



Alexander, S., Smith, G., James, C., Rogers, S. E., Guittard, F., Sagisaka, M., & Eastoe, J. (2014). Low-Surface Energy Surfactants with Branched Hydrocarbon Architectures. *Langmuir*, 30(12), 3413-3421.
10.1021/la500332s

Peer reviewed version

Link to published version (if available):
[10.1021/la500332s](https://doi.org/10.1021/la500332s)

[Link to publication record in Explore Bristol Research](#)
PDF-document

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/pure/about/ebr-terms.html>

Take down policy

Explore Bristol Research is a digital archive and the intention is that deposited content should not be removed. However, if you believe that this version of the work breaches copyright law please contact open-access@bristol.ac.uk and include the following information in your message:

- Your contact details
- Bibliographic details for the item, including a URL
- An outline of the nature of the complaint

On receipt of your message the Open Access Team will immediately investigate your claim, make an initial judgement of the validity of the claim and, where appropriate, withdraw the item in question from public view.

Low Surface Energy Surfactants with Branched Hydrocarbon Architectures

Shirin Alexander,^{*†} Gregory N. Smith,[†] Craig James,[†] Sarah E. Rogers,[‡] Frédéric Guittard,[§]
Masanobu Sagisaka,[‡] and Julian Eastoe^{*†}

[†]*School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK*

[‡]*ISIS-STFC, Rutherford Appleton Laboratory, Chilton, Oxon, OX11 0QX, UK*

[§]*Univ. Nice Sophia Antipolis, CNRS, LPMC, Group surfaces & interfaces, Parc Valrose,
06100 Nice - France*

[‡]*Department of Frontier Materials Chemistry, Graduate School of Science and Technology,
Hirosaki University*

Surface tensiometry and small-angle neutron scattering (SANS) have been used to characterize a new class of Low surface energy surfactants (LSEs): “Hedgehog” surfactants. These surfactants are based on highly branched hydrocarbon (HC) chains as replacements for environmentally hazardous fluorocarbon (FC) surfactants and polymers. Tensiometric analyses indicate that a subtle structural modification in the tails and headgroup, results in significant effects on limiting surface tensions γ_{cm} at the critical micelle concentration (cmc): higher branching and increased counterion size promote an effective surface tension reduction to low values for HC surfactants ($\gamma_{\text{cmc}} \sim 24 \text{ mN m}^{-1}$). These LSEs present a new class of potentially very important materials, which form lamellar aggregates in aqueous solutions independent of dilution.

Keywords: Low Surface Energy, Surfactant, SANS, Surface tension.

1. INTRODUCTION

Low surface energy materials (LSEMs) are obtained by adsorption or attachment of surface layers to substrates.¹ The cause of low surface energy ($\gamma / \text{mN m}^{-1} \equiv \text{J m}^{-2}$) is the underlying chemical structure of the interfacial layers: the ability to control surface properties being the direct consequence of chemical structure. There are numerous applications of LSEMs today, such as printing, painting, adhesion, metal-plating, emulsification/suspension (medicines, cosmetics, food packaging, etc.), washing (electronics, clothes, etc), antifogging and repellent surfaces (self-cleaning windows, water-proof textiles, anti-snow, anti-fog surfaces, papers, fibers, etc.).²⁻⁵ Consequently, development and optimization of LSEMs has attracted much

*Corresponding authors. Email:shirin.alexander@bristol.ac.uk, Julian.eastoe@bristol.ac.uk

attention, and a wide variety of useful LSEMs can be obtained by fluorinating surfaces to yield a surface energies of $\gamma \sim 15 \text{ mN m}^{-1}$ for $-\text{CF}_3$ groups and $\gamma \sim 25 \text{ mN m}^{-1}$ for $-\text{CF}_2$.⁶⁻⁸ Unfortunately, this has important environmental consequences because of the persistence, bioaccumulation, and toxicity of Fluorocarbons (FCs)^{9,10}.

The link between limiting surface energy and chemical structure of the layer depends on various factors, as can be seen by inspection of Table 1 which is a compilation of literature data on aqueous surfactant solutions. (For chemical structures see Table S1). Surfactants bearing fluorocarbon or siloxane chains can promote very low limiting surface tension (γ_{cmc}) compared to typical linear chain hydrocarbon surfactants such as SDS. However, fluorocarbon surfactants are environmentally hazardous and siloxanes maybe hydrolytically unstable. Also included in Table 1 are literature data for branched chain HC surfactants. It is interesting to note that chain branching, especially increasing chain tip methylation, leads to lower limiting surface tensions (γ_{cmc}) as compared to linear chain analogues. Table 1 has been generated after extensive literature searches by different investigators, and lists the lowest γ_{cmc} values found for branched-chain HC surfactants. The current “world record” low γ_{cmc} for an HC surfactant is 24.7 mN m^{-1} for the double chain 2,4,4TMC₅-PO₄⁻Na⁺ which may be found in a PhD thesis.¹¹ The lowest γ_{cmc} value reported in the open peer-reviewed literature is 25.4 mN m^{-1} for the tri-chain anionic surfactant (TC) with highly substituted tetrapropylammonium (TPA) cation. These data prompt an interesting question: “what is the lowest surface tension that can be achieved with an HC surfactant?” Surely, the absolute minimum would be the surface tension of the parent hydrocarbon, for example γ_{cmc} SDS with linear nC₁₂ chains is $\sim 35 \text{ mN m}^{-1}$ but $\gamma_{\text{air-liquid}}$ for pure n-dodecane (linear C₁₂ alkane) is $\sim 26 \text{ mN m}^{-1}$.¹² Obviously, the reason why γ_{cmc} for SDS is so much higher than $\gamma_{\text{air-liquid}}$ for n-dodecane is the dipolar effect on γ owing to charged $-\text{SO}_4^- \text{ Na}^+$ groups. The way to obtain soluble and useful low surface energy HC surfactants will be to maximize the van der Waals interactions, and at the same time minimize the dipolar interactions, which are essential for water solubility.

Table 1. Example of surface properties of some of the FC, HC and Trisiloxane surfactants has been published in the literature.

Surfactant	cmc/(10 ⁻³ M) ± 0.03	γ _{cmc} /(mN m ⁻¹) ±1	A _{cmc} /Å ² ±2
<i>Fluorocarbon</i>			
C ₈ FC ₃ -2-C ₃ C ₈ F ^a	0.00593	13.7	91
DiF ₈ -PO ₄ -Na ⁺ ^b	0.18	16.4	-
di-CF ₄ ^c	1.63	17.9	62
<i>Hydrocarbon</i>			
SDS ^d	8.2	35-38	56
NaDEHP ^e	5.12	~32	-
TPA-DS ^f	1.46	31.8	67
AOT ^g	2.56	30.8	75
Double chain carboxylate ^h	0.084	30.0	-
SC ⁱ	91.10	29.8	45
TC ^j	0.0125	29.7	53
AOT ^g	1.10	28.0	70
TC ^j	21.63	27.0	80
TPA-TC ^f	0.075	25.4	136
2,4,4TMC ₅ -PO ₄ -Na ⁺ ^b	57	24.7	-
<i>Trisiloxane</i>			
SS ^k	-	21.5	70
L77 ^l	0.125	~22	66

^aData from Yoshimura.¹³ ^bData from Dickson.¹¹ ^cData collected by Eastoe.¹⁴ ^dData from various research groups.¹⁵⁻¹⁹ ^eData from Akbay.²⁰ ^fData collected by Brown.²¹ ^gData collected by Nave.^{22,23} ^hData collected by Zhu.²⁴ ⁱData collected by Hudson.²⁵ ^jData collected by Mohamed.²⁶ ^kData collected by Goddard.²⁷ ^lData from Rosen.²⁸

Work by Mohamed *et al.*⁸ has indicated that short branched HC surfactants, such as the trichain (TC14), can lower the surface tension of water down to ~ 27 mN m⁻¹, which is very low for a HC surfactant, and comparable to certain dichain fluorocarbon surfactants (e.g. DiHCF₄ = 26.8 mN m⁻¹).^{5,7} However, synthesis of trichain surfactants is time consuming and less straightforward compared to an equivalent single chain surfactant. To overcome these issues, here are developed novel single-chain surfactants (Figure 1) using commercially-available HC alcohols with various low surface energy hyperbranched “hedgehog” tails to establish the best substitutes for FCs. The advantages of this surfactant class are that they are synthesized from non-hazardous, commercially available starting materials and require only a one step reaction with easy purification procedures.

It was recently shown by Brown *et al.*²¹ that tetraalkylammonium (TAA) cations can be used as alternatives to imidazolium-based ions for ionic liquid surfactants. These TAA surfactants and dodecylsulfate (DS), Aerosol-OT(AOT), and Aerosol-OT analogue trichain (TC) anions, gave lower surface energies compared to the same anion surfactants but with Na⁺ as a cation.

Among the surfactants studied, those with tetrapropylammonium (TPA) were shown to have the lowest limiting surface tensions (see Table 1). As a consequence, in this study, the TPA cation has been chosen to examine the effect of counterion type on reducing surface tension.

This study investigates the adsorption/self-assembly behavior of highly branched single-chain surfactant solutions, the results are compared to the non-branched analogues, using surface tensiometry and small-angle neutron scattering (SANS). Double-chain surfactants with the same branched pendant hydrophobic tails were also synthesized in order to examine the effect of chain number on surface energy. The $n\text{-C}_{18}\text{S}$ (normal linear), $i\text{C}_{18}\text{S}(\text{FO-180N})$ and $i\text{C}_{18}\text{S}(\text{FO-180})$, single chain surfactants, and $i\text{C}_{18}\text{SS}(\text{FO-180N})$ and $i\text{C}_{18}\text{SS}(\text{FO-180})$, double chain surfactants, are shown in Figures 1. The normal linear C_{18} has been chosen as a control (in order to examine the effect of branching) and the TPA cation has been chosen as a substituted counterion. The result show it is possible to reduce the limiting surface tension (energy) to 24.7 mN m^{-1} , using a branched single tail anionic surfactant and the TPA counterion for reasons mentioned above.

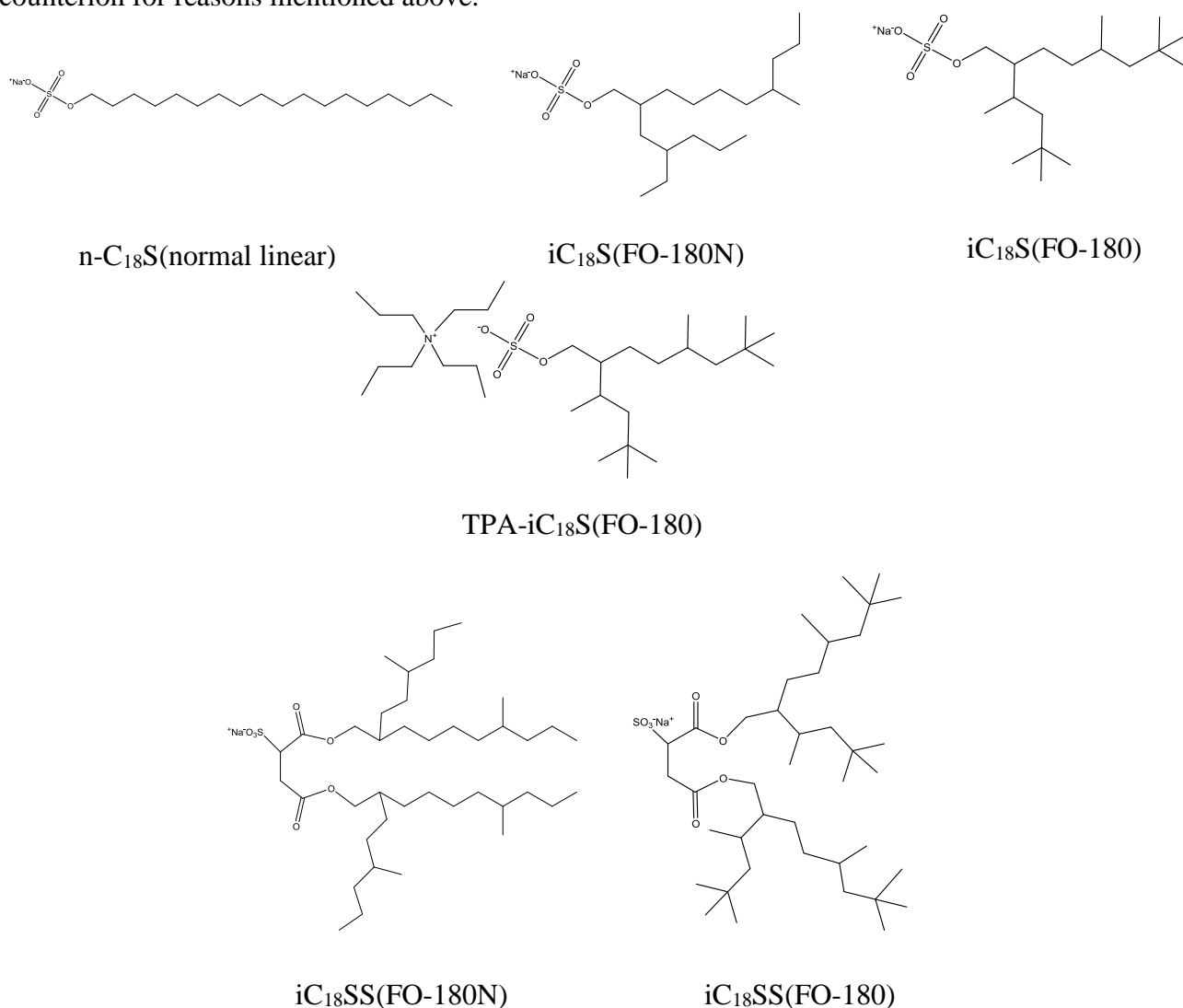


Figure 1. Structure of surfactants synthesized: *Single chain surfactants:* n-C₁₈S(normal linear), iC₁₈S(FO-180N), iC₁₈S(FO-180), and iC₁₈S(FO-180) with TPA cation, and *Double chain surfactants:* iC₁₈SS(FO-180N), and (f) iC₁₈SS(FO-180).

2. EXPERIMENTAL SECTION

Materials. Octadecyl sulfate (n-C₁₈S) was purchased from sigma Aldrich and was purified by crystallization from methanol and Soxhlet extraction.²⁹ The branched isostearyl surfactants (Figure 1) were synthesized as described below. Isostearyl alcohol FO-180N and FO-180 were provided by Nissan Chemical Industries. Maleic anhydride, *p*-Toluenesulfonic acid, chlorosulfonic acid sodium sulfite and sodium metabisulfite, tetrapropylammonium(TPA) hydroxide solutions, D₂O, and *d*₆-DMSO were purchased from Sigma Aldrich and used as received without further purification.

Surfactant Synthesis. For single chain surfactants an appropriate isostearyl alcohol (10 g, 36.96 mmol) was dissolved in dichloromethane (DCM) (150 mL) and the solution was cooled at 0 °C using an ice bath. Chlorosulfonic acid (1 eq. 4.30 g) was diluted by 100 ml of DCM and added dropwise to the isostearyl alcohol solution while maintaining the temperature at 0°C. After the addition was completed, the mixture was allowed to warm up to room temperature and was stirred overnight. It was then neutralized using either saturated sodium hydroxide solution in ethanol for the Na⁺ surfactant or aqueous TPA hydroxide solutions for the ammonium analogue. The solvent was then rotary evaporated and the product was dissolved in ethanol and de-colored by charcoal. The waxy solids were left in the vacuum oven overnight. The dried sample was then dissolved in a small amount of dry acetone and centrifuged for 60 minutes at 1000 rpm. The final product (yield: e.g. 11.5 g, 83.7 %) was obtained by removing the solvent and drying it in the vacuum oven over night at 70 °C. The surfactants were analyzed using ¹H-NMR (300 MHz, CDCl₃, TMS), (δ H/ppm): 0.76-1.79 (multiplet (m), 35H, aliphatic-H), 3.85-4.05 (m, 2H, -OCH₂); and Elemental analysis for C₁₈H₃₇O₄NaS: Calculated C: 58.0, H: 10.0, S: 8.6, and Na: 6.1 and the found: C: 58.7, H: 10.2, S: 7.6, and Na: 5.9.

The synthesis, purification, and characterization of double chain surfactants have been described elsewhere.^{21,30} More data on the characterization of these materials is given in the supporting information.

Surface Tension. Surface tensions for single chain surfactants were determined using a K100 tensiometer at the Krüss Surface Science Centre at the University of Bristol, using the Wilhelmy Plate method, as well as a drop shape analysis system DSA10 Mk2 for comparison. All the measurements for the branched systems were carried out at 298K, and for the linear C₁₈ chain surfactant at 328K to ensure complete solubility. The cleanliness of the glassware and

plate was tested by checking the surface tension of water (Elga, 18.2 M Ω cm) between each measurement.

For each concentration, 10 repeat measurements were obtained. In each case (except surface tension measurements in DMSO) the chelating agent EDTA (99.5% tetrasodium salt hydrate, Sigma) was used at a constant EDTA to surfactant ratio in order to sequester trace impurities of divalent cationic species M²⁺.^{22,23,31} The measurements in DMSO for double chains surfactant were carried out using a drop shape analysis system DSA10 Mk2.

Small-Angle Neutron Scattering. The SANS measurements were carried out on the D11 instrument at the Institute Laue-Langevin (ILL), Grenoble, France, and the LOQ instrument at ISIS facility, Rutherford Appleton Laboratory, UK. D11 uses neutrons with a wavelength of 10 Å and two sample-detector positions (1.2 m and 8 m) were used, to provide a Q -range of 0.002–0.4 Å⁻¹. LOQ is a fixed-sample detector instrument that uses a white neutron beam with wavelengths between 2.2 and 10.0 Å to provide a Q -range of 0.006–1.0 Å⁻¹. All samples were measured in 2 mm path-length rectangular quartz cells, and raw SANS data were normalized by subtracting the scattering of the empty cell and a solvent background. The measurements were carried out at 298K. The LAMP³² and Mantid³³ programs were used for data reduction from D11 and LOQ instrument respectively. SANS data were fitted using the fitting program SansView³⁴ which uses an iterative, least-squares fitting process. For high concentrations of nC₁₈S(normal linear) the elliptical cylinder (elliptical cross section) and cylinder form factor model (circular cross section) were applied. Data at high concentrations of iC₁₈S(FO-180N) were fitted to a lamella paracrystal model which applies for the scattering from a stack of repeating lamellar structures. And finally data from low concentrations of iC₁₈S(FO-180N), all concentrations of iC₁₈S(FO-180) and TPA-iC₁₈S(FO-180) were fitted to a unilamellar model, with assumption of random distribution in solution and a uniform scattering length density (SLD). The full details of the scattering form factors and parameters of these models can be found in the supporting information as well as the following references: the lamellar paracrystal model by Bergstrom³⁵ and Kotlarchyk³⁶, the lamellar model by Berghausen³⁷ and Nallet³⁸, and the elliptical cylinder (elliptical cross-section) and cylinder (circular cross-section) model by Feigin³⁹ and SansView³⁴ program.

3. RESULTS AND DISCUSSION

3.1. Effect of branching on absorption isotherms and self-assembly of single chain surfactants.

Surface Tension Measurements. The cmc determination using the surface tension method relies on the observation that increasing the surfactant concentration leads to a decrease in surface tension up to a break point, as is shown in Figure 2. The pre-cmc surface tension data

were fitted to quartic functions to calculate the **limiting** surface excess concentration ($\Gamma/\text{mol m}^{-2}$) **at the cmc** and thus, **associated** surface area per molecule ($A/\text{\AA}^2$) (eq. 2) using the Gibbs adsorption isotherm (eq. 1).

$$\Gamma = -\left(\frac{1}{mRT}\right)\left(\frac{d\gamma}{d\ln C}\right) \quad (1)$$

$$A = \left(\frac{1}{\Gamma N_A}\right) \quad (2)$$

where $m=2$, is the prefactor for 1:1 dissociating ionic surfactants,⁴⁰ γ (mN m^{-1}) is the surface tension, C ($\text{mole dm}^{-3} \equiv \text{M}$) is the surfactant concentration and N_A is Avogadro's number. Adsorption values derived from the surface tension curves are summarized in Table 2.

The $\log(\text{cmc})$ values are plotted against chain carbon number, as shown in Figure 3. The cmc decreases logarithmically with the linear alkyl chain length of a surfactant, n_c , based on the well-known Klevens equation (eq. 3).^{41,42}

$$\log(\text{cmc}) = A - Bn_c \quad (3)$$

Where A and B are constant and vary according to the charge and type of the head group and contribution of the CH_2 group respectively. For the ionic linear chain surfactants B is approximately 0.3 and A is about 4.49 (obtained from the linear fit in Figure 3). Within the branched series, links between cmc and alkyl carbon number is more complex. Comparison of the individual cmc's in Table 1 indicates that they follow a general trend of increasing cmc with increasing chain branching due to a shorter effective tail.⁴³ If only considering the longest linear portion of these surfactants based on their structure shown in Figure 1, the effective chain length would be 10 and 8 for $\text{Na}^+\text{-iC}_{18}\text{S(FO-180N)}$ and $\text{Na}^+\text{-iC}_{18}\text{S(FO-180)}$ respectively. However, by using the cmc values and the fit for the linear system (Figure 3), the effective thermodynamic chain length can be estimated. For $\text{Na}^+\text{-iC}_{18}\text{S(FO-180N)}$ the effective linear chain length is 15 n_c and for $\text{Na}^+\text{-iC}_{18}\text{S(FO-180)}$ is about **13.6** n_c . This indicates that these branched systems have much better solubility in aqueous solutions (as effective as linear $n\text{-C}_{15}\text{S}$ and $n\text{-C}_{13}\text{S}$) compared to that of linear chain $n\text{C}_{18}\text{S}$, simply due to branching effects.

Studies by Benrraou⁴⁴ suggest that the free energy of micellization becomes increasingly negative with increasing size of the TAA^+ counterion, indicating that micellization is favoured. This is in agreement with the work presented here: The cmc of the surfactant with TAA cation is noticeably lower than for the Na^+ counterion ($\text{cmc} = 2.7 \times 10^{-3} \text{ M}$ for Na^+ and $\text{cmc} = 0.87 \times 10^{-3} \text{ M}$ for TPA) due to the increase of hydrophobicity of the entire surfactant. However, each carbon added to the surfactant in the hydrophobic cations do not contribute to the cmc in the same way as carbon added to the surfactant chains, therefore the effective linear chain length is not greatly affected (from 13.5 for the Na^+ counterion surfactant to 15.5 for the TPA analogue).

More details on the effects of tetraalkylammonium counterions on the properties of ionic surfactants can be found elsewhere.^{21,44-47}

Table 2. Surfactant properties of nC₁₈S, iC₁₈S(FO-180N) and iC₁₈S(FO-180) at 298K unless otherwise stated. The adsorption parameters calculated using Gibbs analyses of γ -ln c curves. *The branching factor for iC₁₈S(FO-180) for example was calculated as follow: approaching the headgroup, 2 methyl in position 2, 1 methyl in position 4, and 7 in position 7 on a C₈ linear chain, i.e., [(2×2)+(1×4)+(7×7)/8]= 7.12²³ **calculated using eq.4. ^a data obtained by Verma⁴⁸, ^b Data collected by Evans⁴⁹

surfactant	Branching factor*	Effective chain length	CMC/(10 ⁻³ M) ± 0.03	γ_{cmc} /(mN m ⁻¹) ± 0.5	A/(Å ² /molecule) ± 2	Surface tension reduction per carbon (C γ)**
Na ⁺ -n-C ₁₈ S (normal linear)	0	18	0.13 (0.1 ^a -0.16 ^b)	33.2	-	2.1
Na ⁺ -iC ₁₈ S(FO-180N)	6.6	15	0.99	27.1	53	2.5
Na ⁺ -iC ₁₈ S(FO-180)	7.1	13.5	2.70	25.4	73	2.6
TPA-iC ₁₈ S(FO-180)	7.1	15.5	0.87	24.6	146	1.6

The effective area per headgroup at the cmc increases significantly on increasing the branching factor (from 53Å² for iC₁₈S(FO-180N) to 73Å² for iC₁₈S(FO-180N)). The parameters in Table 2 indicate that branched and bulky surfactants suffer steric hindrance at the interface which leads to a decrease in the packing efficiency, and therefore higher area per molecule. Areas per molecule also depend on the position and length of the branch on the linear chain. The longer the branch length and/or the closer the branching to the head group, the greater A_{cmc} , as previously observed by Nave²³ for a series of linear and branched AOT surfactants.

In the case of the linear n-C₁₈ surfactant it was not possible to obtain reliable data for A_{cmc} as pre-cmc data shown in Figure 2 were not reproducible. The surface tension measurements were repeated three times and in each case cmc and γ_{cmc} were consistent, however the pre-cmc curve was judged to be of lower reliability and therefore the data were not included in Table 2.

The effect of chain branching on reducing surface tension, limiting surface tension (γ_{cmc}), is a very important point of interest in this study. Comparing γ_{cmc} for the series of surfactants (presented in Table 1), demonstrate that fluorocarbons give rise to the lowest surface energies (13-17 mN m⁻¹), whereas single chain hydrocarbons (e.g SDS with γ_{cmc} ~ 35 mN m⁻¹) have the highest surface limiting tension. Within the hydrocarbon surfactants, trichain surfactants such as TC14 and TPA-TC are the most effective at reducing surface tension (energy) (γ_{cmc} =27 and 25 mN m⁻¹ respectively).

Among the compounds studied here, iC₁₈S(FO-180) has the lowest surface tension of γ_{cmc} =25.4 and γ_{cmc} =24.6 mN m⁻¹ with Na and TPA counterion respectively. As it was shown in Figure 3 these single chain compounds have effective linear tetradecyl and pentadecyl chains, and

therefore the effective limit for the surface tension may be reasonably expected to be the limiting value for the corresponding pure alkane ($\gamma_{\text{pentadecane}}=26.2^{50}$ and $\gamma_{\text{tetradecane}}=24.8 \text{ mN m}^{-1}$ ⁵¹). As can be seen, γ_{cmc} has reached the physical limit of the surface tension reduction and the values are very low indeed for hydrocarbon single chain surfactants (comparable to the trichain hydrocarbon and some dichain fluorocarbon surfactants e.g. DiHCF₄). Note the distinct difference between γ_{cmc} for normal linear hydrocarbon surfactants e.g. n-C₁₈S(normal linear) $\sim 33 \text{ mN m}^{-1}$ in this study, SDS $\sim 35 \text{ mN m}^{-1}$ and, SC4 $\sim 30 \text{ mN m}^{-1}$ from previous studies.²⁵ This remarkable reduction in surface tension is believed to be a direct consequence of increasing the CH₃:CH₂ ratio per headgroup (increase the branching using “hedgehog” tail structures), since the CH₃- has a lower γ_{cmc} than -CH₂- based on the following trend of CF₃- < -CF₂- < CH₃- < -CH₂-.⁵²

The efficiency of these surfactants on reducing the surface tension can also be expressed as surface tension reduction per carbon (C_γ), according to eq.4:

$$C_\gamma = \frac{\gamma_0 - \gamma_{\text{cmc}}}{C_{\text{tot}}} \quad (4)$$

Where γ_0 is surface tension of pure water (72 mN m^{-1}) and C_{tot} is total number of carbons (e.g. 18 for all the Na⁺ surfactants in Figure 1 and 30 for the TPA⁺ surfactant). As can be seen in Table 2, Na⁺-iC₁₈S(FO-180) is the most "material" efficient as it has given the largest decrement in surface tension per carbon (C_γ), consistent with the highest branching factor. On the other hand TPA-iC₁₈S(FO-180) is the least material efficient, which concludes that larger and more hydrophobic cations (e.g TPA) do not contribute to the surface tension reduction with the same efficiency as carbons introduced into the surfactant chains.

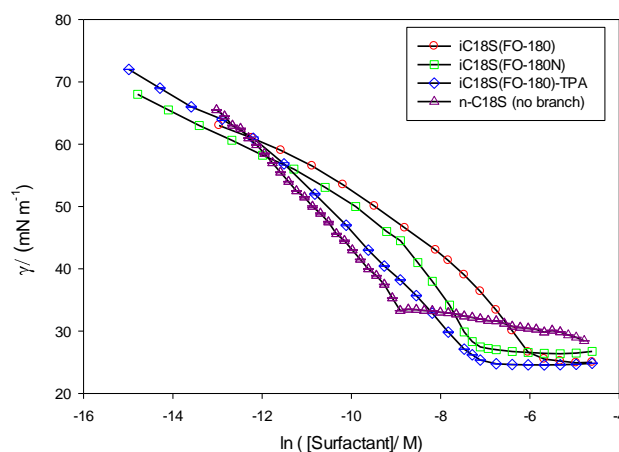


Figure 2. Surface tension behavior of single chain surfactants in water. Polynomial lines fitted to the pre-cmc data were used to calculate the surface excesses.

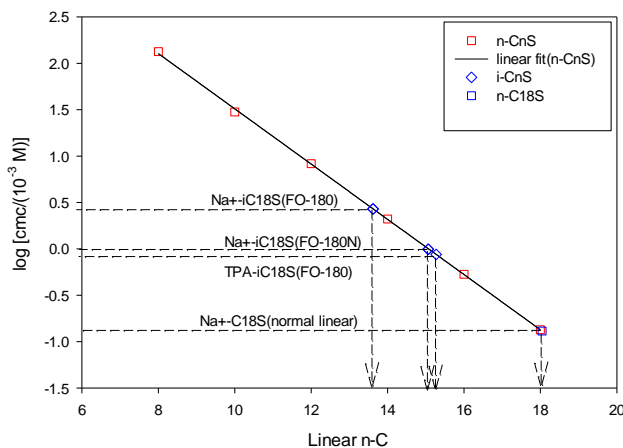


Figure 3. Log cmc vs. the carbon number for linear single chain surfactants (literature data as well as new experimental data for C₁₈), and estimation of effective thermodynamic chain length for branched surfactants. The cmc data for linear surfactant with carbon number C₈₋₁₄ are taken from Ranganathan.⁵³ C₁₆ from Valente⁵⁴ and C₁₈ from Evans.⁴⁹ All the quoted data are at 25°C, except for C₁₈ which is at 40°C.

Aggregation structures. SANS data were collected for all the three single chain surfactants as a function of concentration. For n-C₁₈ (normal linear) measurements were carried out at 328K to ensure the complete solubility in D₂O and for the rest of the surfactants the temperature was 298K. In all cases cmc's obtained by SANS are in good agreement with the surface tension data.

The scattering pattern for the n-C₁₈ (normal linear) surfactant is shown in Figure 4a. At higher concentrations (75 mM and 19 mM), the scattering patterns are consistent with charged elliptical cylinder (elliptical cross section) micelles with parameters including length ($L/\text{Å}$), minor axis ($R_1/\text{Å}$), major axis ($R_2/\text{Å}$), aspect ratio ($X = R_2/R_1$), and the effective micellar charge (Z). At 75 mM the fitted length $L = 155 \text{ Å}$ and the minor axis $R_1 = 18.7 \text{ Å}$ which is consistent of the molecular size of the surfactant (Table 3).

By decreasing the concentration to 19 mM the length of the cylinder decreases to $L = 66 \text{ Å}$, however the fitted R_1 is not greatly affected ($R_1 = 20 \text{ Å}$). The SANS data for concentrations below 4.5 mM were fitted using a model for non-interacting spherical micelles with R_{sphere} of $\sim 21 \text{ Å}$. No clear scattering pattern was observed for the sample at 0.15 mM which is around the surface tension derived cmc for this surfactant (cmc $\sim 0.13 \text{ mM}$). The change in size and shape of micelles with concentration has been reported previously for the common linear C₁₂ surfactant, SDS, that at lower concentrations (above the cmc) spherical micelles and at higher concentrations ellipsoidal/cylindrical micelles and eventually lamellar structures were observed.^{55,56}

Table 3. SANS parameters fitted to the charged elliptical cylinder, charged cylinder, and spherical structure for n-C₁₈ (normal linear) surfactant at 328K.

Concentration/mM	75	19	4.7	1.2	0.6	0.3
L (Å) \pm 1.5	155	65.9	47.4	-	-	-
R_1 (Å) \pm 1.0	18.7	20.3	20.5	-	-	-
X	1.48	1.36	-	-	-	-
R_2 (Å) \pm 0.1	27.6	26.4	-	-	-	-
Z \pm 0.5	15	21	13	-	-	-
R_{sphere} (Å) \pm 1.5	-	-	-	21.8	21.3	21.9

On moving to branched single chain surfactants, the micellar structures (Figure 4b-d) are very different to those seen with the linear chain analogue. The scattering profiles for these surfactants are essentially independent of dilution and intensity scales linearly with volume fraction. Data for higher concentrations of Na⁺-iC₁₈S(FO-180N) (Figure 4b), were fitted to the paracrystal lamellar model with parameters: bilayer thickness D , average distance between two adjacent layers L , distribution of layer distance P , and the number of layers N_{layer} . However, for the same surfactant in the dilute region (9.4 and 4.7 mM), data were fitted to a lamellar form factor with fitted parameter bilayer thickness D . An overview of the parameters obtained using the paracrystal lamellar model and the lamellar structure is given in Table 4. The average number of layers appeared to be rather small, between 1.1 and 1.45, indicating that one or two small unilamellar sheets are in coexistence. As is expected, the average distance between two adjacent layers L , tends to increase upon dilution until the systems become so dilute that only unilamellar sheets are observed, with thickness of around $D = 20$ Å and $D = 23$ Å at concentrations of 9.34 mM and 4.7 mM, respectively. For concentrations around the cmc (2.3 mM and 1.1 mM), data could not be fitted to a single model. However, data at high Q , $0.05 < Q < 0.3$, could be fitted to spherical micelles with radii of ~ 19 Å. Bergström³⁵ observed similar behaviour for the mixed SDS/DTAB surfactants. It was found that on increasing the overall surfactant concentration, stacks of lamellar sheets were formed with the number of layers in a single cluster increasing from 1-3 to infinity.

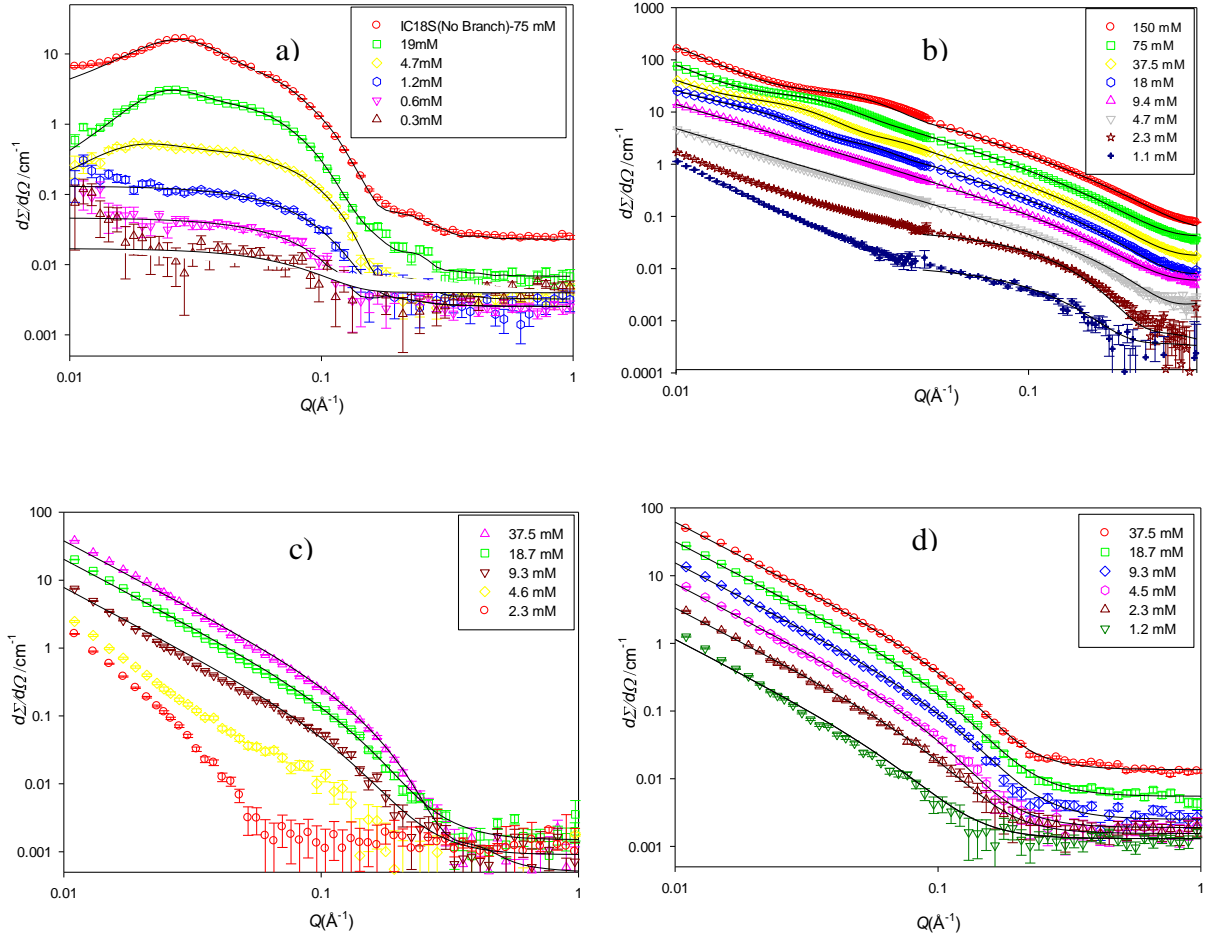


Figure 4. SANS profiles for a) n-C₁₈ (normal linear) surfactant at 328K, b) Na⁺-iC₁₈S(FO-180N) surfactant (data are from D11 at ILL), c) Na⁺-iC₁₈S(FO-180) surfactant, and d) TPA-iC₁₈S(FO-180) surfactant at 298K in D₂O at a range of concentrations, (a), c) and d) data are from LOQ at ISIS).

Data for both Na⁺-iC₁₈S(FO-180) and TPA-iC₁₈S(FO-180) (Figure 4c-d), were fitted to the unilamellar structure with bilayer thickness $D \approx 19 \text{ \AA}$ for the Na⁺ counterion and $D \approx 24 \text{ \AA}$ for TPA⁺ counterion systems with a distribution of bilayer thickness of $\sigma \sim 0.3-0.5$, as is shown in Table 4. The larger bilayer thickness for TPA-iC₁₈S(FO-180) surfactants is consistent and in line with increased counterion size, which demonstrates that ion association can be detected for these single chain surfactants, in contrast to single chain DS surfactants.²¹ Although it has been shown previously that counterion nature can strongly affect the shape of the aggregates,^{21,57} interestingly, counterion size and shape does not significantly influence the shape of the systems studied here, showing the dominant influence of surfactant ion chemical structure on aggregation. The data for Na⁺-iC₁₈S(FO-180) at a dilute concentration of 4.6 mM could not be fitted to a single model as it was stated for the Na⁺-iC₁₈S(FO-180N). The 2.3 mM solution is just below the critical micelle concentration ($\text{cmc} = 2.7 \text{ mM}$) and the SANS data, within the resolution of the intensity scale, demonstrates the absence of any self-assembly structure at

high Q , however, the origin of the scattering at low Q is likely to be residual lamellar fragments.

Table 4. Parameters fitted to SANS data for a paracrystal lamellar model and lamellar structure for $\text{Na}^+\text{-iC}_{18}\text{S(FO-180N)}$ surfactant, and a lamellar structure, for both TPA- $\text{iC}_{18}\text{S(FO-180)}$ and $\text{Na}^+\text{-iC}_{18}\text{S(FO-180)}$ surfactants at 298K.

Surfactant	$\text{Na}^+\text{-iC}_{18}\text{S(FO-180N)}$						TPA- $\text{iC}_{18}\text{S(FO-180)}$						$\text{Na}^+\text{-iC}_{18}\text{S(FO-180)}$		
	Concentration/ mM	150	75	37.5	18	9.4	4.7	37.5	18.7	9.3	4.6	2.3	1.1	37.5	18.7
$D (\text{\AA}) \pm 0.01$	17.5	20	20.4	20.6	20.3	23	22.4	21.2	20.5	25.1	24.9	22.2	19.3	19.4	19.3
$L (\text{\AA}) \pm 0.1$	168.8	210	262	332	-	-	-	-	-	-	-	-	-	-	-
$N_{\text{layer}} \pm 0.006$	1.44	1.44	1.3	1.1	-	-	-	-	-	-	-	-	-	-	-
P	0.22	0.26	0.18	0.12	-	-	-	-	-	-	-	-	-	-	-
σ	-	-	-	-	-	-	0.36	0.39	0.4	0.39	0.30	0.5	0.25	0.41	0.50

3.2. Adsorption isotherms and self-assembly of double chain branched surfactants.

Double chain branched surfactants, $\text{iC}_{18}\text{SS(FO-180N)}$ and $\text{iC}_{18}\text{SS(FO-180)}$ (Figure 1e-f), were synthesized with the intention of pushing the “hedgehog” molecules to the limit of reducing surface energy. However, increasing the number of chains reduces surfactant solubility in aqueous solutions, and therefore it was not possible to dissolve them in water. In order to examine the surface activity of these materials, DMSO which is a polar solvent with a relatively high surface tension ($\gamma = 42 \text{ mN m}^{-1}$)⁵⁸ and dielectric constant of $\epsilon = 49$ was chosen. Both the double chain surfactants were readily soluble in DMSO. The plots of surface tension vs. concentration are shown in Figure 5 and the absorption isotherms data obtained from the graph are shown in Table 5. As can be seen from the graph, surface tension of DMSO solutions decrease from ~ 42.0 to ~ 28.0 and $\sim 27 \text{ mN m}^{-1}$ $\text{iC}_{18}\text{SS(FO-180)}$ and $\text{iC}_{18}\text{SS(FO-180N)}$ respectively and this is clear evidence for solvophobicity and surface-activity in DMSO. However, as DMSO is a much better solvent for these surfactants, the cmc’s are rather high in comparison to those of analogous single chain surfactants in water.

Micelle formation of SDS and cetyltrimethylammoniumbromide (CTAB) in organic solvents including DMSO has been reported and the obtained cmc values in DMSO are higher by a factor of 10-30 compared to water.⁵⁹ As expected for double chain surfactants, addition of a bulkier hydrophobic chain decreases interfacial packing, which in turn increases the molecular area A_{cmc} , as compared to single chain analogues in water (Table 2).

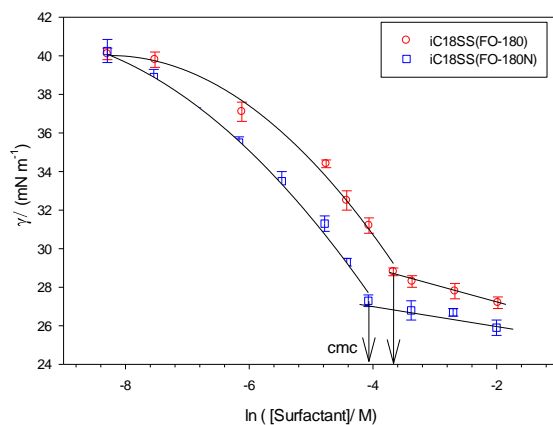


Figure 5. Surface tension behavior for double chain surfactants in DMSO. Polynomial lines fitted to the pre-cmc data were used to calculate the surface excesses.

The SANS patterns and the fitted data in d_6 -DMSO at various concentrations are shown in Figure S5 and Table S2-S3 in the supporting information. The fitting data indicate a weak tendency for aggregation, with low-charge larger aggregates at higher concentrations, and distributions of mainly monomers to trimers at lower concentrations. Similar behaviour was also reported for non-ionic alkyl-fluoroalkyl lipopeptides, in which a low degree of aggregations in DMSO was observed by SANS.⁶⁰ These surface tension results for γ_{cmc} in DMSO are consistent with the findings from studies of aqueous solutions of single branched chain analogues described above. It can be seen that highly branched chains give rise to low limiting surface tensions (energies), at both the air-water and air-DMSO interfaces. Hence, although the double chain analogues are too hydrophobic to be of use in water, the principle that chain branching and chain tip methylation can lead to low surface energy surfactants has been clearly established.

Table 5. Surfactant properties of $iC_{18}SS(FO-180)$ and $iC_{18}SS(FO-180N)$ at 298K. The adsorption parameters calculated using Gibbs analyses of γ - $\ln c$ curves.

surfactant	T/K	CMC/(10^{-3} M) \pm 0.3	γ_{cmc} /(mN m^{-1})	Γ /(mol m^{-2})	A_{cmc} /($\text{\AA}^2/\text{molecule}$)
$iC_{18}SS(FO-180)$	298	20	28.0	9.9×10^{-7}	167
$iC_{18}SS(FO-180N)$	298	17	27.3	8.55×10^{-7}	193

4. CONCLUSIONS

Single and double chain highly branched “hedgehog” anionic surfactants were successfully synthesized and characterized using surface tension and SANS. Single chain surfactants have been previously reported,^{16,25,49,54} with relatively high surface energy compared to fluorocarbon (FC) surfactants^{11,13} and hydrocarbon (HC) tri-chain surfactants.²¹ For the first time it is shown that single hydrocarbon (HC) chain LSEMs can be obtained. These new low surface energy surfactants, synthesized using commercially available feedstock alcohols as convenient

precursors, can lower the surface tension of water as low as $\sim 24 \text{ mN m}^{-1}$: this represents an all-time low value for single chain HC surfactants, and is even lower than certain di-chain FC surfactants (e.g. $\text{DiHCF}_4 = 26.8 \text{ mN m}^{-1}$)⁶ and tri-chain hydrocarbon surfactants (e.g. $\text{TC14} = 27 \text{ mN m}^{-1}$)⁸. This is a remarkable decrease in surface tension can be achieved by increasing branching in the alkyl chains; the higher the branching factor, the lower the surface tension and the higher the aqueous solubility. Self-assembly of these “hedgehog” molecules in water was examined and compared to the normal linear analogue. The results from the branched C_{18} systems showed formation of lamellar sheets, which were independent of dilution; whereas the aggregation structure of linear C_{18} surfactant was concentration dependent and formation of elliptical cylinder, cylindrical and spherical micelles were observed as a function of concentration. Double-chain surfactants with the same branched pendant hydrophobic tails were also synthesized, however the direct comparison to the single chain versions was not possible as these materials were of very low solubility in aqueous solution. Their self-assembly and surface active properties in DMSO indicated very weakly aggregated micelles with ability to reduce the surface tension of DMSO from 42 mN m^{-1} to around 27 mN m^{-1} .

Introduction of chain branching gives rise to two beneficial effects, which serve to improve the properties of surfactants compared to simple linear chain counterparts. Firstly, branching reduces the effective thermodynamic carbon number, increasing the solubility of long chain surfactants in water so that they can perform, and form micelles, at convenient temperatures compared to a linear chain analogue.

Secondly, branched chain architectures promote efficient packing of interfaces, permitting dense surface coverage of $-\text{CH}_2$ and $-\text{CH}_3$ groups. This has an important consequence, since now the alkyl region of adsorbed monolayers can generate densely packed disordered surface layers, to mimic more closely the structure of a neat HC oil, which has a naturally low surface energy (tension). Hence, branched chain surfactants are shown to offer a number of advantages for efficient applications in a variety of fields. Taking all of these results together, the future of replacing costly and environmentally hazardous FC surfactants and polymers with cheap and nontoxic HC LSEMs seems to be within reach.

5. ASSOCIATED CONTENT

Supporting Information. Characterization of synthesized materials by NMR and metal analysis. Additional details of SANS model fitting. This material is available free of charge via the Internet at <http://pubs.acs.org>.

6. AUTHOR INFORMATION

Corresponding Author. *E-mail Julian.Eastoe@bristol.ac.uk; Fax +44 117 9277985

(J.E.), and shirin.alexander@bristol.ac.uk (S.A.)

Notes. The authors declare no competing financial interest.

7. ACKNOWLEDGMENT

S.A. acknowledges the EPSRC for postdoctoral funding through EPSRC EP/K020676/1 under the G8 Research Councils Initiative on Multilateral Research Funding - G8-2012, the STFC for allocation of beam time, travel, and consumables, and Dr Isabelle Grillo at the Institut Laue-Langevin (ILL) is thanked for her support during the experiments. C.J. is supported by EPSRC (grants EP/I018301/1 and EP/I018212/1)

8. REFERENCES

- (1) Celia, E.; Darmanin, T.; Taffin de Givenchy, E.; Amigoni, S.; Guittard, F.: Recent advances in designing superhydrophobic surfaces. *J. Colloid Interface Sci.* **2013**, *402*, 1-18.
- (2) Callow, M. E.; Fletcher, R. L.: The influence of low surface energy materials on bioadhesion — a review. *Int. Biodeterior. Biodegrad.* **1994**, *34*, 333-348.
- (3) Tsibouklis, J.; Nevell, T. G.: Ultra-low surface energy polymers: The molecular design requirements. *Adv. Mater.* **2003**, *15*, 647-650.
- (4) Schmidt, D. L.; Coburn, C. E.; DeKoven, B. M.; Potter, G. E.; Meyers, G. F.; Fischer, D. A.: Water-based non-stick hydrophobic coatings. *Nature* **1994**, *368*, 39-41.
- (5) Matsumoto, Y.; Yoshida, K.; Ishida, M.: A novel deposition technique for fluorocarbon films and its applications for bulk- and surface-micromachined devices. *Sens. Actuators, A* **1998**, *66*, 308-314.
- (6) Eastoe, J.; Nave, S.; Downer, A.; Paul, A.; Rankin, A.; Tribe, K.; Penfold, J.: Adsorption of ionic surfactants at the air–solution interface. *Langmuir* **2000**, *16*, 4511-4518.
- (7) Mohamed, A.; Sagisaka, M.; Hollamby, M.; Rogers, S. E.; Heenan, R. K.; Dyer, R.; Eastoe, J.: Hybrid CO₂-philic surfactants with low fluorine content. *Langmuir* **2012**, *28*, 6299-6306.
- (8) Mohamed, A.; Sagisaka, M.; Guittard, F.; Cummings, S.; Paul, A.; Rogers, S. E.; Heenan, R. K.; Dyer, R.; Eastoe, J.: Low fluorine content CO₂-philic surfactants. *Langmuir* **2011**, *27*, 10562-10569.
- (9) Begley, T. H.; White, K.; Honigfort, P.; Twaroski, M. L.; Neches, R.; Walker, R. A.: Perfluorochemicals: Potential sources of and migration from food packaging. *Food Addit. Contam.* **2005**, *22*, 1023-1031.
- (10) Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H.: Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2005**, *40*, 32-44.
- (11) Dickson, J. L.: Stabilization of Colloidal Dispersions in Supercritical Carbon Dioxide. PhD thesis. The University of Texas 2005.
- (12) Queimada, A. J.; Marrucho, I. M.; Coutinho, J. A. P.: Surface tension of pure heavy n-alkanes: a corresponding states approach. *Fluid Phase Equilib.* **2001**, *183–184*, 229-238.

- (13) Yoshimura, T.; Ohno, A.; Esumi, K.: Equilibrium and dynamic surface tension properties of partially fluorinated quaternary ammonium salt gemini surfactants. *Langmuir* **2006**, *22*, 4643-4648.
- (14) Eastoe, J.; Downer, A.; Paul, A.; Steytler, D. C.; Rumsey, E.; Penfold, J.; Heenan, R. K.: Fluoro-surfactants at air/water and water/CO₂ interfaces. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5235-5242.
- (15) Sakhawat Shah, S.; Muhammad Khan, A.: Determination of critical micelle concentration (cmc) of sodium dodecyl sulfate (sds) and the effect of low concentration of pyrene on its cmc using Origin software. *J. Chem. Soc. Pak.* **2008**, *30*, 186-191.
- (16) Hernáinz, F.; Caro, A.: Variation of surface tension in aqueous solutions of sodium dodecyl sulfate in the flotation bath. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2002**, *196*, 19-24.
- (17) Mysels, K. J.: Surface tension of solutions of pure sodium dodecyl sulfate. *Langmuir* **1986**, *2*, 423-428.
- (18) Taylor, D. J. F.; Thomas, R. K.; Penfold, J.: Polymer/surfactant interactions at the air/water interface. *Adv. Colloid Interface Sci.* **2007**, *132*, 69-110.
- (19) Rana, D.; Neale, G.; Hornof, V.: Surface tension of mixed surfactant systems: lignosulfonate and sodium dodecyl sulfate. *Colloid. Polym. Sci.* **2002**, *280*, 775-778.
- (20) Akbay, C.; Wilmot, N.; Agbaria, R. A.; Warner, I. M.: Characterization and application of sodium di(2-ethylhexyl) sulfosuccinate and sodium di(2-ethylhexyl) phosphate surfactants as pseudostationary phases in micellar electrokinetic chromatography. *J. Chromatogr. A* **2004**, *1061*, 105-111.
- (21) Brown, P.; Butts, C.; Dyer, R.; Eastoe, J.; Grillo, I.; Guittard, F.; Rogers, S.; Heenan, R.: Anionic surfactants and surfactant ionic liquids with quaternary ammonium counterions. *Langmuir* **2011**, *27*, 4563-4571.
- (22) Nave, S.; Eastoe, J.; Heenan, R. K.; Steytler, D.; Grillo, I.: What is so special about Aerosol-OT? 2. Microemulsion systems. *Langmuir* **2000**, *16*, 8741-8748.
- (23) Nave, S.; Eastoe, J.; Penfold, J.: What is so special about Aerosol-OT? 1. Aqueous systems. *Langmuir* **2000**, *16*, 8733-8740.
- (24) Zhu, Y.-P.; Masuyama, A.; Kobata, Y.; Nakatsuji, Y.; Okahara, M.; Rose, M. J.: Double-chain surfactants with two carboxylate groups and their relation to similar double-chain compounds. *J. Colloid Interface Sci.* **1993**, *158*, 40-45.
- (25) Hudson, L.: Structure versus Performance – Surfactants at Interfaces. PhD thesis. University of Bristol, 2008.
- (26) Mohamed, A.; Trickett, K.; Chin, S. Y.; Cummings, S.; Sagisaka, M.; Hudson, L.; Nave, S.; Dyer, R.; Rogers, S. E.; Heenan, R. K.; Eastoe, J.: Universal surfactant for water, oils, and CO₂. *Langmuir* **2010**, *26*, 13861-13866.
- (27) Ananthapadmanabhan, K. P.; Goddard, E. D.; Chandar, P.: A study of the solution, interfacial and wetting properties of silicone surfactants. *Colloids Surf.* **1990**, *44*, 281-297.
- (28) Rosen, M. J.; Wu, Y.: Superspreading of trisiloxane surfactant mixtures on hydrophobic surfaces. 1. Interfacial adsorption of aqueous trisiloxane surfactant-n-alkyl pyrrolidinone mixtures on polyethylene. *Langmuir* **2001**, *17*, 7296-7305.
- (29) Nakamae, M.; Abe, M.; Ogino, K.: The effects of alkyl chain lengths of sodium alkyl sulfates and n-alkanes on microemulsion formation. *J. Colloid Interface Sci.* **1990**, *135*, 449-454.
- (30) Gold, S.; Eastoe, J.; Grilli, R.; Steytler, D.: Branched trichain sulfosuccinates as novel water in CO₂ dispersants. *Colloid. Polym. Sci.* **2006**, *284*, 1333-1337.
- (31) Li, Z. X.; Lu, J. R.; Thomas, R. K.: Neutron reflectivity studies of the adsorption of Aerosol-OT at the air/water interface: The surface excess. *Langmuir* **1997**, *13*, 3681-3685.
- (32) <http://www.ill.eu/instruments-support/computing-for-science/cs-software/all-software/lamp/>.
- (33) http://www.mantidproject.org/Main_Page.
- (34) SasView-2.2.1: <http://www.sasview.org/>.

- (35) Bergström, M.; Pedersen, J. S.; Schurtenberger, P.; Egelhaaf, S. U.: Small-angle neutron scattering (SANS) study of vesicles and lamellar sheets formed from mixtures of an anionic and a cationic surfactant. *J. Phys. Chem. B* **1999**, *103*, 9888-9897.
- (36) Kotlarchyk, M.; Ritzau, S. M.: Paracrystal model of the high-temperature lamellar phase of a ternary microemulsion system. *J. Appl. Crystallogr.* **1991**, *24*, 753-758.
- (37) Berghausen, J.; Zipfel, J.; Lindner, P.; Richtering, W.: Influence of water-soluble polymers on the shear-induced structure formation in lyotropic lamellar phases. *J. Phys. Chem. B* **2001**, *105*, 11081-11088.
- (38) Nallet, F.; Laversanne, R.; Roux, D.: Modelling X-ray or neutron scattering spectra of lyotropic lamellar phases : interplay between form and structure factors. *J. Phys. II France* **1993**, *3*, 487-502.
- (39) Feigin, L. A.; Svergun, D. I.: *Structure Analysis by Small-Angle X-Ray and Neutron Scattering*; Plenum: New York, 1987.
- (40) Eastoe, J.: *Surfactant Chemistry*; Wuhan University Press: China, 2003.
- (41) Klevens, H. B.: Structure and aggregation in dilute solution of surface active agents. *J. Am. Oil Chem. Soc.* **1953**, *30*, 74-80.
- (42) Huibers, P. D. T.: Quantum-chemical calculations of the charge distribution in ionic surfactants. *Langmuir* **1999**, *15*, 7546-7550.
- (43) Rosen, M. J.: *Surfactants And Interfacial Phenomena*; John Wiley & Sons: USA, 1989.
- (44) Benrraou, M.; Bales, B. L.; Zana, R.: Effect of the nature of the counterion on the properties of anionic surfactants. 1. Cmc, ionization degree at the cmc and aggregation number of micelles of sodium, cesium, tetramethylammonium, tetraethylammonium, tetrapropylammonium, and tetrabutylammonium dodecyl sulfates. *J. Phys. Chem. B* **2003**, *107*, 13432-13440.
- (45) Tcacenco, C. M.; Zana, R.; Bales, B. L.: Effect of the nature of the counterion on the properties of anionic surfactants. 5. Self-association behavior and micellar properties of ammonium dodecyl sulfate. *J. Phys. Chem. B* **2005**, *109*, 15997-16004.
- (46) Mukerjee, P.; Mysels, K.; Kapauan, P.: Counterion specificity in the formation of ionic micelles - size, hydration, and hydrophobic bonding effects. *J. Phys. Chem.* **1967**, *71*, 4166-4175.
- (47) Bonilha, J. B. S.; Georgetto, R. M. Z.; Abuin, E.; Lissi, E.; Quina, F.: Exchange between alkylammonium and sodium ions at the surface of dodecylsulfate micelles. *J. Colloid Interface Sci.* **1990**, *135*, 238-245.
- (48) Verma, A.; Purkait, M. K.: Synthesis, characterization and physical properties studies of an anionic surfactant. *Indian J. Chem. Technol.* **2010**, *17*, 233-237.
- (49) Evans, H. C.: 117. Alkyl sulphates. Part I. Critical micelle concentrations of the sodium salts. *J. Chem. Soc.* **1956**, 579-586.
- (50) Shinoda, W.; DeVane, R.; Klein, M. L.: Multi-property fitting and parameterization of a coarse grained model for aqueous surfactants. *Mol. Simul.* **2007**, *33*, 27-36.
- (51) Mejía, A.; Cartes, M.; Segura, H.: Interfacial tensions of binary mixtures of ethanol with octane, decane, dodecane, and tetradecane. *J. Chem. Thermodyn.* **2011**, *43*, 1395-1400.
- (52) Pitt, A. R.; Morley, S. D.; Burbidge, N. J.; Quickenden, E. L.: The relationship between surfactant structure and limiting values of surface tension, in aqueous gelatin solution, with particular regard to multilayer coating. *Colloids Surf., A* **1996**, *114*, 321-335.
- (53) Ranganathan, R.; Tran, L.; Bales, B. L.: Surfactant and salt-induced growth of normal sodium alkyl sulfate micelles well above their critical micelle concentrations. *J. Phys. Chem. B* **2000**, *104*, 2260-2264.
- (54) Valente, A. J. M.; J.S. Dinis, C.; Pereira, R. F. P.; Ribeiro, A. C. F.; Lobo, V. M. M.: Interactions between β -cyclodextrin and some sodium alkyl sulfates and sulfonates as seen by electrical conductivity measurements. *Port. Electrochim. Acta* **2006**, *24*, 129-136.

(55) Rachman, P. E. G.; Abarrul, I.: Nanosize structure of self-assembly sodium dodecyl sulfate: A study by small angle neutron scattering (SANS). *Indo. J. Chem.* **2006**, *6*, 117-120.

(56) Kékicheff, P.; Grabielle-Madelmont, C.; Ollivon, M.: Phase diagram of sodium dodecyl sulfate-water system: 1. A calorimetric study. *J. Colloid Interface Sci.* **1989**, *131*, 112-132.

(57) Eastoe, J.; Towey, T. F.; Robinson, B. H.; Williams, J.; Heenan, R. K.: Structures of metal bis(2-ethylhexylsulfosuccinate) aggregates in cyclohexane. *J. Phys. Chem.* **1993**, *97*, 1459-1463.

(58) Bagheri, A.; Abolhasani, A.; Moghadasi, A. R.; Nazari-Moghaddam, A. A.; Alavi, S. A.: Study of surface tension and surface properties of binary systems of DMSO with long chain alcohols at various temperatures. *J. Chem. Thermodyn.* **2013**, *63*, 108-115.

(59) Singh, H. N.; Saleem, S. M.; Singh, R. P.; Birdi, K. S.: Micelle formation of ionic surfactants in polar nonaqueous solvents. *J. Phys. Chem.* **1980**, *84*, 2191-2194.

(60) Chrisment, J.; Delpuech, J.-J.; Hamdoune, F.; Ravey, J.-C.; Selve, C.; Stebe, M.-J.: Aggregation of amphiphilic compounds in dimethyl sulfoxide: example of non-ionic alkyl-fluoroalkyl lipopeptides. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 927-934.

