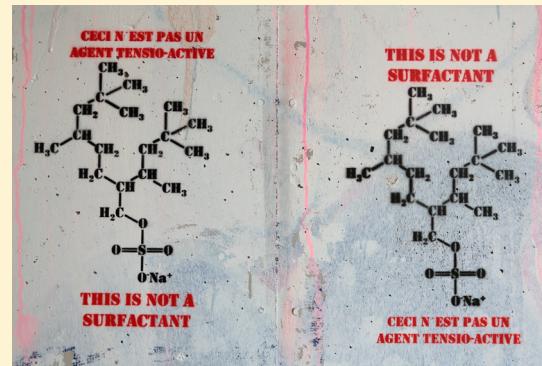


## Surfactants at the Design Limit

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**ABSTRACT:** 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,  $\gamma_{cmc}$ . Particular emphasis is given to how the chemical nature and structure of the hydrophobic tails influence  $\gamma_{cmc}$ . By comparing the three different classes of surfactants, fluorocarbon, silicone, and hydrocarbon, a generalized surface packing index is introduced which is independent of the chemical nature of the surfactants. This parameter  $\phi_{cmc}$  represents the volume fraction of surfactant chain fragments in a surface film at the aqueous cmc. It is shown that  $\phi_{cmc}$  is a useful index for understanding the limiting surface tension of surfactants and can be useful for designing new superefficient surfactants.



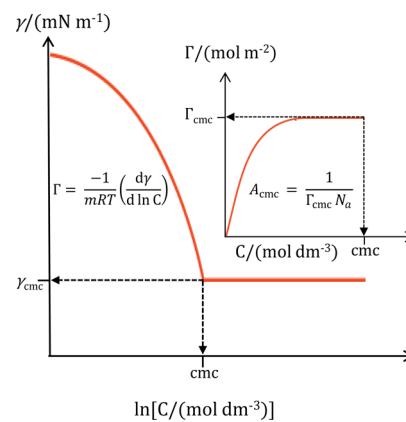
### 1. INTRODUCTION

Surfactants are among 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, and biological and medical technologies.<sup>1–5</sup> The inherent versatility of surfactant molecules originates from their amphiphilic character, and the molecules possess both polar, water-soluble sections (“headgroup”) and nonpolar, 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 from an imbalance of attractive intermolecular interactions at a liquid surface. Molecules in the final surface layer have no neighbors above and consequently are attracted into the bulk. This imbalance of intermolecular attractive interactions creates excess energy at the surface compared to the bulk (the surface free energy), which forces liquid surfaces to contract, reducing the 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  $\gamma$  (units  $J\ m^{-2}$  or  $N\ m^{-1}$ ) is the interfacial free energy per unit area but strictly refers 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  $\gamma$  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 will 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  $\gamma$  is one of the most commonly measured properties of surfactant solutions.<sup>6–8</sup> The critical micelle concentration (cmc), the limiting surface tension at the cmc ( $\gamma_{cmc}$ ), and the dynamics of adsorption are all influenced by the surfactant structure. The hydrophobic tail has a major effect on controlling important physicochemical properties such as the cmc,  $\gamma$ ,  $\gamma_{cmc}$ ,  $\Gamma$ ,  $\Gamma_{cmc}$ , and  $A_{cmc}$  (Figure 1).

To provide a quantitative description of surfactant adsorption, the surface excess ( $\Gamma$ ) is introduced and defined



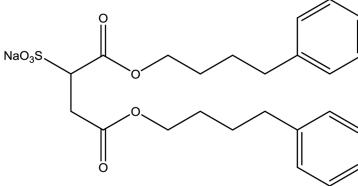
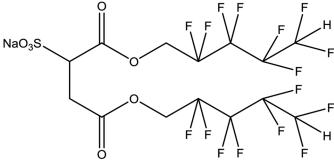
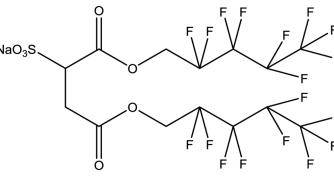
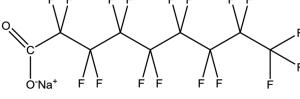
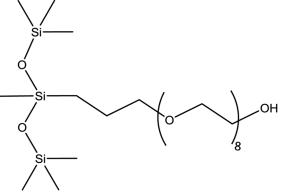
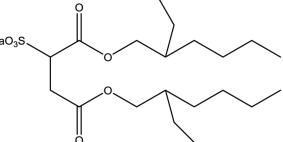
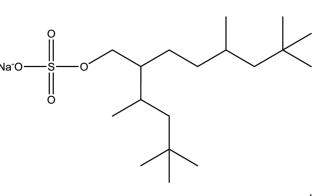
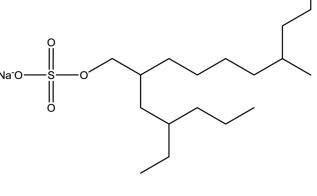
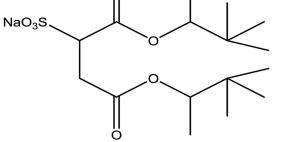
**Figure 1.** Surfactant adsorption at the air–water interface. The surface tension ( $\gamma$ ) is reduced as surfactant molecules adsorb to the air–water interface, simultaneously increasing the surface excess ( $\Gamma$ ) until the cmc is reached, at which point there is generally a plateau.  $A_{cmc}$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

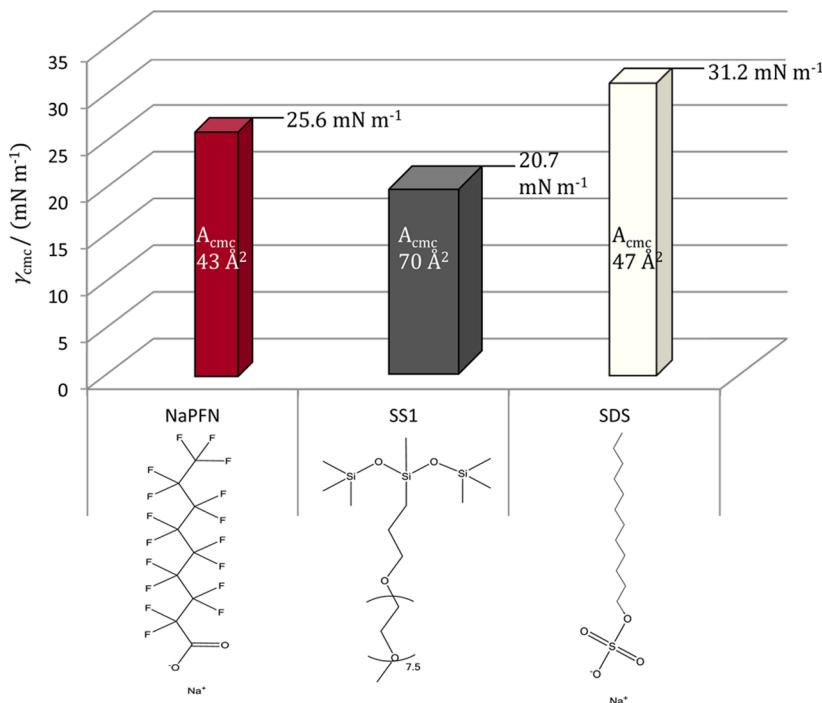
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**Table 1.** Structures of Fluorocarbon, Silicone, and Hydrocarbon Surfactants Discussed in This Article

	Structure	Abbreviation	References
<b>1</b> (Hydro)		di-PhC4SS	16
<b>2</b> (Fluoro)		diHCF4	13, 31, 53
<b>3</b> (Fluoro)		diCF4	13, 31, 53
<b>4</b> (Fluoro)		NaPFN	13
<b>5</b> (Silicone)		M(D'E8OH)M	43, 44
<b>6</b> (Hydro)		AOT	49, 55
<b>7</b> (Hydro)		iC <sub>18</sub> S(FO-180)	57
<b>8</b> (Hydro)		iC <sub>18</sub> S(FO-180N)	57
<b>9</b> (Hydro)		di-BC <sub>6</sub> SS	51



**Figure 2.** Aqueous limiting surface tension and corresponding interfacial molecular area for a typical linear fluorocarbon, silicone, and hydrocarbon surfactant. The column height represents  $\gamma_{cmc}$ , and the column width is proportional to  $A_{cmc}$ . Data from NaPFN,<sup>13</sup> SS1,<sup>14</sup> and SDS.<sup>15</sup>

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 in surface tension with concentration to the amount adsorbed at the surface

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

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

Structure–function relationships on the surface and solution properties have been investigated for many surfactant types.<sup>9–12</sup> This article provides an overview of this area for fluorocarbon (FC), silicone (SiC), and hydrocarbon (HC) surfactants, which are known to generate low  $\gamma_{cmc}$  and also a new class of highly branched HC surfactants also achieving low  $\gamma_{cmc}$  values. Table 1 shows some of the surfactant structures discussed in this article.

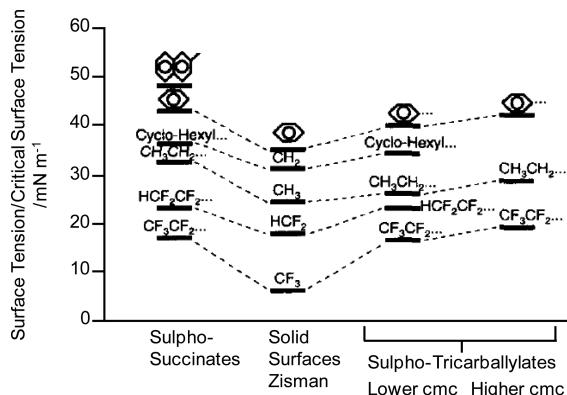
Figure 2 shows the aqueous limiting surface tension,  $\gamma_{cmc}$ , and corresponding molecular area,  $A_{cmc}$ , for examples of common linear fluorocarbon, silicone, and hydrocarbon surfactants. Referring to Figure 2, a large variation in  $\gamma_{cmc}$  is seen, highlighting the importance of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

Pitt et al. highlighted how the hydrophobic tail structure heavily influences the surface tension by investigating the sulfosuccinate and sulfotricarballylate surfactant series.<sup>16</sup> 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 the 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 fluorocarbon, silicone, and hydrocarbon 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.<sup>17</sup> Fowkes suggested that by approximating intermolecular interactions as additive, surface tension  $\gamma$  may be represented by two dominant contributions, one due to dispersion interactions  $\gamma^d$  and the other accounting for all other polar interactions  $\gamma^p$  (i.e.,  $\gamma = \gamma^d + \gamma^p$ ).<sup>18</sup> This concept can be applied directly to the solid/liquid interface to obtain the two separate components of surface tension energy, and analyses of contact angles are conducted using a method pioneered by Zisman and co-workers.<sup>19</sup> 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 ( $\gamma_c$ ), which is defined as the maximum liquid surface tension to fully wet a given solid surface. Pitt compared Zisman's critical surface tension data  $\gamma_c$  to the limiting surface tension values  $\gamma_{cac}$  ( $cac$ , 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  $\gamma^d$  and  $\gamma_{cac}$ , but no correlation was found for the polar component  $\gamma^p$ . This implies



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

that  $\gamma_{cmc}$  (or  $\gamma_{cac}$ ) values depend very strongly on the chemical interactions which are strongly influenced by the chemical identity of the surfactant tails.

### 1.2. Limiting Surface Tension of Surfactant Solutions.

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.<sup>20</sup> Pitt et al. demonstrated how  $\gamma_{cmc}$  of aqueous solutions in a gelatin buffer is influenced by the 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 the chemical nature and structure of hydrophobic tails on limiting surface tension. This was the first study to highlight clearly the strong relationship between the surface activity and the chemistry of the hydrophobic tails. Although the majority of work was conducted using aqueous solutions in a buffer containing 7% (w/w) deionized alkali-processed bone gelatin, the study also demonstrated the same trends with pure aqueous solutions.

By holding the tail carbon number constant to ensure that surfactant cac's (critical aggregation concentrations) were over similar concentration ranges ( $1 \times C12$ ,  $2 \times C7$ ,  $3 \times C5$ , and  $4 \times C4$ ), it was shown that increasing the number of tails (single, double, and triple) caused a lowering of the surface tension. Furthermore, a significant increase in surfactant effectiveness was seen upon changing from one- to two-tail surfactants, whereas a comparatively smaller increase was noted on moving from two-tail to three-tail surfactants. This trend of decreasing  $\gamma_{cmc}$  ( $\gamma_{cac}$ ) with increasing number of tails is a consequence of two effects: an increased packing efficiency of the tail groups versus the electrostatic repulsion between neighboring anionic sulfonate headgroups and an increase in the ratio of CH<sub>3</sub>- to -CH<sub>2</sub>- groups per headgroup, with CH<sub>3</sub>- having a lower surface energy than -CH<sub>2</sub>- on the basis of the following order of increasing surface energy for single-chain carbon-based moieties: CF<sub>3</sub> < CF<sub>2</sub> < CH<sub>3</sub> < CH<sub>2</sub> (ref 19). The reason for the comparatively smaller increase in effectiveness upon 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 headgroups contribute to 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  $\gamma_{cmc}$ : CF<sub>3</sub>-CF<sub>2</sub>- < H(CF<sub>2</sub>CF<sub>2</sub>)- < branched alkyl < single-tail alkyl < phenyl. The influence of a single hydrogen ( $\omega$ -substituted) on an otherwise perfluoroalkyl end group raised the  $\gamma_{cmc}$  by about 6 mN m<sup>-1</sup>. The effect of various tail chemistries on limiting surface tension was extended to four decaglycidol nonionic surfactants (ref 16). Despite being charge neutral, the pattern of behavior and the effects of tail chemistry on  $\gamma_{cmc}$  were of the same order as seen with the anionic surfactants, highlighting clearly the strong relationship between the surface activity and chemistry of the hydrophobic tails.

## 2. FLUOROSURFACTANTS

In the 1950s, an unexpected discovery at 3M highlighted the potential of fluorochemical cleaning products and catalyzed 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 multibillion dollar industry.<sup>21–23</sup> 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.<sup>24</sup>

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 to around 15–25 mN m<sup>-1</sup>. The essential reasons fluorocarbon (FC) surfactants generate low  $\gamma_{cmc}$  are the following: (1) The lower polarizability of fluorine compared to hydrogen results in weaker attractive intermolecular forces. (2) The greater molecular volume of perfluoroalkyl moieties over hydrocarbon moieties makes fluoroalkyl chains more hydrophobic. (3) 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.<sup>25</sup> It has been shown that the bioconcentration and bioaccumulation of perfluorinated acids are directly related to fluorination.<sup>26</sup> Hence, there is now a need to develop replacements for fluorosurfactants. Therefore, an aim of this article is to improve the understanding of structure–function relationships important to guiding the design of replacements for fluorocarbon surfactants.

**2.1. Special Activity of Fluorosurfactants.** The greater surface activity of fluorosurfactants over that of their hydrocarbon counterparts stems from the unique properties of fluorine. The cohesion of a liquid is due to the attractive forces between molecules. Although because of the high electronegativity of fluorine a C–F bond is polarized, a perfluor-

oxygen chain is overall nonpolar and has a zero dipole moment. In nonpolar liquids, only the induced-dipole/induced-dipole dispersion interactions are of relevance. The strength of this interaction is governed by the polarizability of the interacting atoms. Fluorine has a lower polarizability than hydrogen; 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 those of analogous hydrocarbons is the larger volume of perfluoroalkyl moieties. The mean volumes of  $-CF_2-$  and  $CF_3-$  groups have been estimated to be 38 and 92 Å<sup>3</sup>, whereas those of  $-CH_2-$  and  $CH_3-$  are around 27 and 54 Å<sup>3</sup> respectively.<sup>27</sup> Linked to these steric reasons, the average limiting cross-sectional area for a fluorocarbon chain is 27–30 Å<sup>2</sup>, which is larger than the range of 18–21 Å<sup>2</sup> typically achieved for a hydrocarbon chain (ref 27). It is also instructive to examine the free energy of transfer of non-polar carbon moieties from water,  $\Delta G$ , and hence quantify the hydrophobic effect. Table 2 compares the size and

**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<sup>a</sup>**

group	cross-sectional area (Å <sup>2</sup> )	group volume (Å <sup>3</sup> )	$-\Delta G/$ (kJ mol <sup>-1</sup> )
$-CH_2-$	18–21	27	2.60
$-CF_2-$	27–30	38	5.10

<sup>a</sup>Data are from the literature (ref 27).

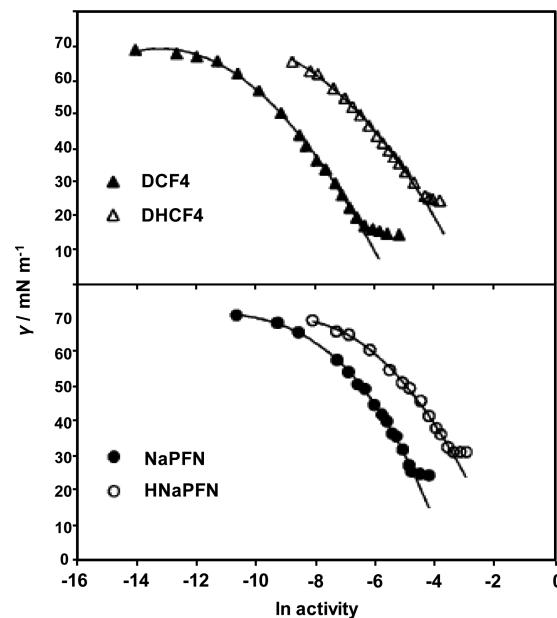
incremental changes in free energy of adsorption for the transfer of a mole of  $-CH_2-$  or  $-CF_2-$  groups from water to the air–water interface. It can be seen that a more favorable free energy of transfer is obtained for  $-CF_2-$  groups and therefore F chains are considerably more hydrophobic than H chains because of their relative larger size. Hence, because of 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.

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, because of 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 for increasing hydrophobicity and hence improving surface properties without increasing the 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 cmc's than expected.<sup>28</sup> Dramé et al. recently synthesized a family of short-tailed anionic gemini surfactants which showed aggregation behavior almost equivalent to those of long-chain (bioaccumulable) perfluoroctyl surfactants, reporting surface tensions from 15 to 33 mN m<sup>-1</sup>.<sup>29</sup>

As highlighted by Pitt et al., the hydrophobic chain structure of a surfactant plays a major role in controlling physiochemical properties such as the surface excess  $\Gamma$ , surface tension  $\gamma$ , and

cmc. It was also shown how with double-chain, partially fluorinated anionic sulfosuccinates the simple difference in a  $CF_3-$  or  $-(CF_2-H)$  terminal group can noticeably affect the physiochemical properties (ref 13). The replacement of a terminal F atom with 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  $\gamma^p$ . This, along with the lower surface excess due to dipolar repulsion, will have the effect of increasing the surface tension for solutions of the  $\omega$ -H surfactants relative to those of the fully fluorinated analogues (Table 1, 3; see Figure 4). The



**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 diHCF<sub>4</sub>, which were at 25 °C. Reprinted with permission from ref 13. Copyright 1999 American Chemical Society.

terminal H atom and the pursuant dipole moment decrease the surfactant tail hydrophobicity which is evident from the higher cmc's compared to those of the fully fluorinated analogues ( $\sim \times 5$  per chain).

Comparable increases in surface tension have also been reported on substitution of chain-terminal F for H.<sup>30</sup> Compared to the equivalent perfluoromethyl-tipped compounds, an increase in  $A_{cmc}$  was observed: 43 Å<sup>2</sup>/51 Å<sup>2</sup> for NaPFN(4)/HNaPFN and 56 Å<sup>2</sup>/65 Å<sup>2</sup> for diCF4(3)/diHCF4(2). The investigations were extended to single-chain nonionics to examine the generality of these reported effects and to compare nonionic behavior with anionics.<sup>31</sup> Almost identical changes in the 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 the interfacial packing ability. Klapper et al. investigated the correlation between the chemical structure of several short-chain fluorosurfactants and the 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.<sup>32</sup>

**Table 3. Static Interfacial Properties of Several Fluorosurfactants with Various Chain Lengths and Numbers of R<sup>F</sup> Groups<sup>a</sup>**

set	fluorinated group	type	static interfacial properties		
			CMC/(10 <sup>-3</sup> g L <sup>-1</sup> )	$\gamma_{cmc}/(mN m^{-1})$	$A_{cmc}/(\text{Å}^2)$
i	3.C <sup>F</sup> <sub>3</sub>	A	10	19.5	61
		B	20	19.5	55
		C	15	19.8	49
ii	2.C <sup>F</sup> <sub>3</sub>	A	30	20.5	239
		B	50	20.3	241
		C	10	21.9	217
iii	2.C <sup>F</sup> <sub>3</sub> OC <sup>F</sup> <sub>2</sub>	A	50	18.1	164
iv	2.C <sup>F</sup> <sub>2</sub>	A	n.o.	24.8	212
		B	n.o.	23.6	213
v	1.C <sup>F</sup> <sub>6</sub>		20	17.4	73

<sup>a</sup>3.C<sup>F</sup><sub>3</sub> corresponds to three perfluoroalkyl chains each composed of three carbons, 2.C<sup>F</sup><sub>3</sub> corresponds to two perfluoroalkyl chains each composed of three carbons, and so forth. Data are from ref 32.

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 those of longer-chain surfactants, which can participate in stronger interactions with neighboring surfactant molecules, pack more densely, and hence lower the surface tension. Furthermore, increasing the number of chains leads to more hydrophobic surfactants with an increased number of chain–chain intermolecular interactions, hence efficient packing, producing surface films composed of low-energy CF<sub>3</sub>–/–CF<sub>2</sub>– groups.

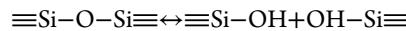
### 3. SILICONE SURFACTANTS

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),<sup>33</sup> ABA copolymers (where B represents the silicone portion),<sup>34</sup> and trisiloxane surfactants (Table 1, 5).<sup>35</sup> 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  $\gamma_{cmc}$  in the range of 20–30 mN m<sup>-1</sup>.<sup>36</sup> The essential reasons silicone (SiC) surfactants generate low  $\gamma_{cmc}$  are the following: (1) the low intrinsic surface activity and lower surface energy of methyl groups (CH<sub>3</sub>–) and (2) 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; therefore, they are widely used in applications such as stabilizers

for polyurethane foams, emulsifiers in cosmetics, agricultural adjuvants, textile conditioning, coating, and ink additives.<sup>37</sup>

The Si–O–Si linkage is susceptible to hydrolysis in the presence of moisture,<sup>38</sup> and the hydrolytic instability of trisiloxane surfactants is an inherent weakness, reducing their performance. This has also lead to discrepancies among published works on supposedly identical compounds.



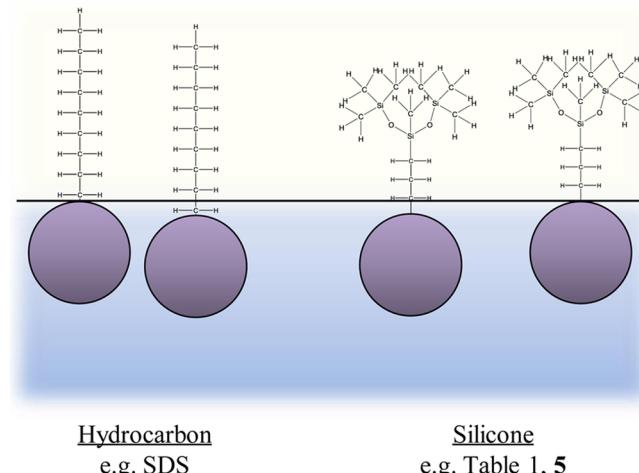
The reaction is catalyzed by acid or base, and the rate is slow near pH 7.0 (ref 38). Residual acidity or basicity on glassware surfaces can catalyze degradation, requiring plasticware or glassware treated by hydrophobic silanization. Furthermore, at sustained temperatures above 70 °C hydrolysis leads to a 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.<sup>39</sup> 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 cmc's (cac's).

**3.1. Surface Activity.** Silicones are effective surfactants able to lower  $\gamma_{cmc}$  to ~20 mN m<sup>-1</sup> (compared to the value of ~30 mN m<sup>-1</sup> for typical hydrocarbon surfactants) and can be surface-active in both aqueous and nonaqueous media.<sup>40</sup> The surface activity of silicone surfactants is due to the nature of both the backbone and pendant organic groups (CH<sub>3</sub>–). 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 groups, compared to typical linear-chain HC surfactants, which promote films with a greater proportion of higher-surface-energy –CH<sub>2</sub>– groups (Figure 5).

The strong intermolecular interactions associated with the inorganic silicate-like backbone are masked by the inter-low-surface-energy organic groups. However, it would be reasonable

–CH<sub>2</sub>– groups dominate the interface,  $A_{cmc} \approx 50 \text{ Å}^2$ ,  $\gamma_{cmc} \approx 30-35 \text{ mN m}^{-1}$

–CH<sub>3</sub> groups dominate the interface,  $A_{cmc} \approx 70 \text{ Å}^2$ ,  $\gamma_{cmc} \approx 20-21 \text{ mN m}^{-1}$



**Figure 5.** Schematic comparison of the surface character of hydrocarbon versus silicone surfactants. Typical values of  $A_{cmc}$  and  $\gamma_{cmc}$  for a linear hydrocarbon and silicone surfactant are provided. Redrawn on the basis of the illustration in ref 37.

to question if the high-surface-energy siloxane backbone directly affects the surface energy. By splitting the surface energy into separate polar and dispersion components, evidence suggests that the backbone has only a minor effect. Using Zisman's contact angle data, Kaelble calculated  $\gamma^d = 20.5 \text{ mN m}^{-1}$  and  $\gamma^p = 1.6 \text{ mN m}^{-1}$  for polydimethylsiloxane.<sup>41</sup> Similar values have been reported elsewhere,<sup>42</sup> showing that the backbone has a small direct effect on the surface energy because 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  $T_g$ ,<sup>43</sup> 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.<sup>44</sup> 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  $\gamma$  on molecular weight indicates that the conformation of polymeric siloxane surfactants at interfaces is a major factor dictating the 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  $\text{CH}_3-$  groups. Thus, the lower surface tensions given by siloxane surfactants can be traced directly to the molecular structure, the unusual flexibility of the siloxane backbone, and the different surface energies of  $\text{CH}_3-$  versus  $-\text{CH}_2-$ .

**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,  $\gamma_c$ , indicating whether a liquid with a known liquid/vapor interfacial tension,  $\gamma_{LV}$ , wets a solid surface. Liquids with  $\gamma_{LV} < \gamma_c$  will spread out over the solid substrate. The surface tension of pure water ( $\gamma_{LV} \approx 72 \text{ mN m}^{-1}$  at 298 K) is much higher than the critical surface tension of typical hydrophobic materials such as leafy surfaces ( $\gamma_c \approx 50 \text{ mN m}^{-1}$  at 298 K); therefore, the spreading of water does not occur on those materials. Hence, reducing the surface tension using surfactants means that solutions are much more likely to wet low-energy surfaces. Young's equation for the contact angle (eq 2) shows that spreading requires both a low surface tension for the surfactant solution ( $\gamma_{LV}$ ) and a low interfacial tension between the liquid and the substrate ( $\gamma_{SL}$ ).

$$0 = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos \theta \quad (2)$$

Fluorocarbon surfactant solutions with limiting aqueous surface tensions of about  $15 \text{ mN m}^{-1}$  do not spread on low-energy hydrocarbon surfaces because the interfacial tensions between fluorocarbon surfactant solutions and hydrocarbon substrates ( $\gamma_{SL}$ ) are relatively 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<sub>8</sub>OH)M (Table 1, S). Hence, because of the unique spreading and low  $\gamma$  of silicone surfactants, they have wide applications as adjuvants for agrochemicals, facilitating the spreading of crop spray formulations over hydrophobic/waxy leaf surfaces.<sup>45</sup>

#### 4. HYDROCARBON SURFACTANTS

The link between the limiting tension (energy)  $\gamma_{cmc}$  and chemical structure in the interfacial film depends on various factors. Table 4 shows a compilation of literature data on selected fluorocarbon, silicone, and hydrocarbon surfactants.

**Table 4. Surface Properties of Some Fluorocarbon, Silicone, and Hydrocarbon Surfactants from the Literature**

surfactant	$\gamma_{cmc}/(\text{mN m}^{-1}) \pm 1$	$A_{cmc}/(\text{\AA}^2) \pm 2$
<b>Fluorocarbon</b>		
NaPFN (4) <sup>a</sup>	25.6	43
diCF <sub>4</sub> (3) <sup>b</sup>	17.9	62
C <sub>8</sub> FC <sub>3</sub> -2-C <sub>3</sub> C <sub>8</sub> F <sup>c</sup>	13.7	91
<b>Hydrocarbon</b>		
TPA-DS <sup>d</sup>	31.8	67
AOT (6) <sup>e</sup>	30.8	75
TCl4 <sup>f</sup>	27.0	80
TPA-TC <sup>d</sup>	25.4	136
di-BC <sub>9</sub> SS <sup>g</sup>	24.5	120
<b>Silicone</b>		
L77 <sup>h</sup>	~22	66
SS1 <sup>i</sup>	20.7	70

<sup>a</sup>Data from Eastoe.<sup>13</sup> <sup>b</sup>Data from Dickson.<sup>46</sup> <sup>c</sup>Data from Yoshimura.<sup>47</sup> <sup>d</sup>Data from Brown.<sup>48</sup> <sup>e</sup>Data from Nave.<sup>49</sup> <sup>f</sup>Data from Mohamed.<sup>50</sup> <sup>g</sup>Data from Penfold.<sup>51</sup> <sup>h</sup>Data from Rosen.<sup>52</sup> <sup>i</sup>Data from Goddard (ref 14). Structures for C<sub>8</sub>FC<sub>3</sub>-2-C<sub>3</sub>C<sub>8</sub>F, L77, and SS1 can be found in Figure 9; for compounds with bold numbers, the structures are in Table 1. (TPA-DS), tetrapropylammonium dodecylsulfate; (TCl4), trichain anionic surfactant; (TPA-TC), tetrapropylammonium trichain anionic; and (di-BC<sub>9</sub>SS), sodium bis(1-isobutyl-3,5-dimethyl-hexyl)-2-sulfosuccinate.

As previously highlighted, perfluorocarbon surfactants provide lower surface tensions than hydrocarbon analogues because of (1) the low polarizability of fluorine and (2) the larger volume of a fluorocarbon chain. Furthermore, surfactants bearing siloxane chains have been shown to generate lower  $\gamma_{cmc}$  values than those of typical linear-chain hydrocarbon surfactants because of the unique flexibility of the siloxane backbone. Initially, it would appear that hydrocarbon surfactants are somewhat inferior. However, because of 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  $\gamma$  (ref 51), and the essential reasons these hydrocarbon (HC) surfactants generate low  $\gamma_{cmc}$  are the

following: (1) the low intrinsic surface energy of methyl groups ( $\text{CH}_3-$ ) and (2) highly branched tails generating dense surface layers composed of  $\text{CH}_3-$  groups with weaker tail–tail interactions compared to those of 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  $\gamma_{\text{cmc}}$  values comparable to those of certain fluorosurfactants.<sup>53</sup> However, the synthesis of trichain surfactants is time-consuming and not so straightforward, limiting their commercial applications. It has been shown that the chain branching of hydrocarbon surfactants, especially an increasing level of chain tip methylation (Table 1, 6–9), can lead to  $\gamma_{\text{cmc}}$  values lower than those for linear chain analogues.<sup>54</sup> This approach to packing the hydrocarbon chain termini with low-surface-energy  $\text{CH}_3-$  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 because of its high versatility, rich aqueous-phase behavior, and ability to form cosurfactant-free microemulsions. Investigations of the relationship between the surfactant molecular structure and phase behavior have been performed with 16 different aerosol-OT-related surfactants. AOT with a limiting surface tension of  $\gamma_{\text{cmc}} = 30.8 \text{ mN m}^{-1}$  and an effective area per molecule of  $A_{\text{cmc}} = 75 \text{ \AA}^2$  was shown to behave in a very similar fashion to a range of related analogues.<sup>55</sup> However, these studies revealed that the hydrocarbon backbone structure dictates the interfacial packing. The branched-chain compounds demonstrated a significant increase in  $A_{\text{cmc}}$  of between 10 and 20  $\text{\AA}^2$  over those found for equivalent carbon number linear-chain surfactants. Furthermore, slight variations in  $A_{\text{cmc}}$  were detected, reflecting changes in packing owing to differing extents of chain branching.

In effect, the limiting  $\gamma$  that could be achieved with an HC surfactant would be that for the parent hydrocarbon. For example, the  $\gamma_{\text{cmc}}$  of SDS with linear  $n\text{C}_{12}$  chains is  $\sim 35 \text{ mN m}^{-1}$ , but  $\gamma_{\text{air–liquid}}$  for pure  $n$ -dodecane is  $\sim 26 \text{ mN m}^{-1}$ .<sup>56</sup> The reason for the difference is that the water-soluble headgroups sterically hinder the surfactant tails from achieving a dense surface and increase the dispersion contribution  $\gamma^d$  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  $\text{CH}_3-$  and  $-\text{CH}_2-$  groups while at the same time minimizing dipolar interactions, which are essential, and unavoidable, to promoting water solubility. Hence, the net limiting surface tension  $\gamma_{\text{cmc}}$  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, 7–9) have been examined in terms of  $\gamma_{\text{cmc}}$  to explore structure–function correlations and optimize the molecular design.<sup>57</sup> 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)<sup>58</sup>

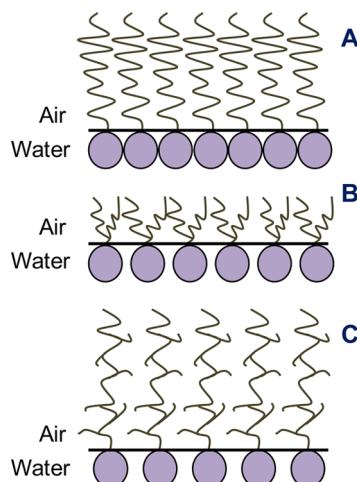
$$\log(\text{cmc}) = A - Bn_c \quad (3)$$

where  $A$  and  $B$  are constants which vary according to the charge and type of headgroup and contribution of the  $-\text{CH}_2-$  groups, respectively. Within a series of branched surfactants, links between the 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 in  $\gamma_{\text{cmc}}$  with an increasing carbon number which reflects an increase in the chain density in the surface films. Among the compounds studied,  $i\text{C}_{18}\text{S(FO-180)}$  (Table 1, 7) gave the lowest surface tension, with values of 25.4 and 24.6  $\text{mN m}^{-1}$  with  $\text{Na}^+$  and  $\text{TPA}^+$  (tetrapropylammonium) counterions, respectively. These values compare favorably with, for example, a pure alkane such as tetradecane for which  $\gamma_{\text{tetradecane}} = 24.8 \text{ mN m}^{-1}$ .<sup>59</sup> Therefore, it can be seen that  $\gamma_{\text{cmc}}$  has reached a natural limit of surface tension reduction. This remarkable reduction is believed to be a direct consequence of the increase in the  $\text{CH}_3-/-\text{CH}_2-$  ratio per headgroup based on the following order of increasing surface energy for single-carbon-based moieties:  $\text{CF}_3 < \text{CF}_2 < \text{CH}_3 < \text{CH}_2$  (ref 19). These values suggest that the surface layers of hedgehog molecules are more densely packed with  $\text{CH}_3-$  and  $-\text{CH}_2-$  groups compared to the linear-chain surfactant counterparts, and as a result,  $\gamma_{\text{cmc}}$  values are reduced.

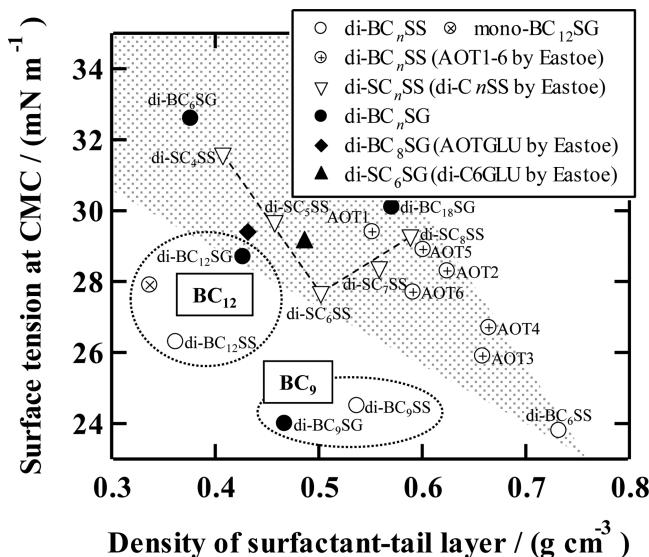
To develop HC surfactants with surface tensions as low as can be obtained for FC surfactants, dense surfactant films are needed. Hence, the optimal thickness of a surfactant layer (i.e., the optimal length of a surfactant tail) for attaining very low  $\gamma$  must be considered. If the tails are too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

One of the clearest ways of characterizing an adsorbed layer is in terms of the limiting surface excess,  $\Gamma_{\text{cmc}}$ , and area per headgroup,  $A_{\text{cmc}}$ , because these give an indication of the molecular packing efficiency. As shown, the minimum effective molecular area  $A_{\text{cmc}}$  directly affects the effective mass density of the surfactant film, and this depends on the branching position and length of the tail. However, to relate  $\gamma_{\text{cmc}}$  to the density of the surfactant HC-tail layers, the apparent mass densities of surface films can be estimated using  $\rho_{\text{layer}} = m/(A_{\text{cmc}} \times \tau)$ , where  $m$  is the weight of the surfactant double tail and  $\tau$  is the 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<sup>60</sup>). Figure 7 shows the relationship between  $\gamma_{\text{cmc}}$  and  $\rho_{\text{layer}}$  for a series of aerosol-OT-analogue surfactants (sulfosuccinate-type di- $\text{BC}_n\text{SS}$  and sulfoglutamate-type di- $\text{BC}_n\text{SG}$ ) with highly branched alkyl double tails, where  $n$  represents the carbon number (ref 51).

It can be seen that  $\rho_{\text{layer}}$  is an important property affecting  $\gamma_{\text{cmc}}$ , with a higher  $\rho_{\text{layer}}$  leading to a lower  $\gamma_{\text{cmc}}$ . The lowest  $\gamma_{\text{cmc}}$



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



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

of 23.8 mN m<sup>-1</sup> is obtained at the highest  $\rho_{\text{layer}}$  of 0.73 g cm<sup>-3</sup> for di-BC<sub>6</sub>SS (Table 1, 9). It is interesting that pure liquid *n*-decane has properties of  $\gamma = 23.7$  mN m<sup>-1</sup> at 293 K and a

density of 0.73 g cm<sup>-3</sup>.<sup>61</sup> It should also be noted that these  $\gamma_{\text{cmc}}$  values for branched HC surfactants are approaching those of common linear FC surfactants, such as NaPFN (Table 4). Figure 7 shows that the hedgehog BC<sub>9</sub> and BC<sub>12</sub> tails give much lower  $\gamma_{\text{cmc}}$  values, even at low  $\rho_{\text{layer}}$  values. This might be because the order parameter of the layer is small in BC<sub>9</sub> and BC<sub>12</sub> tails, quantifying the degree of parallel ordering of anisotropic molecules along their longitudinal axes i.e., low-surface-energy surfaces of pure liquid alkanes of ~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 an all-trans conformation of C–C bonds will give an order parameter of ~1. The symmetric structure of the individual units composing the BC<sub>9</sub> and BC<sub>12</sub> tails is likely to produce high isotropy in C–C bond ordering (i.e., a low order parameter of ~0).

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

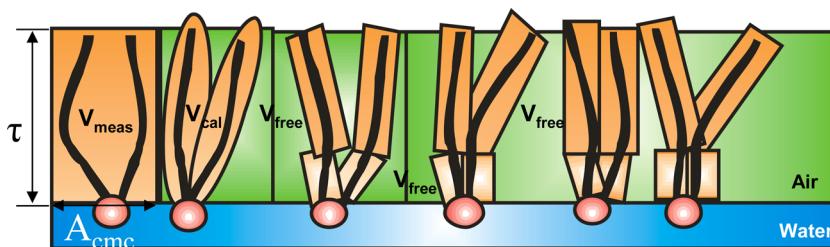
Above, the effect of surfactant structure on aqueous  $\gamma_{\text{cmc}}$  has been reviewed for fluorocarbon, siloxane, and hydrocarbon surfactants. It has been shown that each class of surfactant possesses unique chemical properties which are at the heart of notable performance. Furthermore, there are many compounds that are highly effective at reducing the 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  $\gamma_{\text{cmc}}$ ? An index to assess the surface coverage at the cmc,  $\Phi_{\text{cmc}}$ , is introduced (eq 4):

$$\Phi_{\text{cmc}} = \frac{V_{\text{cal}}}{V_{\text{meas}}} \quad (4)$$

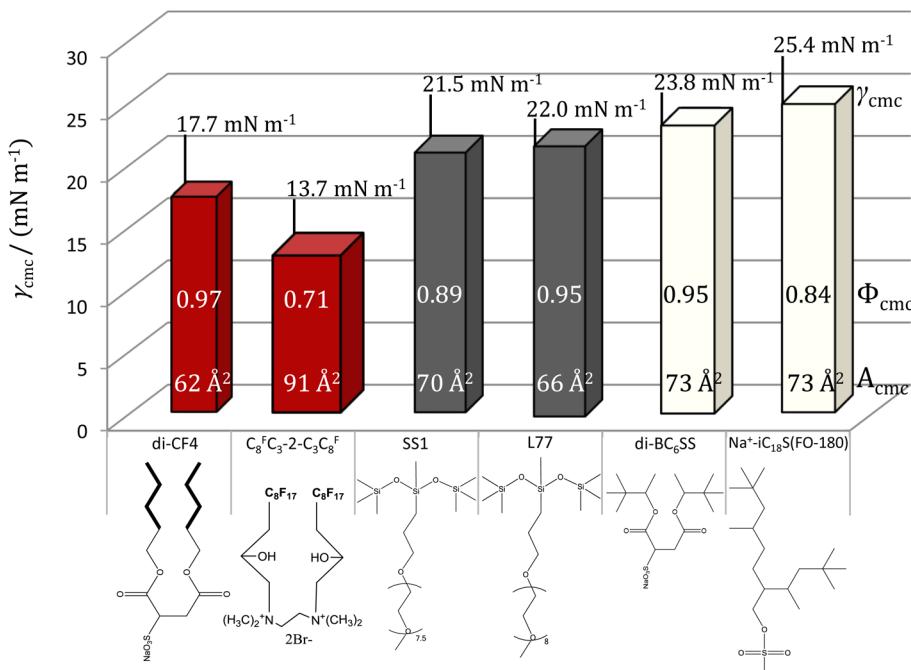
where  $V_{\text{cal}}$  is the total physical volume of surfactant molecular fragments (values taken from refs 62–64) and  $V_{\text{meas}}$  is the total volume occupied by a molecule at the reference air–water interface, calculated using experimental values (eq 5):

$$V_{\text{meas}} = A_{\text{cmc}} \tau \quad (5)$$

$A_{\text{cmc}}$  corresponds to the surfactant headgroup area (which can be determined tensiometrically), and  $\tau$  is an interfacial thickness which can be found with 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.** Visual representation of surfactants at the air–water interface, showing the different fragment and interfacial volumes used in the calculation of  $\Phi_{\text{cmc}}$ . The measured surfactant molecular volume is  $V_{\text{meas}}$ , the calculated volume based on the summation of fragments is  $V_{\text{cal}}$ , and  $V_{\text{free}}$  represents the free space in the film. Reprinted with permission from ref 53. Copyright 2011 American Chemical Society.



**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 (gray), and hydrocarbon (cream) surfactants. The column height shows  $\gamma_{cmc}$  and the column width represents  $A_{cmc}$ . Chains and end groups in bold represent perfluoroalkyl chains. Data from the literature: di-CF<sub>4</sub> (ref 46),  $C_8^F C_3-2-C_3 C_8^F$  (ref 47), SS1 (ref 14), L77 (ref 52), di-BC<sub>6</sub>SS (ref 51), and  $Na^+ \cdot iC_{18}S(\text{FO-180})$  (ref 57).

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  $\Phi_{cmc}$  is indicative of efficiently packed surfactant monolayers with little free space.

As an example, for the common SDS,  $\gamma = 31.2\ mN\ m^{-1}$ ,  $A_{cmc} = 47\ \text{\AA}^2$ , and  $\phi_{cmc} = 0.49$ , showing that the majority of the surface layer is in fact free space. Another common surfactant, AOT (Table 1, 6) with aqueous  $\gamma_{cmc} = 30.8\ mN\ m^{-1}$  and  $A_{cmc} = 75\ \text{\AA}^2$ , has a corresponding  $\Phi_{cmc} = 0.63$ . In comparison, di-CF<sub>2</sub>, a linear dichain fluorocarbon AOT-based analogue, has  $\gamma_{cmc} = 22.4\ mN\ m^{-1}$  and  $A_{cmc} = 65\ \text{\AA}^2$ , giving a surface coverage value of  $\Phi_{cmc} = 0.79$  (data from ref 53). The values obtained for  $\Phi_{cmc}$  are independent of both the surfactant geometry and chemistry of the surfactants. Therefore, by comparing  $\Phi_{cmc}$  alongside  $\gamma_{cmc}$  and  $A_{cmc}$  for three main classes of low-surface-energy surfactants, it is possible to identify a general property that accounts for low  $\gamma_{cmc}$ . Simply put, an efficiently packed surface monolayer is required for low  $\gamma_{cmc}$ , consistent with a high value of  $\Phi_{cmc}$ .

Figure 9 shows an illustration of aqueous limiting surface tensions,  $\gamma_{cmc}$ , corresponding areas per molecule at the surface,  $A_{cmc}$ , and film-packing volume fractions,  $\Phi_{cmc}$ , for some of the most effective fluorocarbon, silicone, and hydrocarbon surfactants covered in this article. The column height represents  $\gamma_{cmc}$ , and the column width represents  $A_{cmc}$ . Surface coverage  $\Phi_{cmc}$  is also given in each column. From Figure 9, it can be seen that all classes of these superefficient surfactants generate high interfacial coverages  $\Phi_{cmc}$ .

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 and 20  $\text{\AA}^2$ , respectively (ref 27). A greater number of perfluoroalkyl chains and longer chain length result in greater surface activity. For example,  $C_8^F C_3-2-C_3 C_8^F$  containing longer

perfluoroalkyl chains than di-CF<sub>4</sub> can form denser surface layers composed of low-surface-energy  $-CF_2-$  and  $CF_3-$  groups. Siloxane surfactants typically achieve aqueous  $\gamma_{cmc}$  values lower than those of hydrocarbon surfactants, accounted for by the flexibility of the siloxane backbone.

Compared to linear hydrocarbons, dense surfaces can be formed that are dominated by  $CH_3-$  groups, by employing branched chains instead. To generate low  $\gamma_{cmc}$  hydrocarbon surfactants must be able to pack sufficiently to create dense surface layers predominated by lower-surface-energy  $CH_3-$  groups while 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 while 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 coverage at the cmc,  $\Phi_{cmc}$ , 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 limiting equilibrium surface tension,  $\gamma_{cmc}$  (ref 16). This new article represents an up-to-date review of structure–activity relationships of fluorocarbon, silicone, and hydrocarbon surfactants.

Fluorocarbon surfactants provide the lowest  $\gamma_{cmc}$  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 neighboring 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  $\text{CF}_3-$  chain tip groups. Furthermore, a greater number of fluoroalkyl chains will also produce more “hydrophobic” surfactants which will reduce  $\gamma$ . 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 the 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  $\gamma_{cmc}$  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  $\text{CH}_3-$  groups (based on the trend in the surface energy of single-carbon-based moieties ( $\text{CF}_3 < \text{CF}_2 < \text{CH}_3 < \text{CH}_2$  (ref 19))), which explains the typical  $\gamma_{cmc}$  values achieved by siloxane surfactants. Smaller siloxane groups enable 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 the surface tension.

Hydrocarbon surfactants provide the highest aqueous  $\gamma_{cmc}$  values of the three classes. Chain branching of a hydrocarbon can lead to lower  $\gamma_{cmc}$  values over those of linear analogues (ref 54). Recently, it was demonstrated with AOT analogues how the structure of the hydrocarbon backbone dictates interfacial packing (ref 55). By designing highly branched surfactants (hedgehog surfactants) to increase the  $\text{CH}_3-/-\text{CH}_2-$  ratio per headgroup, it was shown that low surface tensions can be achieved by trying to mimic the densities of pure alkanes (refs 51 and 57). Long hydrocarbon tails result in poor water solubility and stronger tail–tail interactions which increase  $\gamma_{cmc}$  but also drive  $A_{cmc}$  lower. Counterbalancing this, chain branching drives  $A_{cmc}$  higher because of 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  $\Phi_{cmc}$ , which is independent of molecular geometry and composition, it has been possible to identify a general property of all effective surfactants. Namely, a reduction in surface tension is achieved by a high surface coverage (i.e., large  $\Phi_{cmc}$ ). This general structure–property relationship of surfactants has not been highlighted before, and it points to new ways of controlling the surface energy through the design of superefficient, environmentally acceptable, and commercially viable surfactants.

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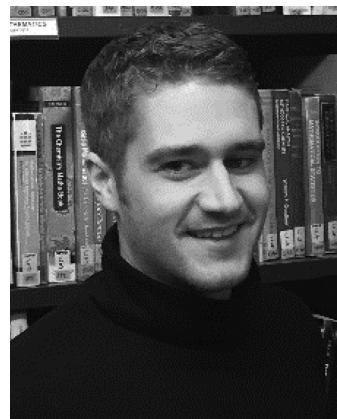
### Notes

The authors declare no competing financial interest.

### Biographies



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## ■ REFERENCES

- (1) Nelson, R. C. Applications of surfactants in the petroleum industry. *J. Am. Chem. Soc.* **1982**, *59*, 823A–826A.
- (2) 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.
- (3) Banat, I. M.; Makkar, R. S.; Cameotra, S. S. Potential commercial applications of microbial surfactants. *Appl. Microbiol. Biotechnol.* **2000**, *53*, 495–508.
- (4) Mulligan, C. N. Environmental applications for biosurfactants. *Environ. Pollut.* **2005**, *133*, 183–198.
- (5) Heertje, I.; Roijers, E. C.; Hendrickx, H. A. C. M. Liquid crystalline phases in the structuring of food products. *Food. Sci. Technol.* **1998**, *31*, 387–396.
- (6) Zhu, B. Y.; Rosen, M. J. Synergism in binary mixtures of surfactants: IV. Effectiveness of surface tension reduction. *J. Colloid Interface Sci.* **1984**, *99*, 435–442.
- (7) Abe, M.; Morikawa, K.; Ogino, K.; Sawada, H.; Matsumoto, T.; Nakayama, M. Reduction of surface tension of pure m-xylene by novel fluorinated surfactants. *Langmuir* **1992**, *8*, 763–764.
- (8) Manglik, R. M.; Wasekar, M. W.; Zhang, J. Dynamic and equilibrium surface tension of aqueous surfactant and polymeric solutions. *Exp. Therm. Fluid Sci.* **2001**, *25*, 55–64.
- (9) Rekvig, L.; Kranenburg, M.; Hafskjold, B.; Smit, B. Effect of surfactant structure on interfacial properties. *Europhys. Lett.* **2003**, *63*, 902–907.
- (10) Svitova, T.; Hoffmann, H.; Hill, R. M. Trisiloxane surfactants: surface/interfacial tension dynamics and spreading on hydrophobic surfaces. *Langmuir* **1996**, *12*, 1712–1721.
- (11) Rosen, M. J.; Cohen, A. W.; Dahanayake, M.; Hua, X. Y. Relationship of structure to properties in surfactants. 10. Surface and thermodynamic properties of 2-dodecyloxypoly (ethenoxyethanol)<sub>n</sub>, C<sub>12</sub>H<sub>25</sub>(OC<sub>2</sub>H<sub>4</sub>)<sub>n</sub>OH, in aqueous solution. *J. Phys. Chem.* **1982**, *86*, 541–545.
- (12) Morán, C.; Clapés, P.; Comelles, F.; García, T.; Pérez, L.; Vinardell, P.; Mitjans, M.; Infante, M. R. Chemical structure/property relationship in single-chain arginine surfactants. *Langmuir* **2001**, *17*, 5071–5075.
- (13) Downer, A.; Eastoe, J.; Pitt, A. R.; Simister, E. A.; Penfold, J. Effects of hydrophobic chain structure on adsorption of fluorocarbon surfactants with either CF<sub>3</sub>- or H-CF<sub>2</sub>-terminal groups. *Langmuir* **1999**, *15*, 7591–7599.
- (14) Ananthapadmanabhan, K. P.; Goddard, E. D.; Chandar, P. A study of the solution, interfacial and wetting properties of silicone surfactants. *Colloids Surf., A* **1990**, *44*, 281–297.
- (15) Lu, J. R.; Marrocco, A.; Su, T. J.; Thomas, R. K.; Penfold, J. Adsorption of Dodecyl Sulfate Surfactants with Monovalent Metal Counterions at the Air-Water Interface Studied by Neutron Reflection and Surface Tension. *J. Colloid Interface Sci.* **1993**, *158*, 303–316.
- (16) 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.
- (17) Fowkes, F. M. Additivity of intermolecular forces at interfaces. I. Determination of the contribution to the surface and interfacial tensions of dispersion forces in various liquids. *J. Phys. Chem.* **1963**, *67*, 2538–2541.
- (18) Fowkes, F. M. Attractive forces at interfaces. *Ind. Eng. Chem.* **1964**, *56*, 40–52.
- (19) Fowkes, F. M.; Zisman, W. A. Contact Angle, Wettability and Adhesion. *Adv. Chem. Ser.* **1964**, *43*, 1–51.
- (20) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989.
- (21) Kissel, E. *Fluorinated Surfactants: Synthesis, Properties and Applications*; Marcel Dekker: New York, 1994.
- (22) Porter, M. R. *Handbook of Surfactants*, 2nded.; Blackie: London, 1994.
- (23) Renner, R. The long and the short perfluorinated replacements. *Environ. Sci. Technol.* **2006**, *40*, 12–13.
- (24) Roa, N. S.; Baker, B. E. Textile finishes and fluorosurfactants. *Top. Appl. Chem.* **1994**, 321–338.
- (25) Giesy, J. P.; Kannan, K. Peer reviewed: Perfluorochemical Surfactants in the Environment. *Environ. Sci. Technol.* **2002**, *36*, 146A–152A.
- (26) Conder, J. M.; Hoke, R. A.; Wolf, W. D.; Russell, M. H.; Buck, R. C. Are PFCAs Bioaccumulative? A Critical Review and Comparison with Regulatory Criteria and Persistent Lipophilic Compounds. *Environ. Sci. Technol.* **2008**, *42*, 995–1003.
- (27) Krafft, M. P.; Riess, J. G. Chemistry, Physical Chemistry, and Uses of Molecular Fluorocarbon– Hydrocarbon Diblocks, Triblocks, and Related Compounds–Unique “Apolar” Components for Self-Assembled Colloid and Interface Engineering. *Chem. Rev.* **2009**, *109*, 1714–1792.
- (28) Zana, R.; Xia, J. *Gemini Surfactants: Synthesis, Interfacial and Solution-Phase Behavior, and Applications*; CRC Press, 2003.
- (29) Drame, A.; Taffin de Givenchy, E.; Dieng, S. Y.; Amigoni, S.; Oumar, M.; Diouf, A.; Darmanin, T.; Guittard, F. One F-octyl versus two F-butyl chains in surfactant aggregation behaviour. *Langmuir* **2013**, *29*, 14815–14822.
- (30) Achilefu, S. A.; Selve, C.; Stebe, M. J.; Ravey, J. C.; Delpuech, J. J. Monodisperse Perfluoroalkyl Oxyethylene Nonionic Surfactants with Methoxy Capping – Synthesis and Phase behavior of Water/Surfactant Binary Systems. *Langmuir* **1994**, *10*, 2131–2138.
- (31) Eastoe, J.; Paul, A.; Rankin, A.; Wat, R.; Penfold, J.; Webster, J. R. Fluorinated nonionic surfactants bearing either CF<sub>3</sub>- or H-CF<sub>2</sub>-terminal groups: Adsorption at the surface of aqueous solutions. *Langmuir* **2001**, *17*, 7873–7878.
- (32) Schuster, T.; Krumpfer, J. W.; Schellenberger, S.; Friedrich, R.; Klapper, M.; Müllen, K. Effects of chemical structure on the dynamic and static surface tensions of short-chain, multi-arm nonionic fluorosurfactants. *J. Colloid Interface Sci.* **2014**, *428*, 276–285.
- (33) Kim, D. W.; Noh, S. T.; Jo, B. W. Effect of salt and pH on surface active properties of comb rake-type polysiloxane surfactants. *Colloids Surf., A* **2006**, *287*, 106–116.
- (34) Owen, M. J.; Kendrick, T. C. Surface activity of polystyrene-polysiloxane-polystyrene ABA block copolymers. *Macromolecules* **1970**, *3*, 458–461.
- (35) Chengara, A.; Nikolov, A.; Wasan, D. Surface tension gradient driven spreading of trisiloxane surfactant solution on hydrophobic solid. *Colloids Surf., A* **2002**, *206*, 31–39.
- (36) Wagner, R.; Richter, L.; Wu, Y.; Weißmüller, J.; Kleewein, A.; Hengge, E. Silicon-modified carbohydrate surfactants. VII: Impact of different silicon substructures on the wetting behaviour of carbohydrate surfactants on low-energy surfaces—distance decay of donor–acceptor forces. *Appl. Organomet. Chem.* **1998**, *12*, 265–276.
- (37) Hill, R. M. *Silicone Surfactants*; Marcel Dekker: New York, 1999; p 86.
- (38) Knoche, M.; Tamura, H.; Bukovac, M. J. Performance and stability of the organosilicon surfactant L-77 - Effect of pH,

- Concentration, and Temperature. *J. Agric. Food. Chem.* **1991**, *39*, 202–206.
- (39) Robb, I. D. *Specialist Surfactants*; Blackie: London, 1996.
- (40) Li, X.; Washenberger, R. M.; Scriven, L. E.; Davis, H. T.; Hill, R. M. Phase behavior and microstructure of water/trisiloxane E6 and E10 polyoxyethylene surfactant/silicone oil systems. *Langmuir* **1999**, *15*, 2278–2289.
- (41) Kaelble, D. H. Dispersion-Polar surface tension properties of organic solids. *J. Adhes.* **1970**, *2*, 66–81.
- (42) Owen, M. J. The Surface Activity of Silicones: A Short Review. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 97–103.
- (43) Lee, W. A.; Rutherford, R. A.; Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley: New York, 1975; pp 111–139.
- (44) Kanner, B.; Reid, W. G.; Petersen, I. H. Synthesis and Properties of Siloxane-Polyether Copolymer Surfactants. *Ind. Eng. Chem. Prod. Res. Dev.* **1967**, *6*, 88–92.
- (45) Stevens, P. J. Organosilicone surfactants as adjuvants for agrochemicals. *Pestic. Sci.* **1993**, *38*, 103–122.
- (46) Dickson, J. L. Stabilization of Colloidal Dispersions in Supercritical Carbon Dioxide. Ph.D. Thesis, The University of Texas, August 2005.
- (47) 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.
- (48) 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.
- (49) 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.
- (50) 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 CO<sub>2</sub>. *Langmuir* **2010**, *26*, 13861–13866.
- (51) Sagisaka, M.; Narumi, T.; Niwase, M.; Narita, S.; Ohata, A.; James, C.; Yoshizawa, A.; Taffin de Givenchy, E.; Guittard, F.; Alexander, S.; Eastoe, J. Hyperbranched Hydrocarbon Surfactants Give Fluorocarbon-like Low Surface Energies. *Langmuir* **2014**, *30*, 6057–6063.
- (52) 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.
- (53) Mohamed, A.; Sagisaka, M.; Guittard, F.; Cummings, S.; Paul, A.; Rogers, S. E.; Heenan, R. K.; Dyer, R.; Eastoe, J. Low fluorine content CO<sub>2</sub>-philic surfactants. *Langmuir* **2011**, *27*, 10562–10569.
- (54) Wormuth, K. R.; Zushma, S. Phase behavior of branched surfactants in oil and water. *Langmuir* **1991**, *7*, 2048–2053.
- (55) Nave, S.; Eastoe, J.; Penfold, J. What is so special about Aerosol-OT? 1. Aqueous systems. *Langmuir* **2000**, *16*, 8733–8740.
- (56) 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*, 229–238.
- (57) Alexander, S.; Smith, G. N.; James, C.; Rogers, S. E.; Guittard, F.; Sagisaka, M.; Eastoe, J. Low-surface energy surfactants with branched hydrocarbon architectures. *Langmuir* **2014**, *30*, 3413–3421.
- (58) Klevens, H. B. Structure and aggregation in dilute solution of surface active agents. *J. Am. Oil Chem. Soc.* **1953**, *30*, 74–80.
- (59) Mejia, 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.
- (60) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed.; Wiley: New York, 1980.
- (61) Korosi, G.; Kovats, E. S. Density and surface tension of 83 organic liquids. *J. Chem. Eng. Data* **1981**, *26*, 323–332.
- (62) Li, Z. X.; Lu, J. R.; Thomas, R. K.; Penfold, J. Neutron Reflectivity Studies of the Adsorption of Aerosol-OT at the Air-Water Interface: The structure of the Sodium Salt. *Phys. Chem. B* **1997**, *101*, 1615–1620.
- (63) Berr, S. S.; Jones, R. R. M. Small-Angle Neutron Scattering from Aqueous Solutions of Sodium Perfluoroctanoate above the Critical Micelle Concentration. *J. Phys. Chem.* **1989**, *93*, 2555–2558.
- (64) Tanford, C. Micelle Shape and Size. *J. Phys. Chem.* **1972**, *76*, 3020–3024.