, thus giving rise to negative interfacial curvature and hence reverse micelles.³ In this framework, W/CO₂ microemulsions are only stabilized for surfactants with a EPP > 1, and the interfacial curvature becomes more planar if EPP $\sim$ 1 leading to formation low curvature reverse microemulsions or macroemulsions.²⁴ For all W_0 values, the triple tail TMS and FC surfactants have CPP > 2 as would be expected due to the observed formation of stable W/ CO₂ microemulsions. TCSiC also displays a decrease in EPP with increasing W_0 , reaching a constant EPP value of ~ 2.3 at $W_0 = 20$. It implies that a lowest limit of packing parameter for a triple tail surfactant are > 2.0 in W/CO₂ microemulsions due to the bulkiness of the triple tail structure: this puts a limit on the solubilizing capacity to less than 30 (even with appropriate CO₂-philicity for a high water-content microemulsion with $W_0 = 30$ or more). On the other hand, the double tail structure can generate EPP values less than 2, tending to form larger water μE droplets,

given sufficient CO₂-philicity to stabilize the microemulsions as found with double fluorocarbon tail surfactants, but not with double TMS-tail analogues.

Figure 6. Changes in aggregation number (N_{agg} , upper) and effective packing parameter (EPP, lower) for double and triple tail fluorocarbon and TMS surfactant W/CO₂ μ Es as a function of W_0 at 45 °C and 350 bar.

Conclusions

Technologies and applications employing supercritical CO₂ (scCO₂) have been continuously developed for various chemical industries such as extraction, organic synthesis, polymerization, nanomaterial processing etc.^{1-3,5} It is believed that formation of stable W/CO₂ dispersions will lead to advances, improving efficiency and effectiveness, as well as promoting other uses of CO₂ insoluble materials. Previous studies found that the most efficient formation of stable W/CO₂ μ Es is achieved using long and/or multiple fluorinated tail surfactants or hybrid surfactants containing both fluorocarbon (FC) and hydrocarbon (HC) moieties in the surfactant tail.^{3,12,24} Although this is a step in the right direction, there still remains a clear incentive to completely move away from the use of FC surfactants in industrial processes.²² To achieve this practically, there must be clear alternatives which provide the desired interfacial properties, such as form stable W/CO₂ μ Es. Here, novel double and triple tail surfactants bearing trimethylsilyl (TMS) groups in the tail structure have been synthesized and compared to analogous HC and FC tail surfactants in terms of interfacial performance and W/CO₂ μ E formation. This is a systematic study whereby all surfactants have the same headgroup, and each class of double/triple tail surfactant (HC, FC and TMS) have the same tail structure (see **Table 1**). Therefore, additional relationships of how tail group chemistry and number of surfactant tails affects these properties can be explored.

Surface tension measurements were employed to characterize the surfactants in terms of critical micelle concentrations (CMCs), surface tension at CMC (γ_{CMC}) and minimum area per molecule (A_{min}). Previous literature has consistently shown that γ_{CMC} is an important parameter for predicting the solubilizing ability of surfactants in scCO₂ and is therefore crucial for a comprehensive understanding.^{24,41} Low γ_{CMC} and CMC values were recorded for all studied double and triple tail surfactants, with γ_{CMC} being $\leq 26 \text{ mN m}^{-1}$ in all cases. For all studied surfactants, addition of a third tail group produced further reductions in both γ_{CMC} and CMC compared to the double tail analogues. Within the series of surfactants, the FC amphiphiles produced the largest reductions in aqueous γ (lowest value = 18.0 mN m^{-1} for 4FS(EO)₂). Although this is the case, it is important to note that both

the TMS and HC surfactants gave γ_{CMC} values lower than a double tail FC surfactant DiHCF4 (26.8 mN m⁻¹), which has been shown to stabilize W/CO₂ μEs .¹² Considering the series of surfactants, the following trend in observed surface activity for both double and triple tail surfactants was found: FC > TMS > HC. This echoes previous literature that demonstrated the improved performance of surfactants with TMS groups in place of *t*-butyl for reasons associated with increases in surface coverage (Φ_{cmc}), tail volume and atomic radius of Si compared to C.²⁹

To investigate how both the tail group chemical architecture and the absolute number of tails affects the observed interfacial properties, minimum area per molecule (A_{min}) and surfactant tail density in the monolayers (ρ_{layer}) were considered. It is known that design of surfactants with highly dense layers will lead to lower packing densities and hence γ_{CMC} values.^{26,43–45} In all cases, the triple tail surfactants have lower A_{CMC} values than the double tail counterparts, demonstrating the increased packing efficiency through addition of a third tail group.²⁰ For the series of double tail surfactants, ρ_{layer} values were 0.62, 0.58 and 0.40 g/cm³ for the HC, TMS and FC surfactants, respectively. Further enhancements in ρ_{layer} are also possible through increasing the length of the tail group.^{20,29} Addition of a third surfactant tail group leads to formation of highly dense and effective layers for all studied surfactant systems. However, these data also demonstrated that larger ρ_{layer} do not necessarily predict reductions in γ_{CMC} , instead it has been shown that the surface energies of the chemical moieties within the tail groups have much more of a significant effect.

High pressure small-angle neutron scattering (HP-SANS) was used to characterise the formation of stable W/ CO₂ μEs . For the HC surfactants, stable W/CO₂ μEs were not formed, whereas in the case of the double tail surfactant AOTtBE, however stable μEs were generated up to $W_0 = 10$ for the triple tail surfactant TCtBE. This similar pattern has been seen previously for the double and triple tail HC surfactants, AOT14 and TC14 and this emphasises the improvements in CO₂ compatibility achieved through addition of a third surfactant tail.^{20,46} Significantly, triple tail surfactants vastly improve the space-filling efficiency of the surfactant tails, as shown by the substantial increases in ρ_{layer} compared to double tail analogues, and therefore favour the formation

of reversed micelles through better separation between CO₂ and water across the interface.¹⁹ Furthermore, for the first time TMS surfactants have been shown as successful W/ CO₂ μ E stabilizers, with AOTSiC and TCSiC being stable up to $W_0 = 5$ and 25, respectively. The triple tail TMS surfactant being stable up to $W_0 = 25$ is a very important step in the right direction for guiding design of novel fluorine-free surfactants for CO₂.

Overall, this study has provided important insight into the structure performance relationship of double and triple tail surfactants in terms of interfacial properties and ability to perform as successful W/CO₂ μ E stabilizers. Importantly, TMS surfactants have emerged as a new class of potential W/CO₂ μ E stabilizers and therefore represent novel, commercially viable and environmentally responsible 21st century surfactants. It is becoming clear now, that to develop more efficient CO₂-philic solubilizers without fluorine requires a combination in one molecule of two important properties: (a) widely-tuneable effective parking parameter (EPP), such as found with double tail surfactants and (b) high CO₂-philicity characteristic of triple tail surfactants.

ASSOCIATED CONTENT

Supporting information. Synthetic schemes for the double and triple tail surfactants, including characterization data. Calculation of scattering length densities of reverse micelle shells (ρ_{shell}), aqueous cores (ρ_{core}), and CO₂ (ρ_{CO_2}) in the D₂O/CO₂ μ Es. Structural models and tail lengths of 4FS(EO)₂ and AOTSiC anions. Aqueous SANS profiles of double and triple tail TMS surfactants in D₂O at 20 x CMC. Additional W/CO₂ SANS profiles for additional fluorocarbon surfactants, used for comparison in this work. Estimation of D₂O core radii in double and triple tail FC/ TMS surfactants/D₂O/CO₂ reverse micelles with different W_0 values at 350 bar and 45 °C by Guinier and Porod analyses of SANS data. SANS profiles of double/triple tail HC/TMS surfactants/W/heptane microemulsion and associated modelling parameters. Estimation of aggregation number, area per surfactant molecule, and effective packing parameter of the D₂O/CO₂ μ Es with FC and TMS surfactants.

This material is available free of charge via the Internet at “<http://pubs.acs.org>.”

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ACKNOWLEDGEMENTS

CH acknowledges Japan Society for the Promotion of Science (JSPS) for support as a JSPS International Research Fellow (Graduate School of Science and Technology, Hirosaki University). This project was supported by JSPS [KAKENHI, Grant-in-Aid for Scientific Research (B), No. 19H02504, Fostering Joint International Research (A), No. 15KK0221, Grant-in-Aid for Challenging Research (Exploratory), No.17K19002], and Leading Research Organizations (RCUK [through EPSRC EP/I018301/1]) under the G8 Research Councils Initiative for Multilateral Research

Funding–G8-2012. We also acknowledge STFC for the allocation of beam time, travel, and consumables grants at ISIS. This work benefited from the use of the SasView application, originally developed under NSF award DMR-0520547. SasView contains code developed with funding from the European Union’s Horizon 2020 research and innovation programme under the SINE2020 project, grant agreement No 654000. The authors acknowledge Shared Facility Center for Science and Technology, Hirosaki University (SFCST) for ^1H -NMR and FT-IR spectra measurements and elemental analysis.

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