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Surfactants at the Design Limit

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This article analyzes how the individual structural elements of surfactant molecules affect surface properties. In particular, the point of reference defined by the limiting surface tension at the aqueous cmc, γ_{cmc}. Particular emphasis is given to how the chemical nature and structure of the hydrophobic tails influences γ_{cmc}. By comparing the three different classes of surfactants, fluoro-, silicone and hydro-carbon, a generalized surface packing index is introduced which is independent of the chemical nature of the surfactants. This parameter ϕ_{cmc} represents the volume fraction of surfactant chain fragments in a surface film at the aqueous cmc. It is shown that ϕ_{cmc} is a useful index for understanding the limiting surface tension of surfactants and can be useful for designing new super-efficient-surfactants.

1. Introduction

Surfactants are amongst the most versatile chemicals, being key components in a diverse range of products and technologies such as the petroleum industry, pharmaceuticals, detergents, firefighting foams, inks, paints, electronic printing, bio- and medical technologies.[1-5] The inherent versatility of surfactant molecules originates from their amphiphilic character, the molecules possess both polar, water-soluble sections ("head group") and non-polar, water-insoluble moieties ("tail"). The dual characteristics of surfactant molecules give them a wide range of properties, connected to two key features – adsorption at interfaces and self-assembly in bulk solution.

Surface tension arises due to an imbalance of attractive intermolecular interactions at a liquid surface. Molecules in the final surface layer have no neighbours above, and consequently are attracted into the bulk. This imbalance of intermolecular attractive interactions creates an excess energy at the surface compared to the bulk (the surface free energy), which forces liquid surfaces to contract, reducing exposed surface area. When present at low concentrations, surfactant adsorption to the air-water interface is a spontaneous process resulting in an oriented monolayer, which alters the surface free energy. The surface tension of a liquid γ (units: J m^{-2} or N m^{-1}) is the interfacial free energy per unit area but strictly referring to a gas-liquid interface (by convention interfacial tension refers to liquid-liquid, or liquid-solid interfaces). To expand, a minimum amount of work (W_{min}) is required to create the additional surface, which is a product of the surface tension γ and increase in the surface (interfacial) area dA, so $W_{min} = \gamma\, dA$. A surfactant is a substance that will adsorb to a surface, significantly altering the surface (interfacial) tension and therefore change the work required to expand the liquid surface.

Pure water has a surface tension of about 72 mN m^{-1} (298 K), and the extent of reduction of γ is one of the most commonly measured properties of surfactant solutions.[6-8] The critical micelle concentration (cmc), the limiting surface tension at the cmc (γ_{cmc}) and the dynamics of adsorption are all influenced by surfactant structure. The hydrophobic tail has a major effect on controlling important physiochemical properties such as cmc, γ, γ_{cmc}, Γ, Γ_{cmc} and A_{cmc} (Figure 1).

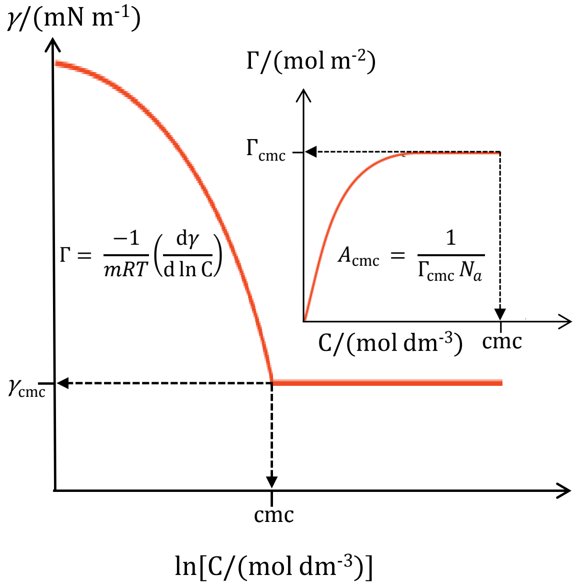


Figure 1. Surfactant adsorption at the air-water interface. The surface tension (γ) is reduced as surfactant molecules adsorb to the air-water interface, simultaneously increasing the surface excess (Γ) until the cmc is reached. At which point there is generally a plateau. A_{cmc} corresponds to the area per surfactant molecule at the air-water interface at the reference concentration, cmc.

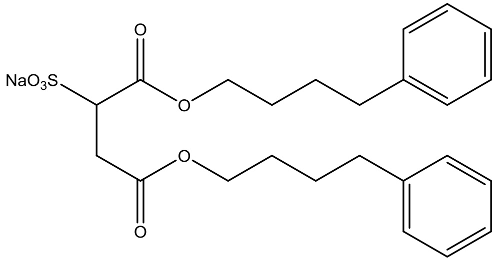
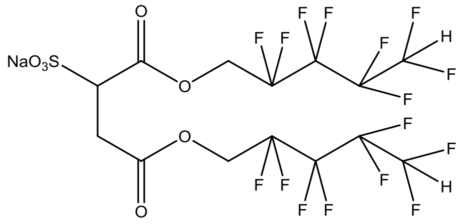
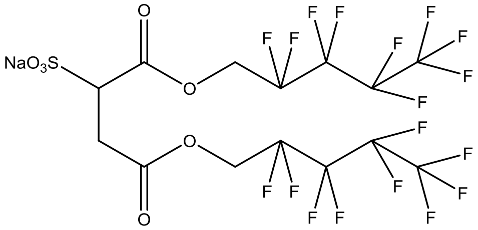
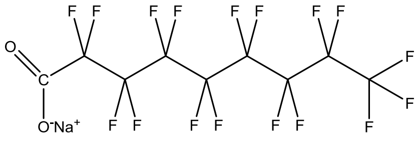
In order to provide a quantitative description of surfactant adsorption, surface excess (Γ) is introduced. Defined as the concentration of surfactant molecules in a surface plane, relative to that at a similar plane in the bulk. The Gibbs adsorption equation (eq. 1) relates the change of surface tension with concentration to the amount adsorbed at the surface:

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

Where m is the number of adsorbing species, R is the ideal gas constant, T is temperature, γ is surface tension and C is the surfactant concentration. Hence, by application of the Gibbs analysis, measurement of γ as a function of C allows a quantitative determination of the absorbed amount $\Gamma(C)$.

Structure-function relationships on surface and solution properties have been investigated for many surfactant types.[9-12] This article provides an overview of this area for fluoro-carbon (FC), silicone (SiC) and hydro-carbon (HC) surfactants, which are known to generate low γ_{cmc}, and also a new class of highly branched HC surfactants also achieving low γ_{cmc} values. Table 1 shows some of the surfactant structures discussed in this article.

Table 1. Structures of fluoro-, silicone and hydro-carbon surfactants discussed in this article.

	Structure	Abbreviation	References
1 (Hydro)		di-PhC4SS	16
2 (Fluoro)		diHCF4	13, 31, 53
3 (Fluoro)		diCF4	13, 31, 53
4 (Fluoro)		NaPFN	13

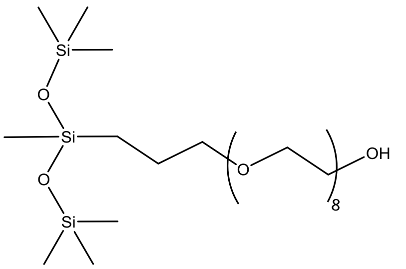
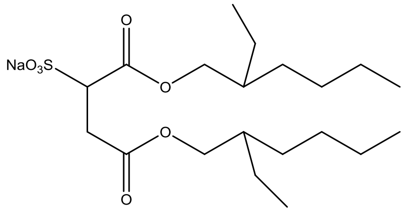
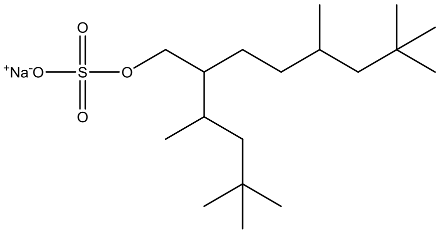
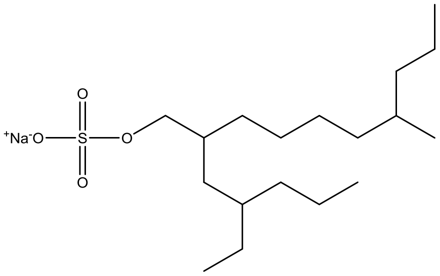
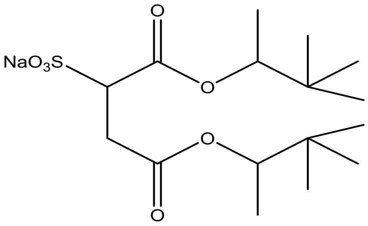
5 (Silicone)		M(D'E$_8$OH)M	43, 44
6 (Hydro)		AOT	49, 55
7 (Hydro)		iC$_{18}$S(FO-180)	57
8 (Hydro)		iC$_{18}$S(FO-180N)	57
9 (Hydro)		di-BC$_6$SS	51

Figure 2 shows the aqueous limiting surface tension, γ_{cmc}, and corresponding molecular area, A_{cmc}, for examples of common linear fluoro-, silicone and hydro-carbon surfactants. Referring to Figure 2 a large variation in γ_{cmc} is seen, highlighting the importance of chemical structure. Note, the common linear chain sodium dodecylsulfate (SDS) is a poor performer on this scale, suggesting such simple HC surfactants are inefficient. This article shows how the performance of HC surfactants can be significantly improved by controlled design of the chain architecture.

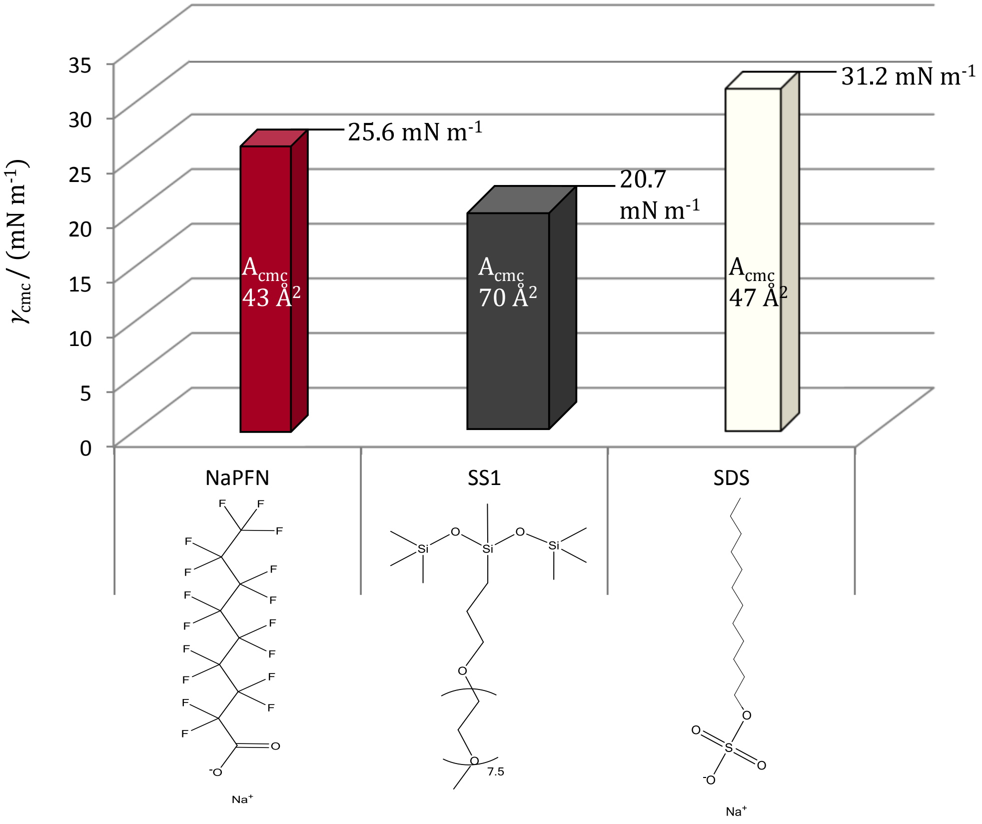


Figure 2. Aqueous limiting surface tension and corresponding interfacial molecular area for a typical linear fluoro-, silicone and hydro-carbon surfactant. Column height represents γ_{cmc} and column width is proportional to A_{cmc}. Data from NaPFN,[13] SS1,[14] and SDS.[15]

Pitt et al. highlighted how the hydrophobic tail structure heavily influences surface tension by investigating sulfosuccinate and sulfotricarballylate surfactant series.[16] By comparing two classes of surfactants (hydrocarbon and fluorocarbon) it was possible to identify some general properties which are required by surfactant molecules to effectively reduce surface tension. The aim of this article is to identify additional properties and this is achieved by identifying and comparing the structure-property relationships of fluoro-, silicone and hydro-carbon surfactants in aqueous systems.

1.1 Surface tension as a sum of parts

The surface tension of a liquid is intimately related to intermolecular interactions.[17] Fowkes suggested that by approximating intermolecular interactions as additive, surface tension γ may be represented by two dominant contributions, one due to dispersion interactions γ^d and the other accounting for all other polar interactions γ^p, i.e. $\gamma = \gamma^d + \gamma^p$.[18] This concept can be applied directly to the solid/liquid interface to obtain the two separate components of surface tension energy, analyses of contact angles are conducted using a method pioneered by Zisman and co-workers.[19] The studies of Zisman et al. amassed a large body of data for contact angles of many liquids on low-energy surfaces such as polymers. This also introduced the concept of the critical surface tension of a solid substrate (γ_c), which is defined as the maximum liquid surface tension to fully wet a given solid surface. Pitt compared Zisman's critical surface tension data γ_c to the limiting surface tension values γ_{cac} (cac - critical aggregation concentration corresponds to the surfactant concentration at which aggregates of surfactant start to form on polymers) taken from the sulfosuccinate and sulfotricarballylate series, and found a good correlation within any given surfactant class (ref.16), see Figure 3.

The polar, and dispersive components of the sulfosuccinate and sulfotricarballylate surfactant series were investigated further by contact angle analyses of surface coated systems. Surface free energies were then compared with the limiting surface tensions of aqueous solutions. For both surfactant series a strong correlation was seen between the dispersive component of the solid free energy γ^d and γ_{cac}, but no correlation was found for the polar component γ^p. This implies γ_{cmc} (or

γ_{cac}) values depend very strongly on the chemical interactions which are strongly influenced by the chemical identity of the surfactant tails.

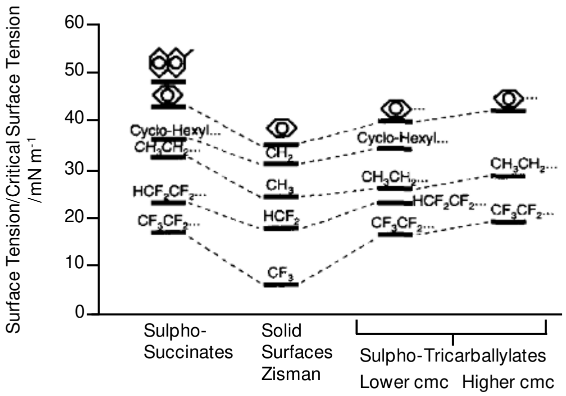


Figure 3. Comparison between limiting surface tension values of surfactants in aqueous gelatin buffer solution (7% (w/w) deionised) and critical surface tension γ_c data for solid substrates with a chemical identity of terminal groups (example sulphosuccinate surfactant with phenyl tip, Table 1. **1**). Reprinted with permission from (ref 16). Copyright 1996 Elsevier Science B.V.

1.2 Limiting surface tension of surfactant solutions

In order to help compare the performance of surfactants, Rosen et al. provided specific definitions of the efficiency (i.e. the bulk concentration required to produce a significant reduction in surface tension) and effectiveness (i.e. the maximum reduction in tension regardless of the bulk concentration) of surfactant molecules.[20] Pitt et al. demonstrated how γ_{cmc} of aqueous solutions in a gelatin buffer is influenced by surfactant chemical structure, comparing hydrocarbon and fluorocarbon surfactants (ref. 16). This interesting approach expanded on a review by Rosen (ref. 20), but with a particular emphasis on the influences of chemical nature and structure of hydrophobic tails on limiting surface tension. This was the first study to highlight clearly the strong relationship between surface activity and chemistry of the hydrophobic tails. Although the majority of work was conducted using aqueous solutions in a buffer containing 7% (w/w) deionised alkali-processed bone gelatin, the study also demonstrated the same trends with pure aqueous solutions.

By holding the tail carbon number constant to ensure surfactant cacs (critical aggregation concentrations) were over similar concentration ranges (1 x C12, 2 x C7, 3 x C5 and 4 x C4), it was shown increasing the number of tails (single, double, triple - Table 1. **4** and **6** for example single and double tail structure respectively) caused a lowering of surface tension. Furthermore, for both surfactant classes a significant increase in surfactant effectiveness was seen changing from single to two-tail surfactants, whereas a comparatively smaller increase was noted on moving from two-tail to three-tail surfactants. This trend of decreasing γ_{cmc} (γ_{cac}) with increased number of tails is a consequence of two effects: an increased packing efficiency of the tail groups versus the electrostatic repulsion between neighbouring anionic sulfonate head groups, and an increase in the ratio of CH_3- to $-CH_2$- groups per headgroup. CH_3- being of lower surface energy than $-CH_2$-, based on the following order of increasing surface energy for single carbon based moieties: $CF_3 < CF_2 < CH_3 < CH_2$ (ref. 19). The reason for the comparatively smaller increase in effectiveness changing from a two-tail to three-tail surfactant was considered to be linked to the underlying polar groups. The thinner the packed hydrocarbon tail layer region, the more the polar head groups contribute towards increased surface energy. A wide structural variation of two-tail and three-tail sulfosuccinate surfactants was investigated. The terminal chain groups were varied to include fluoroalkyl, alkyl and aryl groups (Table 1. **1**) showing the following trend for γ_{cmc}: CF_3-CF_2- < $H(CF_2CF_2)$- < branched alkyl < single-tail alkyl < phenyl. The influence of a single hydrogen (ω-substituted) on an otherwise perfluoroalkyl endgroup raised the γ_{cmc} by about 6 mN m^{-1}. The effect of various tail chemistries on limiting surface tension was extended to four decaglycidol non-ionic surfactants (ref. 16). Despite being charge neutral the pattern of behaviour as well as the effects of tail chemistry on γ_{cmc} were in the same order as seen with the anionic surfactants, highlight clearly the strong relationship between surface activity and chemistry of the hydrophobic tails.

2. Fluorosurfactants

In the 1950s an accidental discovery at 3M highlighted the potential of fluorochemical cleaning products and catalysed the development of fluorosurfactants. Fluorosurfactants now constitute an important class and appear in a diverse range of applications including biomedicine, firefighting applications, cosmetics, lubricants, paints, polishes, and adhesives, representing a multi-billion dollar industry.[21-23] Furthermore, the hydrophobic tails of fluorosurfactants display both oil and water repellency and because of this, fluorosurfactants are used as low surface energy coatings, for example on textiles or paper.[24]

In fluorinated surfactants, at least one hydrogen in the hydrophobic tail has been replaced by fluorine. Both the extent of fluorination and position of the fluorine atoms affect the characteristics of the surfactants. Fluorosurfactants can be described as perfluorinated, where all hydrogen in the hydrophobic tail has been replaced by fluorine, or as partially fluorinated. Fluorosurfactants display greater surface activities than their hydrocarbon counterparts and can lower surface tensions effectively at very low concentrations, typically lowering the surface tension of water from 72 mN m^{-1} to around 15-25 mN m^{-1}. The essential reasons fluorocarbon (FC) surfactants generate low γ_{cmc} are:-

- The lower polarisability of fluorine compared to hydrogen results in weaker attractive intermolecular forces.
- The greater molecular volume of perfluoroalkyl moieties over hydrocarbon moieties makes fluoroalkyl chains more hydrophobic.

- The larger cross section of fluorocarbon chains makes the packing density per unit area lower and hence so are the intermolecular forces.

More recently it has been identified that fluorinated compounds with C8-C15 chain lengths are hazardous pollutants.[25] It has been shown that bioconcentration and bioaccumulation of perfluorinated acids are directly related to fluorination.[26] Hence there is now a need to develop replacements for fluorosurfactants. Therefore, an aim of this article, to improve understanding about structure-function relationships important to guiding design of replacements for fluorocarbon surfactants.

2.1 The special activity of fluorosurfactants

The greater surface activity of fluorosurfactants over their hydrocarbon counterparts stems from the unique properties of fluorine. The cohesion of a liquid is due to the attractive forces between molecules. Although due to the high electronegativity of fluorine a C-F bond is polarised, a perfluorocarbon chain is overall non-polar and has a zero dipole moment. In non-polar liquids only the induced-dipole/induced-dipole dispersion interactions are of relevance. The strength of this interaction is governed by the polarisability of the interacting atoms. Fluorine has a lower polarisability than hydrogen and therefore the total dispersion interaction is lower for the interaction between fluorine atoms. Hence, perfluoroalkane liquids are expected to have weaker attractive intermolecular forces than similar hydrocarbons.

The other principal reason for the lower surface tensions exhibited by perfluoroalkane liquids in comparison to analogous hydrocarbons is the larger volume of perfluoroalkyl moieties. The mean volumes of -CF_2- and CF_3- groups have been estimated as 38 $Å^3$ and 92 $Å^3$, whereas those of -CH_2- and CH_3- are around 27 $Å^3$ and 54 $Å^3$ respectively.[27] Linked to these steric reasons, the average limiting cross sectional area for a fluorocarbon chain is 27-30 $Å^2$, which is larger than the range of 18-21 Å^2 typically achieved for a hydrocarbon chain (ref. 27). It is also instructive to examine the free energy of transfer of a non-polar carbon moiety into water, ΔG, and hence quantify the hydrophobic effect. Table 2 compares the size and incremental changes in free energy of adsorption for the transfer of a mole of -CH_2- or -CF_2- groups from water to the air-water interface. It can be seen that a more favourable free energy of transfer is obtained for -CF_2- groups and therefore, *F*-chains are considerably more hydrophobic than *H*-chains due to their relative larger size. Hence, due to the 'bulk' of fluorocarbon surfactants, they will show an enhanced tendency to segregate, self-assemble, and collect at the air-water interface to alter the surface free energy.

Table 2. Comparison of size and free energy of transfer from water to the air/water interface at 298.15 K for one mole of -CH_2- and -CF_2- groups. Data from literature, (ref. 27).

Group	Cross sectional area (Å^2)	Group Volume (Å^3)	-ΔG/ (kJ mol^{-1})
-CH_2-	18-21	27	2.60
-CF_2-	27-30	38	5.10

The larger cross section of a fluorocarbon chain also means that the molecular packing density *per unit area* is lower than for hydrocarbon chains and hence so are the intermolecular interactions. Hence, due to the unique chemistry of fluorine over hydrogen, it can now be understood why fluorocarbon surfactants possess greater surface activities over hydrocarbon analogues, and why longer fluoroalkyl chain lengths give the lowest reported surface energies.

2.2 Structure-property relationships

One strategy to increase hydrophobicity and hence improve surface properties without increasing chain length is to increase the number of perfluoroalkyl chains. Gemini surfactants (i.e. two surfactant molecules chemically bonded together by a spacer) have led to greater surface activity and lower cmcs than expected.[28] Dramé *et al.* recently synthesized a family of short tailed anionic gemini surfactants which showed aggregation behaviour almost equivalent to those of long chain (bioaccumulable) perfluorooctyl surfactants, reporting surface tensions from 15 to 33 mN m^{-1}.[29]

As highlighted by Pitt et al., the hydrophobic chain structure of a surfactant plays a major role in controlling physiochemical properties such as surface excess Γ, surface tension γ, and cmc. It was also shown how with double-chain, partially fluorinated anionic sulfosuccinates, the simple difference of a CF_3- and -(CF_2-H) terminal group can noticeably affect physiochemical properties (ref. 13). The replacement of a terminal F atom for an H atom introduces a notable permanent dipole moment into the chain tip (Table 1. **2**) which leads to higher surface tensions by increasing the polar contribution γ^p. This, along with the lower surface excess because of dipolar repulsion, will have the effect of increasing the surface tension for solutions of the ω-H surfactants relative to those of the fully fluorinated analogues (Table 1. **3**), see Figure 4. The terminal H atom, and the pursuant dipole moment, decreases the surfactant tail hydrophobicity which is evident from the higher cmcs compared to the fully fluorinated analogues (~ x 5 per chain).

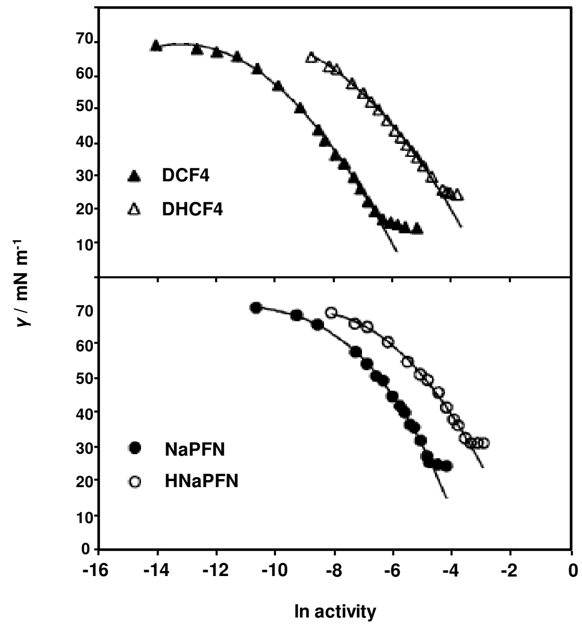


Figure 4. Surface tension measurements of diCF4 (**3**), diHCF4 (**2**), NaPFN (**4**) and HNaPFN in aqueous solution (**3** and **4** have chain terminal CF_3- groups, whereas **2** and HNaPFN have chain termini bearing -(CF_2-H) moieties). Measurements were made at 30 °C except those for diHCF4 which were at 25 °C. Reprinted with permission from (ref. 13). Copyright 1999 American Chemical Society.

Comparable increases in surface tension have also been reported on substitution of chain terminal F for H.[30] Compared to the equivalent perfluoromethyl-tipped compounds an increase in A_{cmc} was observed: 43 Å^2/51 Å^2 for NaPFN(**4**)/HNaPFN and 56 Å^2/65 Å^2 for diCF4(**3**)/diHCF4(**2**) respectively. The investigations were extended to single chain nonionics to examine the generality of these reported effects, and compare nonionic behaviour with anionics.[31] Almost identical changes in cmc, limiting molecular area and surface tension were observed for both surfactant series. Hence, regardless of headgroup there is a strong structure-function relationship, dependent on the differences in the fluorocarbon chain structure only. Such large changes in surfactant properties cannot be so easily achieved with hydrocarbon amphiphiles, highlighting the unusually sensitive structure-activity relationship of fluorosurfactants.

The limiting molecular area, A_{cmc}, is a measure of the ability to form packed layers at the interface. There is no definitive conclusion pertaining to the effect of chain length on observed A_{cmc} but it is generally accepted that lower interfacial molecular areas indicate an increase in interfacial packing ability. Klapper et al. investigated the correlation between chemical structure of several short chain fluorosurfactants and resulting surface properties by comparing a wide range of surfactants which could be split into three structural classes: Type A with thio-linkages, Type B with triazole-linkages, and Type C without spacers, see Table 3.[32]

Table 3. Static interfacial properties of several fluorosurfactants with various chain lengths and number of R^F groups. $3.C^F_3$ corresponds to three perfluoroalkyl chains each composed of three carbons, $2.C^F_3$ corresponds to two perfluoroalkyl chains each composed of three carbons etc. Data from (ref. 32).

Set	Fluorinated Group	Type	Static interfacial properties		
			CMC / (10^{-3} g L^{-1})	γ_{cmc} / (mN m^{-1})	A_{cmc} / ($Å^2$)
i	$3.C^F_3$	A	10	19.5	61
		B	20	19.5	55
		C	15	19.8	49
ii	$2.C^F_3$	A	30	20.5	239
		B	50	20.3	241
		C	10	21.9	217
iii	$2.C^F_3OC^F_2$	A	50	18.1	164
iv	$2.C^F_2$	A	n.o.	24.8	212
		B	n.o.	23.6	213
v	$1.C^F_6$	-	20	17.4	73

From the A_{cmc} values in Table 3 it is shown that surfactants with short chains (sets ii and iv) cannot pack as efficiently showing increased A_{cmc} values compared to longer chain surfactants (set iii), which can form greater interactions with neighbouring surfactant molecules, pack more densely and hence, lower surface tension. Furthermore, increasing the number of chains leads to more hydrophobic surfactants with increased chain-chain intermolecular interactions, hence efficient packing, producing surface films composed of low energy CF_3-/-CF_2- groups.

3. Silicone Surfactants

Silicone surfactants, also commonly referred to as siloxane surfactants, comprise permethylated siloxane hydrophobic groups coupled to one or more hydrophilic polar groups. There are three common molecular structures for silicone surfactants, rake-type copolymers (comb or graft copolymers),[33] ABA copolymers ("B" represents the silicone portion),[34] and trisiloxane surfactants (Table 1. **5**).[35] Although the polar groups can be nonionic, anionic, cationic or zwitterionic, nonionic groups based on polyoxyethylene (PEO) and polyoxypropylene (PPO) are the most common. Silicone surfactants can effectively reduce aqueous surface tensions, achieving γ_{cmc} in the range 20-30 mN m^{-1}.[36] The essential reasons silicone (SiC) surfactants generate low γ_{cmc} are:-

- The low intrinsic surface activity and lower surface energy of methyl groups (CH_3-).
- The unique flexibility of the siloxane backbone which can adopt conformations to present available organic groups to their best advantage, i.e. a surface that is dominated by methyls.

These systems also display unique spreading properties, and as of such, are widely used in applications such as stabilizers for polyurethane foams, emulsifiers in cosmetics, agricultural adjuvants, textile conditioning, coating, and ink additives.[37]

The Si-O-Si linkage is susceptible to hydrolysis in the presence of moisture,[38] and the hydrolytic instability of trisiloxane surfactants is an inherent weakness, reducing their performance. This has also lead to discrepancies between published works on supposedly identical compounds.

$\equiv$Si-O-Si$\equiv$ $\leftrightarrow$ $\equiv$Si-OH + OH-Si$\equiv$

The reaction is catalysed by acid or base and the rate is slow near pH 7.0 (ref. 38). Residual acidity or basicity of glass-ware surfaces can catalyse the degradation requiring plasticware or glassware treated by hydrophobic silanization. Furthermore, at sustained temperatures above 70 ^{o}C hydrolysis leads to rapid loss of surfactancy for most trisiloxane surfactants (ref. 38). The rate of hydrolysis is higher for free molecules than for those aggregated in micelles.[39] Thus, concentrated solutions may appear to be stable for long periods of time and polymeric siloxane surfactants are generally more hydrolytically stable owing to low cmcs (cacs).

3.1 Surface Activity

Silicones are effective surfactants able to lower γ_{cmc} to $\approx$ 20 mN m^{-1} (compared to the value of $\approx$ 30 mN m^{-1} for typical hydrocarbon surfactants) and can be surface active in both aqueous and nonaqueous media.[40] The surface activity of silicone surfactants is due to both the nature of the backbone and pendant organic groups (CH_3-). The -O-Si-O-Si- backbone serves as a flexible framework on which to attach multiple methyl groups. The low intrinsic surface energy of methyl groups (ref. 19), coupled with the unique flexibility of the siloxane backbone enables the surfactants to adopt a variety of configurations, and to present surfaces that are dominated by methyl, compared to typical linear chain HC surfactants, which promote films with a greater proportion of higher surface energy -CH_2- groups (Figure 5).

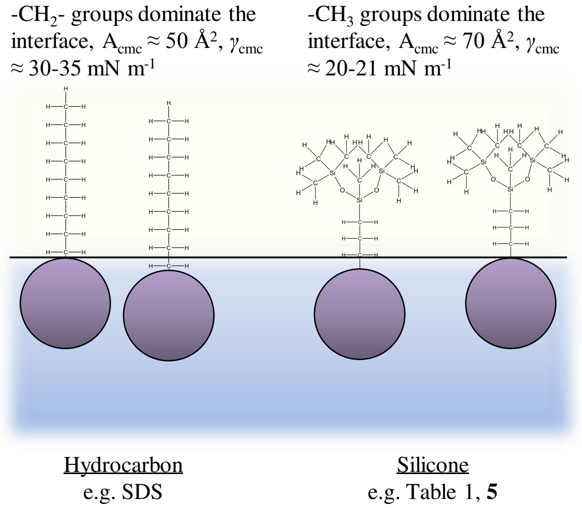


Figure 5. Schematic comparison of the surface character of hydrocarbon versus silicone surfactants. Typical values of A_{cmc} and γ_{cmc} for a linear hydrocarbon and silicone surfactant provided. Redrawn based on illustration from (ref. 37).

The high intermolecular forces associated with the inorganic silicate-like backbone are masked by the inter low-surface-energy organic groups. However, it would be reasonable to question if the high surface energy siloxane backbone directly affects surface energy. By splitting the surface energy into separate polar and dispersion components, evidence suggests the backbone has only a minor effect. Using Zisman's contact angle data Kaelble calculated γ^d 20.5 mN m^{-1} and γ^p 1.6 mN m^{-1} for polydimethlysiloxane.[41] Similar values have been reported elsewhere,[42] showing the backbone has a small direct effect on surface energy as the polar component is low. The prime role of the backbone is to present available organic groups to their best advantage which is achieved by virtue of its unique flexibility.

In most hydrocarbon systems the bond angles are constrained, and steric packing considerations often prevent the available methyl groups from adopting their lowest surface energy orientations. Because of the electron orbital interactions between silicon and oxygen present in the siloxane backbones, an extended flexible chain system is preferred. This freedom to rotate about bonds is reflected in the glass transition temperature of polymers (T_g), where a low T_g is indicative of a flexible polymer. Lee and Rutherford investigated T_g for several polymers with polydimethylsiloxane giving the lowest T_g,[43] a direct consequence of the many orientations that the polymer can adopt as a result of the unique freedom of rotation.

To determine the effects of siloxane backbone flexibility on surface activity, Kanner et al. prepared a number of low molecular weight siloxane polyoxyethylene surfactants.[44] The most surface active were those with the smallest siloxane groups, having two to five silicon atoms in the chains. Branching of the siloxane hydrophobe and variation of the EO chain length had only minor effects on the surface activity. Replacing methyl groups with longer alkyl groups resulted in a decreased surface activity. The dependence of γ on molecular weight indicates that the conformation of polymeric siloxane surfactants at interfaces is a major factor dictating surface energy in these systems. The lower surface tensions provided by smaller siloxane groups and shorter alkyl chains on the backbones suggest efficient organization at the interface to produce dense surface films packed with CH_3- groups. Thus the lower surface tensions given by siloxane surfactants can be traced directly to molecular structure, the unusual flexibility of the siloxane backbone, and the different surface energies of CH_3- versus -CH_2-.

3.2 Wetting and spreading

The spreading and wetting (ability of a liquid to maintain contact with a solid surface) of liquids over solid substrates is extremely important. Silicone surfactants are often called “superspreaders” so at this point in the article it is appropriate to briefly introduce the topic. As stated above, Zisman and co-workers introduced the critical surface tension, γ_c, indicating whether a liquid with a known liquid/vapour interfacial tension, γ_{LV}, wets a solid surface or not. Liquids with $\gamma_{LV} < \gamma_c$ will spread out over the solid substrate. The surface tension of pure water ($\gamma_{\mathrm{LV}} \approx 72$ mN m^{-1} at 298 K) is much higher than the critical surface tension of typical hydrophobic materials such as leafy surfaces ($\gamma_{\mathrm{c}} \approx 50$ mN m^{-1} at 298 K), and therefore, spreading of water does not occur on those materials. Hence, reducing the surface tension using surfactants means solutions are much more likely to wet low-energy surfaces. Young's equation for contact angle (eq. 2) shows that spreading requires both a low surface tension for the surfactant solution (γ_{LV}) and a low interfacial tension between the liquid and the substrate (γ_{SL}).

$$0 = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} - \gamma_{\mathrm{LV}} cos\theta_c \tag{2}$$

Fluorocarbon surfactant solutions with limiting aqueous surface tensions of about 15 mN m^{-1} do not spread on low energy hydrocarbon surfaces because the interfacial tensions between fluorocarbon surfactant solutions and hydrocarbon substrates (γ_{SL}) are large. Certain siloxane surfactants greatly enhance the ability of aqueous mixtures to rapidly spread over and wet highly hydrophobic (leafy) surfaces, termed superspreaders. For example, the surfactant denoted as M(D´E_8OH)M (Table 1. **5**). Hence, due to the unique spreading and low γ of silicone surfactants, they have wide applications as adjuvants for agrochemicals facilitating spreading of crop spray formulations over hydrophobic/waxy leaf surfaces.[45]

4. Hydrocarbon Surfactants

The link between the limiting tension (energy) γ_{cmc} and chemical structure in the interfacial film depends on various factors. Table 4 shows a compilation of literature data on selected fluoro-, silicone and hydro-carbon surfactants.

Table 4. Surface properties of some fluoro-, silicone and hydro-carbon surfactants from literature. [a]Data from Eastoe (ref. 13). [b]Data from Dickson.[46] [c]Data from Yoshimura.[47] [d]Data from Brown.[48] [e]Data from Nave.[49] [f]Data from Mohamed.[50] [g]Data from Penfold.[51] [h]Data from Rosen.[52] [i]Data from

Goddard (ref. 14). Structures for C_8FC_3-2-C_3C_8F, L77 and SS1 can be found in Figure 9, compounds with bold numbers structures in Table 1. (TPA-DS) - Tetrapropylammonium dodecylsulfate; (TCl4) – trichain anionic surfactant; (TPA-TC) - Tetrapropylammonium trichain anionic; (di-BC_9SS) - sodium bis(1-isobutyl-3,5,dimethyl-hexyl)-2-sulfosuccinate.

Surfactant	γ_{cmc} / (mN m^{-1})	A_{cmc} / ($Å^2$) ± 2
Fluorocarbon		
NaPFN [a] (**4**)	25.6	43
$diCF_4$ [b] (**3**)	17.9	62
C_8FC_3-2-C_3C_8F [c]	13.7	91
Hydrocarbon		
TPA-DS [d]	31.8	67
AOT [e] (**6**)	30.8	75
TCl4 [f]	27.0	80
TPA-TC [d]	25.4	136
di-BC_9SS [g]	24.5	120
Silicocarbon		
L77 [h]	~22	66
SS1 [i]	20.7	70

As previously highlighted perfluorocarbon surfactants provide lower surface tensions than hydrocarbon analogues due to 1) the low polarisability of fluorine and 2) the larger volume of a fluorocarbon chain. Furthermore, surfactants bearing siloxane chains have shown to generate lower γ_{cmc} values than those of typical linear chain hydrocarbon surfactants, due to the unique flexibility of the siloxane backbone. Initially, it would appear that hydrocarbon surfactants are somewhat inferior. However, due to the low hydrolytic stability of trisiloxane surfactants, and the environmentally hazardous nature of fluorocarbons, hydrocarbon surfactants might provide possible alternatives, being both stable and generally environmentally acceptable. Recently, highly branched HC surfactants have been synthesized which provide low γ (ref. 51), and the essential reasons these hydrocarbon (HC) surfactants generate low γ_{cmc} are:-

- The low intrinsic surface energy of methyl groups (CH_3-).
- Highly branched tails generate dense surface layers composed of CH_3- groups with weaker tail- tail interactions compared to linear chain HC tails.

By examining and developing structure-function properties for hydrocarbon surfactants, could viable replacements be found to the most commonly used silicone and fluorocarbon surfactants?

4.1 Structure-property relationships

Work by Mohamed et al. indicated that trichain HC surfactants could provide γ_{cmc} values comparable to those of certain fluorosurfactants.[53] However, synthesis of trichain surfactants is time consuming and not so straightforward, limiting their commercial applications. It has been shown that chain branching of hydrocarbon surfactants, especially an increasing level of chain tip methylation (see Table 1. **6** and **7**), can lead to γ_{cmc} lower than linear chain analogues.[54] This approach to pack the hydrocarbon chain termini with low surface energy CH_3- groups mirrors the architecture of the very effective siloxane surfactants mentioned in the previous section.

Aerosol-OT (or AOT, Table 1. **6**) is one of the most studied surfactants due to its high versatility, rich aqueous-phase behaviour and ability to form cosurfactant-free microemulsions. Investigations of the relationship between surfactant molecular structure and phase behaviour have been performed with sixteen different Aerosol-OT related surfactants, AOT with a limiting surface tension $\gamma_{cmc} = 30.8$ mN m^{-1} and an effective area per molecule $A_{cmc} = 75$ Å^2 was shown to behave in a very similar fashion to a range of related analogues.[55] However, these studies revealed that the hydrocarbon backbone structure dictates interfacial packing. The branched chain compounds demonstrated a significant increase in A_{cmc}, of between 10 and 20 Å^2 over those found for equivalent carbon number linear chain surfactants. Furthermore, slight variations in A_{cmc} were detected reflecting changes in packing owing to differing extents of chain branching.

In effect, the limiting γ that could be achieved with a HC surfactant would be that for the parent hydrocarbon. For example, the γ_{cmc} of SDS with linear nC12 chains is ~35 mN m^{-1} but $\gamma_{air\text{-}liquid}$ for pure n-dodecane is ~ 26 mN m^{-1}.[56] The reason for the difference is because the water-soluble headgroups sterically hinder the surfactant tails from achieving a dense surface, and increase the dispersion contribution γ^d to the total tension by introducing dipolar interactions,. Therefore, to obtain soluble and useful low-surface energy HC surfactants, the van der Waals dispersion interactions must be maximized to promote dense surface packing of CH_3- and -CH_2- groups, whilst at the same time minimizing dipolar interactions, which are essential, and unavoidable, to promote water solubility. Hence, the net limiting surface tension γ_{cmc} is a result of the balance between these two opposing effects.

One approach is to replace linear hydrocarbon chains with highly branched bulkier groups, also referred to as "hedgehog" surfactants owing to their unusual spiky brushlike structures. In these systems, branched alkyl moieties help to generate high densities of pure liquid alkanes at the air-water interface. Several novel surfactants based on AOT, but with more highly branched alkyl tails (Table 1. **7**, **8** and **9**) have been examined in terms of γ_{cmc} to explore structure-function correlations, and optimize molecular design.[57] For linear surfactants the cmc decreases logarithmically with the linear alkyl chain length of a surfactant, n_c, based on the well-known Klevens equation (eq. 3).[58]

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

where A and B are constants which vary according to the charge and type of the headgroup and contribution of the -CH_2- groups, respectively. Within a series of branched surfactants, links between cmc and alkyl carbon number are more complex. However, the general trend of an increasing cmc with an increasing level of chain branching due to a shorter effective tail was observed. With linear chains, the general trend is a decrease of γ_{cmc} with increasing carbon number which reflects an increase in the chain density in the surface films. Among the compounds studied, $iC_{18}S$(FO-180) (Table 1. **7**) gave the lowest surface tension, with values of 25.4 and 24.6 mN m^{-1} with Na^+ and TPA^+ (tetrapropylammonium) counterions respectively. These values compare favorably with an example pure alkane, tetradecane for which $\gamma_{tetradecane}$ = 24.8 mN m^{-1}.[59] Therefore, it can be seen, γ_{cmc} has reached a natural limit of surface tension reduction. This remarkable reduction is believed to be a direct consequence of the increase in the CH_3- : -CH_2- ratio per headgroup based on the following order of increasing surface energy for single carbon based moieties: $CF_3 < CF_2 < CH_3 < CH_2$ (ref. 19). These values suggest the surface layers of hedgehog molecules are more densely packed with CH_3- and -CH_2- groups compared to the linear chain surfactant counterparts, and as a result γ_{cmc} values are reduced.

To develop HC surfactants with surface tensions as low as can be obtained for FC surfactants, dense surfactant films are needed, hence, the optimal thickness of a surfactant layer (i.e. the optimal length of surfactant tail) to attain very low γ must be considered. If the tails are too long the surfactant will only have a poor solubility in water owing to the hydrophobic effect, stronger tail-tail interactions will result in surfactants that are too hydrophobic, with low cmcs, tending to insolubility. On the other hand, too short a tail is insufficiently hydrophobic. The chain branching of hedgehog surfactants drives A_{cmc} to be high due to the increase in bulkiness of the tail, optimal surface packing and therefore, weaker tail-tail interactions, illustrated in Figure 6. The effective area per headgroup at the cmc increases from 53 Å^2 for $iC_{18}S$(FO-180N) (Table 1. **8**) to 73 Å^2 for $iC_{18}S$(FO-180) (**7**) due to an increase in chain branching.

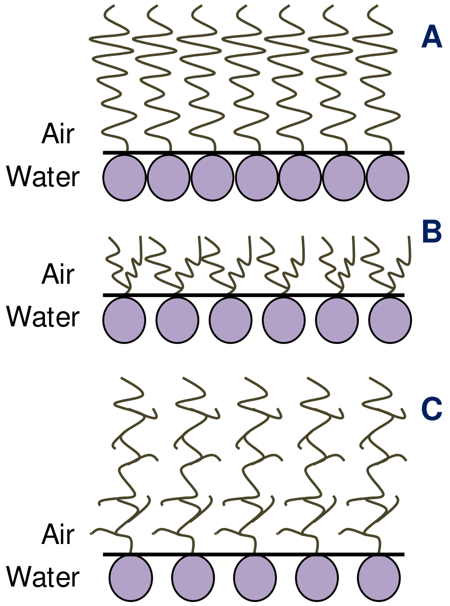


Figure 6. Illustration of the differences in packing adopted by: A - linear, B - dichain and C - highly branched hydrocarbon surfactants.

One of the clearest ways of characterizing an adsorbed layer is in terms of the limiting surface excess, Γ_{cmc}, and area per headgroup, A_{cmc}, since these give an indication about molecular packing efficiency. As shown the minimum effective molecular area A_{cmc} directly affects the effective mass density of the surfactant film, and this depends on branching position and length of tail. However, to relate γ_{cmc} to the density of the surfactant HC-tail layers, the apparent mass densities of surface films can be estimated using $\rho_{layer} = m / (A_{cmc} \times \tau)$, where m is the weight of the surfactant double tail and τ is surfactant tail length (obtained by the Tanford equation: $\tau = 1.5 + 1.256x$, where x is the carbon number of the longest alkyl chain in the tail.[60]). Figure 7 shows the relationship between γ_{cmc} and ρ_{layer} for a series of Aerosol-OT-analogue surfactants (sulfosuccinate-type di-BC$_n$SS and sulfoglutarate-type di-BC$_n$SG) with highlybranched alkyl double tails, where n represents carbon number (ref. 51).

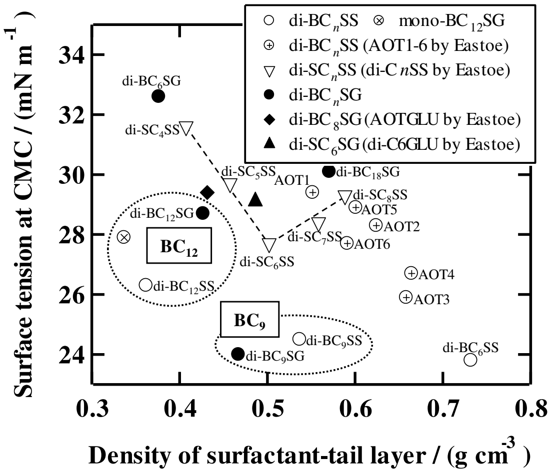


Figure 7. Relationship between γ_{cmc} and density of surfactant-tail layer ρ_{layer} calculated with A_{cmc} and tail length at 35 °C, (AOT1 and di-BC$_6$SS Table 1. **6** and **9** respectively). Structures for other AOT analogues and hedgehog surfactants can be found in (ref. 55 and 51) respectively. Reprinted with permission from (ref. 51). Copyright 2014 American Chemical Society.

It can be seen that ρ_{layer} is an important property affecting γ_{cmc}, with a higher ρ_{layer} leading to a lower γ_{cmc}. The lowest γ_{cmc} of 23.8 mN m^{-1} is obtained at the highest ρ_{layer} of 0.73 g cm^{-3} for di-BC$_6$SS (Table 1. **9**), it is interesting to note that pure liquid n-decane $\gamma = 23.7$ mN m^{-1} at 293 K and a density of 0.73 g cm^{-3}.[61] It should also be noted that these γ_{cmc} values for branched HC surfactants are approaching those of common linear FC surfactants, like NaPFN (Table 4.). Figure 7 shows that the hedgehog BC$_9$ and BC$_{12}$ tails give much lower γ_{cmc}, even at low ρ_{layer} values. This might be because the order parameter of the layer is small in BC$_9$ and BC$_{12}$ tails, quantifying the degree of parallel ordering of anisotropic molecules along their longitudinal axes, i.e. low surface energy surfaces of pure liquid alkanes ≈ 0, when the state changes to solid (crystal) ≈ 1. Here the order parameter is defined as the degree of the average C-C bond ordering; the ordering of *n*-alkyl-tails with all trans-conformation of C-C bonds will give an order parameter of ~1. The symmetric structure of the individual units composing the BC$_9$ and BC$_{12}$ tails are likely to produce high isotropy in C-C bond ordering, i.e. a low order parameter ~0. When incorporating order parameter theory into designing low surface energy surfactant tails, the order parameter should be as close to 0 as possible.

These results suggest that highly branched tail structures can generate dense surface layers, which mimic the surfaces of pure alkane analogues. Hence, hydrocarbon surfactants could be developed to achieve equilibrium surface tensions which match those of fluorocarbon or silicone surfactants.

5. Comparison of different surfactants

Above, the effect of surfactant structure on aqueous γ_{cmc} has been reviewed for fluorocarbon, siloxane and hydrocarbon surfactants. It has been shown that each class of surfactant possesses unique chemical properties which are at the heart of notable performance. Furthermore, there are many compounds that are highly effective at reducing surface tension. However, by comparing widely different classes of surfactants, is it possible to identify a general property, independent of the chemical type or structure, which explains low γ_{cmc}? An index to assess surface coverage at the cmc, Φ_{cmc} is introduced (eq. 4):

$$\Phi_{\mathrm{cmc}} = {}^{\mathrm{V_{cal}}}\!/_{\mathrm{V_{meas}}} \qquad (4)$$

where V_{cal} is the total physical volume of surfactant molecular fragments (values taken from literature[62-64]), and V_{meas} is the total volume occupied by a molecule at the reference air-water interface, calculated using experimental values (eq. 5):

$$V_{\text{meas}} = A_{\text{cmc}} \times \tau \tag{5}$$

A_{cmc} corresponds to the surfactant headgroup areas (which can be determined tensiometrically), and τ is an interfacial thickness which can be found by the Tanford Equation (ref. 60), or determined by Neutron Reflectivity (ref. 15). An illustration of these volumes and dimensions is depicted in Figure. 8.

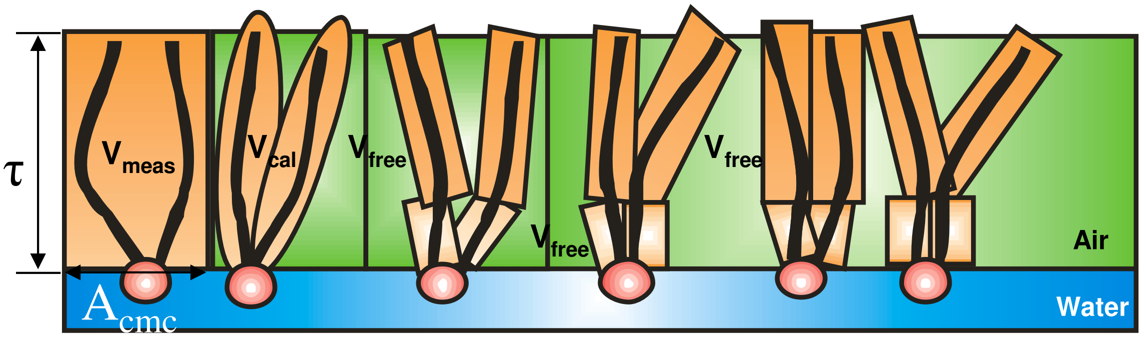


Figure. 8 A visual representation of surfactants at the air-water interface, showing the different fragment and interfacial volumes used in the calculation of Φ_{cmc}. The measured surfactant molecular volume is V_{meas}, the calculated volume based on summation of fragments is V_{calc} and V_{free} represents the free space in the film. Reprinted with permission from (ref. 53). Copyright 2011 American Chemical Society.

The part of the interfacial layer which is not occupied by molecular fragments is free space, $V_{\text{free}} = V_{\text{meas}} - V_{\text{cal}}$. Assuming the layer is uniform, a high Φ_{cmc} is indicative of efficiently packed surfactant monolayers, with little free space.

As an example, for the common SDS, $\gamma = 31.2$ mN m^{-1}, $A_{\text{cmc}} = 47$ Å^2 and $\phi_{\text{cmc}} = 0.49$, showing the majority of the surface layer is in fact free space. Another common surfactant, AOT (Table 1. **6**) with aqueous $\gamma_{\text{cmc}} = 30.8$ mN m^{-1} and $A_{\text{cmc}} = 75$ Å^2 has a corresponding $\Phi_{\text{cmc}} = 0.63$. In comparison di-CF2, a linear dichain fluorocarbon AOT-based analogue, $\gamma_{\text{cmc}} = 22.4$ mN m^{-1} and

A_{cmc} = 65 Å^2, giving a surface coverage value of Φ_{cmc}= 0.79 (data from ref. 53). The values obtained for Φ_{cmc} are independent of both the surfactant geometry and chemistry of the surfactants, therefore, by comparing Φ_{cmc} alongside γ_{cmc} and A_{cmc} for three main classes of low surface energy surfactants, it is possible to identify a general property that accounts for low γ_{cmc}. Simply put, an efficiently packed surface monolayer is required for low γ_{cmc}, consistent with a high value of Φ_{cmc}.

Figure 9 shows an illustration of aqueous limiting surface tensions, γ_{cmc}, corresponding areas per molecule at the surface, A_{cmc}, and film packing volume fractions Φ_{cmc} for some of the most effective fluoro-, silicone and hydro-carbon surfactants covered in this article. Column height represents γ_{cmc} and column width represents A_{cmc}. Surface coverage Φ_{cmc} is also given on each column. From Figure 9 it can be seen that all classes of these super-efficient surfactants generate high interfacial coverages Φ_{cmc}.

An important reason fluorosurfactants give the lowest surface energies is due to the 'fatness', which is reflected in typical cross sectional areas for fluorocarbon and hydrocarbon chains, 27 Å^2 and 20 Å^2 respectively (ref. 27). A greater number of perfluoroalkyl chains and longer chain length result in greater surface activity. For example, $C_8^FC_3$-2-$C_3C_8^F$ containing longer perfluoroalkyl chains than di-CF4 can form denser surface layers composed of low surface energy -CF_2- and CF_3-groups. Siloxane surfactants typically achieve aqueous γ_{cmc} values lower than hydrocarbon surfactants, accounted for owing to the flexibility of the siloxane backbone.

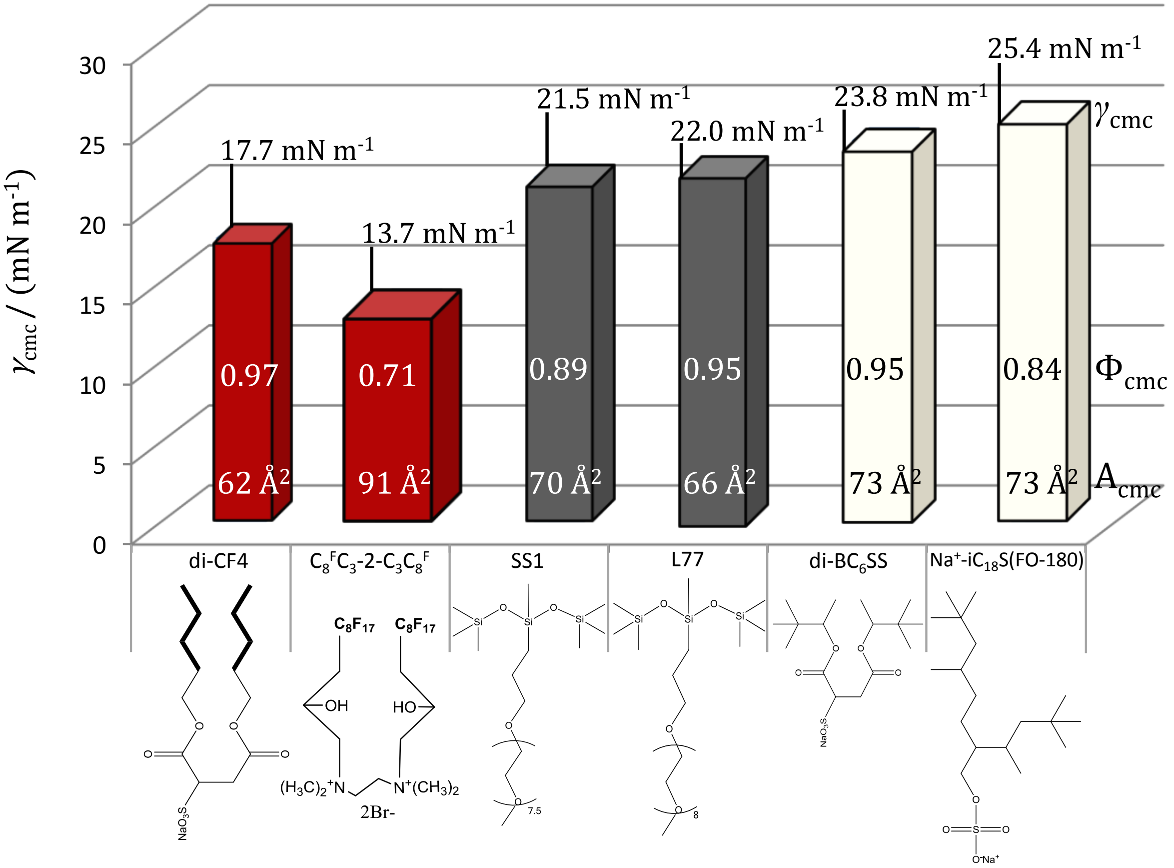


Figure 9. Comparison of the aqueous surface tension, area per molecule and surface coverage at the cmc for some of the most effective fluorocarbon (red), silicone (grey) and hydrocarbon (cream) surfactants. Column length shows γ_{cmc} and column width represents A_{cmc}. Chains and endgroups in bold represent perfluoroalkyl chains. Data from literature: di-CF4 (ref. 46), $C_8{}^FC_3$-2-$C_3C_8{}^F$ (ref. 47), SS1 (ref. 14), L77 (ref. 52), di-BC$_6$SS (ref. 51), Na$^+$-iC$_{18}$S(FO-180) (ref. 57).

Compared to linear hydrocarbons dense surfaces can be formed dominated by CH_3- groups. In order to generate low γ_{cmc} hydrocarbon surfactants must be able to pack sufficiently to create dense surface layers predominated by lower surface energy CH_3- groups, whilst also keeping tail-tail interactions low. Normal linear hydrocarbon chains present packed surface layers dominated by -CH_2- groups, resulting in comparably higher surface energies. However, chain branching causes a sufficient reduction in packing efficiency to decrease tail-tail interactions, whilst maintaining the all important high (CH_3-) : (-CH_2-) ratio per headgroup.

The limiting aqueous surface tension depends on the ability of surfactant hydrophobic tails to form dense surface layers, regardless of surfactant type. This has been identified by evaluating surface tension in terms of surface coverages at the cmc, Φ_{cmc}, where the most effective surfactants known all show high surface coverages. Hence, it can be said that for all classes of surfactants a general structure-property relationship exists - low aqueous surface tensions are achieved through efficient surface packing and hence, superior coverages at the air-water interface.

6. Conclusions

The surface tension of a liquid is a direct measure of the intermolecular interactions stabilizing the liquid phase. The reduction of surface tension is one of the most commonly measured properties of surfactants in solution. Pitt et al. examined and compared how the different chemical structures of fluorocarbon and hydrocarbon surfactants affect the aqueous static limiting surface tension, γ_{cmc} (ref. 16). This new article represents an up to date review of structure-activity relationships of fluoro-, silicone and hydro-carbon surfactants.

Fluorocarbon surfactants provide lowest γ_{cmc} values over the three classes of surfactants. This is due to weaker intermolecular forces, and the larger molecular volumes of perfluoroalkyl moieties over hydrocarbon groups. The greater the fluoroalkyl chain length, the lower the surface tension (ref. 32). Longer chains can form more group-to-group interactions with neighbouring chains, pack more densely (lower A_{cmc}), and hence locate more distinctly at the air-water interface to produce surfaces with a greater proportion of low surface energy CF_3- chain tip groups. Furthermore, a greater number of fluoroalkyl chains will also produce more 'hydrophobic' surfactants which will reduce γ. On the other hand, branching of the tails will result in a greater difficulty in packing at the interface, thus producing inferior equilibrium properties. Regardless of headgroup there is a strong structure-function relationship dependent on differences in fluorocarbon chain structure only (ref. 13).

Silicone surfactants are the most efficient spreading agents and typically achieve aqueous γ_{cmc} values in-between those of FC and HC surfactants. The Si-O groups provide a highly flexible Si-O-Si backbone which presents available organic groups to their best advantage. The air-water interface is dominated by lower energy CH_3- groups (based on the trend for surface energy of single carbon based moieties: $CF_3 < CF_2 < CH_3 < CH_2$ (ref. 19)) which explains the typical γ_{cmc} values achieved by siloxane surfactants. Smaller siloxane groups promote the surfactants to form the lowest surface energy conformations. On the other hand inhibiting efficient packing by replacing the backbone methyl groups with longer alkyl groups, results in a decreased ability to lower surface tension.

Hydrocarbon surfactants, provide the highest aqueous γ_{cmc} values of the three classes. Chain branching of a hydrocarbon can lead to lower γ_{cmc} values over linear analogues (ref. 54). Recently, it was demonstrated with AOT analogues how structure of the hydrocarbon backbone dictates interfacial packing (ref. 55). By designing highly branched surfactants ("hedgehog surfactants") to increase the (CH_3-) : (-CH_2-) ratio per headgroup, it was shown that low surface tensions can be achieved, by trying to mimic the densities of pure alkanes (ref. 51 and 57). Long hydrocarbon tails result in poor water solubility and stronger tail-tail interactions which increase γ_{cmc}, but also drives A_{cmc} lower. Counterbalancing this, chain branching drives A_{cmc} higher due to increased bulkiness of the tails, causing a decrease in packing efficiency and therefore, weaker tail-tail interactions between chains, resulting in the lowest aqueous surface tensions achieved for hydrocarbon surfactants.

By comparing the performance of three classes of surfactants in terms of the packing index Φ_{cmc}, which is independent of molecular geometry and composition, it has been possible to identify a general property of all effective surfactants. Namely, reduction of surface tension is achieved by a high surface coverage (i.e. large Φ_{cmc}). This general structure-property relationship of surfactants has not been highlighted before, and it points to new ways of controlling surface energy through design of super efficient, environmentally acceptable and commercially viable surfactants.

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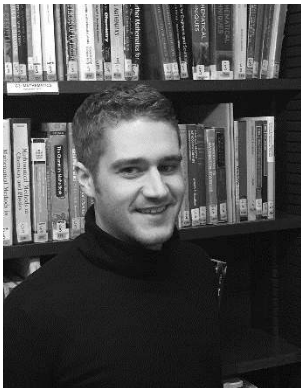

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