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# Hyperbranched Hydrocarbon Surfactants Give Fluorocarbon-like Low Surface Energies

Masanobu Sagisaka,[*,†] Tsuyoshi Narumi,[†] Misaki Niwase,[†] Shioki Narita,[†] Atsushi Ohata,[†] Craig James,[†] Atsushi Yoshizawa,[†] Elisabeth Taffin de Givenchy,[‡] Frédéric Guittard,[‡] Shirin Alexander,[§,∥] and Julian Eastoe[§]

[†]Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan

[‡]CNRS, Equipe Surfaces et Interfaces, Univ. Nice Sophia-Antipolis, Parc Valrose, 06100 Nice, France

[§]School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

[∥]Energy Safety Research Institute (ESRI), College of Engineering, Swansea University, Swansea SA2 8PP, U.K.

Ⓢ Supporting Information

**ABSTRACT:** Two series of Aerosol-OT-analogue surfactants (sulfosuccinate-type di-BC$_n$SS and sulfoglutarate-type di-BC$_n$SG) with hyperbranched alkyl double tails (so-called "hedgehog" groups, carbon number $n$ = 6, 9, 12, and 18) have been synthesized and shown to demonstrate interfacial properties comparable to those seen for related fluorocarbon (FC) systems. Critical micelle concentration (CMC), surface tension at the CMC ($\gamma_{CMC}$), and minimum area per molecule ($A_{min}$) were obtained from surface tension measurements of aqueous surfactant solutions. The results were examined for relationships between the structure of the hedgehog group and packing density at the interface. To evaluate $A$ and $B$ values in the Klevens equation for these hedgehog surfactants, log-(CMC) was plotted as a function of the total carbon number in the surfactant double tail. A linear relationship was observed, producing $B$ values of 0.20−0.25 for di-BC$_n$SS and di-BC$_n$SG, compared to a value of 0.31 for standard double-straight-tail sulfosuccinate surfactants. The lower $B$ values of these hedgehog surfactants highlight their lower hydrophobicity compared to double-straight-tail surfactants. To clarify how hydrocarbon density in the surfactant-tail layer ($\rho_{layer}$) affects $\gamma_{CMC}$, the $\rho_{layer}$ of each double-tail surfactant was calculated and the relationship between $\gamma_{CMC}$ and $\rho_{layer}$ examined. As expected for the design of low surface energy surfactant layers, $\rho_{layer}$ was identified as an important property for controlling $\gamma_{CMC}$ with higher $\rho_{layer}$, leading to a lower $\gamma_{CMC}$. Interestingly, surfactants with BC$_9$ and BC$_{12}$ tails achieved much lower $\gamma_{CMC}$, even at low $\rho_{layer}$ values of <0.55 g cm$^{-3}$. The lowest surface energy surfactant studied here was di-BC$_6$SS, which had a $\gamma_{CMC}$ of only 23.8 mN m$^{-1}$. Such a low $\gamma_{CMC}$ is comparable to those obtained with short FC-tail surfactants (e.g., 22.0 mN m$^{-1}$ for the sulfosuccinate-type FC-surfactant with R = F(CF$_2$)$_6$CH$_2$CH$_2$−).
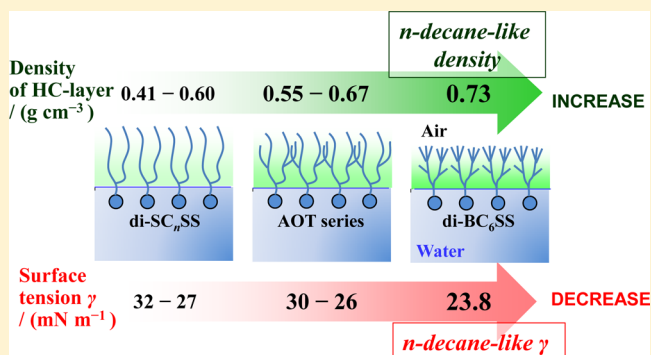
## 1. INTRODUCTION

Low surface energy materials (LSEMs) are key to a wide range of technologies and processes, from high volume products, food packaging, and protective or antiadhesion coatings for fabrics and metals (e.g., PTFE cookware) to high-end applications in photovoltaics, supercapacitors, and uranium enrichment.[1−5] One promising application of LSEMs is as efficient and effective solubilizers for water-in-supercritical CO$_2$ (W/CO$_2$) microemulsions.[6] As a supercritical fluid (SCF), CO$_2$ is unique in that it is readily available from natural resources, being also recyclable and biocompatible. The potential for dense supercritical CO$_2$ in environmental-friendly technologies has been an active area of research over the past two decades.[6] The most flexible way to modify CO$_2$ properties, such as surface tension, wettability, and viscosity, is to add self-assembling surfactants or amphiphilic polymers. New advances in surfactant molecular design have found LSE surfactants to be effective in CO$_2$, even stabilizing ultralow interfacial tension water-in-CO$_2$ microemulsions.[6] This opens up the possibility of introducing micellar self-assembly structures into dense CO$_2$, transforming it from a very weak (next to useless) solvent medium into a universal environmentally benign fluid, capable of carrying numerous CO$_2$-phobic materials.[6] Surfactant-modified CO$_2$-based solvents are expected to have widespread chemical engineering applications including reactions, separations,

extractions, nanomaterial synthesis, material processing, dyeing, metal plating, and dry cleaning.

The development and optimization of LSEMs has attracted much attention, and a wide variety of useful LSEMs can be obtained by fluorinating surfaces. Unfortunately, fluorocarbons (FCs) have significant environmental risks: recent studies[7,8] highlight the persistence and bioaccumulation hazards of FCs, and the sources of these contaminants are unquestionably fluorinated components used in today's LSEMs. This study challenges the commonly held belief that LSEMs can only be attained using biohazardous expensive FCs. Fluorinated surfactants used for LSEMs are also typically expensive and environmentally burdensome. Therefore, low surface energy hydrocarbon surfactants should be developed and used as substitutes for fluorinated surfactants in chemical industries.

For common linear HC surfactants, such as sodium dodecyl sulfate (SDS)[9] in water, the limiting surface tensions $\gamma_{min}$ are around 35 mN m$^{-1}$, a value much higher than for a typical liquid alkane (e.g., hexane 18.4 mN m$^{-1}$ at 20 °C). The reason for this is that for surfactants the water-soluble headgroups sterically hinder the surfactant tails from achieving the dense surface packing which is found in the analogous pure liquid alkane. The question then arises, "how does one modify the HC chain structure of surfactants to promote dense surface packing of the CH$_3$- and CH$_2$- groups?". This modification will promote low $\gamma$ approaching those of typical LSEMs. In an attempt to address this, the following strategy has been developed whereby linear HC chains in the surfactant molecules have been replaced with highly branched bulky groups. Here, hyperbranched HCs are called "hedgehog molecules", owing to their unusual spiky brushlike structures. 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 the limiting surface energies/tensions are reduced.

It has been recently reported that single-, double-, and triple-HC-tail anionic surfactants coupled with different ammonium cations (N$^+$R$'_4$: R$'$ = H, CH$_3$–(TMA), CH$_3$CH$_2$–(TEA), and CH$_3$CH$_2$CH$_2$–(TPA)) were able to generate low $\gamma_{min}$ in the region of 25 mN m$^{-1}$—the range normally found for FC surfactants.[10] Recently, branching of HC-only chains was found to generate LSEMs, with surface energies as low as ~24 mN m$^{-1}$.[11] Furthermore, it is known that even small changes in spacer length $n$ (from sulfosuccinate to sulfogultarate) can lead to greater LSEM efficiencies.[6]

These new discoveries[6,10,11] about low surface energy hedgehog molecules represent the key innovation: it is possible to replace fluorine in LSE surfactants with certain kinds of HC chains, counterions, and surfactant backbones and yet still achieve comparable surface properties. This study describes synthesis of novel surfactants with hyperbranched alkyl tails (Tables 1 and 2) as hydrophobic groups and variations of the linking and hydrophilic groups. The surface tensions of aqueous solutions of the hedgehog surfactants were measured to explore structure−function correlations and optimize molecular design. The molecular design strategy is to pack into the molecules as many low surface energy groups as possible, to attain efficient LSEMs, while also retaining water solubility and interfacial activity. The outputs of this study will lead to a new generation of environmentally friendly and low-cost materials and at the same time stimulate new avenues of research to design and generate alternative fluorine-free LSEMs.

**Table 1. Branched Alkyl Tails and Branching Factor**

| Branched-tail | Structure | Branching factor |
|---|---|---|
| BC$_6$ |  | 2.33 |
| BC$_9$ |  | 4.50 |
| BC$_{12}$ |  | 5.00 |
| BC$_{18}$ |  | 7.12 |
| AOT1 |  | 1.67 |
| AOT2 |  | 1.60 |
| AOT3 |  | 2.40 |
| AOT4 |  | 1.33 |
| AOT5 |  | 2.80 |
| AOT6 |  | 1.33 |

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** The surfactants were sodium bis(3,3-dimethyl-2-butyl)-2-sulfosuccinate (di-BC$_6$SS), sodium bis(2,6-dimethyl-4-heptyl)-2-sulfosuccinate (di-BC$_9$SS), sodium bis(1-isobutyl-3,5-dimethylhexyl)-2-sulfosuccinate (di-BC$_{12}$SS), sodium bis[5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octyl]-2-sulfosuccinate (di-BC$_{18}$SS), sodium bis-(3,3-dimethyl-2-butyl)-2-sulfoglutarate (di-BC$_6$SG), sodium bis(2,6-dimethyl-4-heptyl)-2-sulfoglutarate (di-BC$_9$SG), sodium bis(1-isobutyl-3,5-dimethylhexyl)-2-sulfoglutarate (di-BC$_{12}$SG), sodium bis[5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octyl]-2-sulfogultarate (di-BC$_{18}$SG), and a mixture of sodium 5-methoxy-1,5-dioxo-1-((2,6,8-trimethyl-nonan-4-yl)oxy)pentane-2-sulfonate and sodium 1-methoxy-1,5-dioxo-5-((2,6,8-trimethylnonan-4-yl)oxy)pentane-2-sulfonate (mono-BC$_{12}$SG). These surfactants have highly branched alkyl tails shown in Tables 1 and 2 and were synthesized to examine the effects of the tail structure (BC$_n$) and length of methylene spacer (sulfosuccinate SS or sulfogultarate SG) (see Supporting Information for syntheses). Sodium bis(tetradecyl)-2-sulfosuccinate (di-SC$_{14}$SS) was also synthesized previously (see Supporting Information) and was used as a control.

3,3-Dimethyl-2-butanol (Tokyo Chemical Industry), 2,6-dimethyl-4-heptanol (Tokyo Chemical Industry), 1-isobutyl-3,5-dimethylhexanol (Tokyo Chemical Industry), and 5,7,7-trimethyl-2-(1,3,3-trimethylbutyl)octanol (isostearyl alcohol FO-180, Nissan Chemical Industries) were employed as raw materials for branched hydrocarbon tails BC$_6$, BC$_9$, BC$_{12}$, and BC$_{18}$, respectively. Dimethyl glutaconate (Aldrich) was used without further purification.

Reagent grade acetone, dichloromethane, hexane, 1,4-dioxane, toluene, $p$-toluenesulfonic acid monohydrate, chloroform, chloroform-$d$, trifluoroacetic acid, isopropanol, fumaric acid, and sodium hydrogen sulfite were commercially obtained from Wako Pure Chemical Industries and employed as received. Surfactant structures are shown in Tables 1 and 2 with interfacial properties of aqueous solutions obtained by measurements as described in section 2.2. As compared to di-BC$_n$SS, di-BC$_n$SG has an extra −CH$_2$− spacer between the BC$_n$ chain and the sulfonate group. Ultrapure water with a resistivity of 18.2 MΩ cm, obtained from a Millipore Milli-Q Plus system, was used in the experiments.

**2.2. Measurement of Surface Tension, Surface Pressure, and Krafft Temperature.** Surface tensions of aqueous surfactant solutions were measured using a Wilhelmy tensiometer (CBVP-Z, Kyowa Interface Science) equipped with a platinum plate. The measurements were performed at 35 ± 0.1 °C until constant values of the surface tension of the aqueous surfactant solutions were obtained; the experimental error was less than 0.1 mN m$^{-1}$. The critical micelle concentration (CMC) was obtained from the point of intersection of

**Table 2. Interfacial Properties of Branched-Alkyl-Tail Surfactants in Water at 35 °C**

| Main structure | Surfactant | $R_x$ and $R_y$ | Kraft temp. / °C | CMC [a] / M | $\gamma_{CMC}$ [b] / (mN m$^{-1}$) | $A_{min}$ [c] / Å$^2$ |
|---|---|---|---|---|---|---|
| $R_xO-\overset{O}{\overset{\|}{C}}-CH_2$ $\|$ $R_yO-\underset{O}{\overset{\|}{C}}-CHSO_3Na$ | di-BC$_6$SS | BC$_6 \times 2$ | < 0 | $1.62 \times 10^{-2}$ | 23.8 | 73 |
| | di-BC$_9$SS | BC$_9 \times 2$ | < 0 | $2.84 \times 10^{-3}$ | 24.5 | 120 |
| | di-BC$_{12}$SS | BC$_{12} \times 2$ | 24 | $7.94 \times 10^{-5}$ | 26.3 | 171 |
| | di-BC$_{18}$SS | BC$_{18} \times 2$ | 56 | – | – | 146 [e] |
| | di-SC$_{14}$SS | $n$-C$_{14}$H$_{29} \times 2$ | 56 | – | 31.9 [d] | 58 [e] |
| $R_xO-\overset{O}{\overset{\|}{C}}-(CH_2)_2$ $\|$ $R_yO-\underset{O}{\overset{\|}{C}}-CHSO_3Na$ | di-BC$_6$SG | BC$_6 \times 2$ | < 0 | $1.58 \times 10^{-2}$ | 32.6 | 142 |
| | di-BC$_9$SG | BC$_9 \times 2$ | < 0 | $6.31 \times 10^{-4}$ | 24.0 | 138 |
| | di-BC$_{12}$SG | BC$_{12} \times 2$ | < 35 | $2.40 \times 10^{-5}$ | 28.7 | 145 |
| | di-BC$_{18}$SG | BC$_{18} \times 2$ | > 80 | – | 30.1 [d] | 127 [e] |
| | mono-BC$_{12}$SG | BC$_{12}$ + CH$_3$ | < 0 | $1.17 \times 10^{-3}$ | 27.9 | 100 |

[a]Critical micelle concentration in water. [b]Surface tension at CMC. [c]Minimum effective molecular area obtained by using the Gibbs adsorption equation. The uncertainties of $A_{min}$ are ±5 Å$^2$. [d]Data estimated from the equation $\gamma = \gamma_{water} - \pi_{max}$, where $\gamma_{water}$ is a surface tension of pure water (70.4 mN m$^{-1}$ at 35 °C) and $\pi_{max}$ is a collapse pressure obtained from Figure 3. [e]Data obtained from Figure 3 (shown by arrows).

the curves in the graph of surface tension versus logarithm of the surfactant concentration.

Minimum effective molecular area $A_{min}$ at the CMC was calculated by[10,11]

$$A_{min} = \frac{1}{N_A \Gamma_{CMC}} \quad (1)$$

where $N_A$ is the Avogadro constant and $\Gamma_{CMC}$ is the surface excess per unit area ($\Gamma$) at the CMC. If the interface and bulk phases are in (thermodynamic) equilibrium and the thermodynamic properties of the dilute solutions are assumed to be ideal, $\Gamma$ can be obtained by the Gibbs adsorption equation:[10,11]

$$\Gamma = -\frac{1}{2.303 nRT}\left(\frac{d\gamma}{d \log C}\right) \quad (2)$$

where $R$ is the gas constant, $n$ is the number of absorbing species and is 2 for a monoionic surfactant (accounting for the simultaneous adsorption of both cation and anion), $T$ is the temperature, and $C$ is the concentration of the surfactant. The value of $d\gamma/d \log C$ at CMC was obtained from the local tangents to the $\gamma-\log C$ plot on the low-concentration side. All surfactants synthesized with sodium hydrogen sulfite may contain not only Na$^+$ counterions but also other cations such as Ca$^{2+}$ due to possible impurities in the reagents.[11] Multivalent metal ions are known to enhance the surface activity of surfactants compared with sodium ions.[11] However, as the syntheses of these hedgehog surfactants was carried out with the common reagent of sodium hydrogen sulfite, this study assumed the effect of the other counterions on the surfactant surface activity is negligible. Surfactant properties were evaluated and discussed on the assumption that all surfactant molecules bear only the Na$^+$ counterion.

Surface pressure−area isotherms were measured on a KSV minitrough (KSV 2000, KSV Instruments Ltd.) equipped with a platinum Wilhelmy plate at 35 °C. In each experiment, 10 $\mu$L of a chloroform solution of surfactant was spread on the water surface. 15 min was allowed for solvent evaporation before compression. The barrier was moved at a speed of 10 mm min$^{-1}$.

The Krafft temperature was determined by observing dissolution of surfactant precipitate/water at surfactant concentration of 10 times higher than the CMC on heating.

## 3. RESULTS AND DISCUSSION

### 3.1. Surface Tension Lowering Ability of Hedgehog Surfactants.
Surface tension ($\gamma$) measurements of aqueous solutions of hedgehog surfactants were made as a function of concentration $C$ and branched group structure, thus determining the CMC and the surface tension at the CMC ($\gamma_{CMC}$) and identifying the optimal subset of chain and backbone structures. The maximum interfacial density (packing) or minimum effective molecular area $A_{min}$ are other important parameters that can be obtained from $\gamma-C$ (and $\gamma-\log C$) measurements, giving insight into intermolecular arrangements and interactions in the interfacial layers. The parameter $\gamma_{CMC}$ is especially important in predicting the solubilizing ability of the surfactant in scCO$_2$; this is because (1) the water/air and water/CO$_2$ interfacial properties of the surfactant are correlated[6] and (2) microemulsions generally form at interfacial tensions below 1 mN m$^{-1}$.[12]

Figure 1 shows the aqueous surface tensions of the hedgehog surfactants at various concentrations and 35 °C. The surface tension of all surfactant solutions decreased with concentration; however, it was almost invariant above a certain concentration, the threshold defined as the CMC. The $A_{min}$ was also calculated
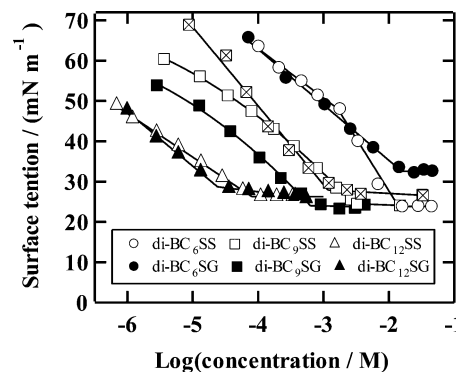


**Figure 1.** Change in surface tension for aqueous hedgehog surfactant solutions as a function of logarithm of concentration at 35 °C.

using the eqs 1 and 2 and local tangents of the $\gamma-\log C$ plot below the CMC. The values of CMC, $\gamma_{CMC}$, and $A_{min}$ are listed in Table 2 with Kraft temperature ($T_K$) data. $T_K$s increased with increasing carbon number $n$ (and therefore increasing hydrophobicity). The $T_K$ of $BC_{18}$ surfactants were $\geq 56$ °C, which makes the surfactant almost insoluble in water at the 35 °C employed for surface tension measurements. As compared with the $T_K$ of double FC-tail surfactants $n$FS(EO)$_2$ (FC length $n =$ 4, 6, and 8, tail = CF$_3$(CF$_2$)$_{n-1}$CH$_2$CH$_2-$) with a sulfosuccinate headgroup,[13] the $T_K$ of di-BC$_{12}$SS is close to that of 6FS(EO)$_2$ ($T_K = 26$ °C), and therefore the $T_K$ of di-BC$_{18}$SS could be similar to that of 7FS(EO)$_2$ given the value of 73 °C for 8FS(EO)$_2$. As $T_K$ is one of the measures of surfactant hydrophobicity, as well as CMC, the hydrophobicity between BC$_{12}$ and CF$_3$(CF$_2$)$_5$CH$_2$CH$_2$- or BC$_{18}$ and CF$_3$(CF$_2$)$_6$CH$_2$CH$_2$- is suggested to be almost same; namely, BC$_{10}$ and BC$_{16}$ correspond to C$_6$F$_{13}$- and C$_7$F$_{15}$- chains, respectively. In comparison, for branched-HC-tail and straight-HC-tail surfactants, di-BC$_{18}$SS has the same $T_K$ as for the straight-HC-tail di-SC$_{14}$SS (56 °C), clearly indicating that branching of HC-tail makes $T_K$ lower as reported in earlier papers.[14]

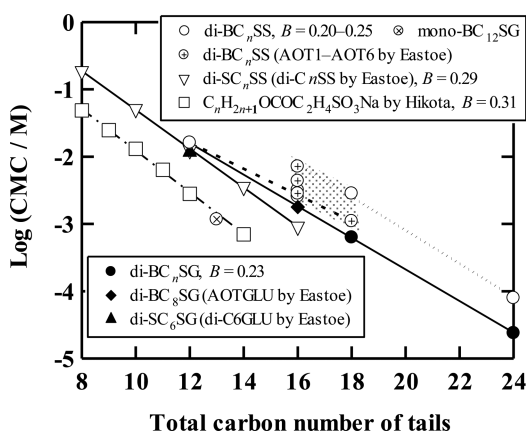**3.2. Effect of Branched Chain Structure on Critical Micelle Concentration (CMC).** Figure 2 shows variations in



**Figure 2.** Relationship between log(CMC) and total carbon number in surfactant tails. Fitted lines to experimental values were used to obtain $A$ and $B$ values in the Klevens equation for each surfactant family. Data for AOT1–AOT6, AOTGLU, di-C6GLU, and di-C$_n$SS reported by Eastoe et al.[15,16] and single-tail surfactants by Hikota et al.[17,18] were plotted for comparison with hedgehog surfactants synthesized in this study.

log(CMC) as a function of total carbon number ($n_{total}$) of the surfactant tails (namely, $2n$ for di-BC$_n$SS, di-BC$_n$SG, di-SC$_n$SS, and di-SC$_n$SG, 13 (= 12 + 1) for mono-BC$_{12}$SS, and $n$ for C$_n$H$_{2n+1}$OCOCH$_2$CH$_2$SO$_3$Na).[15–18] The log(CMC) data of the single straight-HC-tail surfactant C$_n$H$_{2n+1}$OCOCH$_2$CH$_2$SO$_3$Na at 30 ($n =$ 9, 11)[17] and 40 °C ($n =$ 8, 10, 12, 14)[18] were also plotted for comparison with the sulfosuccinate surfactants. Eastoe et al. reported CMC data at 25 °C of di-BC$_n$SS and di-BC$_n$SG analogues, which are five double-straight-HC-tail sulfosuccinates di-SC$_n$SS (synonymous di-C$_n$SS, $n =$ 4–8),[15] a double-straight-C6-tail sulfogultarate di-SC$_6$SG (synonymous with di-C6GLU),[16] six different double-branched-HC-tail sulfosuccinates di-BC$_n$SS (synonymous with AOT1-AOT6; the BC tails shown in Table 1),[15] and a double-branched-C$_8$-tail sulfogultarate di-BC$_n$SG (synonymous with

AOTGLU; the BC tail is the same as AOT1 shown in Table 1).[16] These CMC data are also displayed to examine the difference in CMC between straight and branched tails.

In general, CMC varies logarithmically with a carbon number based on the well-known Klevens equation (eq 4)[19,20]

$$\log(cmc) = A - Bn_{total} \tag{4}$$

where $A$ and $B$ are constants and vary according to the charge and type of the headgroup and contribution of the CH$_x$ ($x =$ 0, 1, 2, 3) group, respectively. For the single-straight-HC-tail surfactant and the double-straight-HC-tail di-SC$_n$SS, the $A$ and $B$ values obtained from the linear fits in Figure 2 are 1.18 and 0.31 for the single tail and 1.59 and 0.29 for the double tail, respectively. This indicates that the number of surfactant tails also affects $A$ and $B$ values even if the same headgroup is employed. On the other hand, the double-branched-tail surfactant di-BC$_n$SG has a $B$ value of 0.23. The smaller $B$ value compared with the straight-tail surfactants is due to the branching of HC tails, resulting in a better affinity with water. Interestingly, as shown for in log(CMC) data of di-BC$_n$SS with AOT1-AOT6, di-BC$_n$SS shows a discontinuity in the Klevens plots appearing at $n =$ 8–9 (i.e., total carbon numbers 16–18). If di-BC$_n$SS has a $B$ value of 0.20–0.25 similar to that of di-BC$_n$SG, the $A$ value should change with $n$ and range from 0.90 to 1.86. This may be due to a change in molecular shape (i.e., critical packing parameter) caused by bulkiness of hyper-branched tails and the narrow space of the succinate group preventing the double bulky tails to stand perpendicularly. This suggestion is supported by the larger $A_{min}$ of di-BC$_n$SS with bulky tails ($n =$ 12 and 18) compared to the smaller value seen with small tails ($n =$ 6 and 9), as compared with di-BC$_n$SG with the same $n$.

Figure 2 shows the CMCs of di-BC$_n$SG are lower than those of di-BC$_n$SS surfactants, resulting from the stronger hydrophobicity of di-BC$_n$SG caused by the addition of an extra methylene unit. Focusing on the hydrophobic effects of one methylene unit in the linking group (succinate $\rightarrow$ gultarate) and in the tail, the change in log(CMC) by addition of one methylene, $\Delta$ log(CMC), was found to be smaller in the former case. For example, $\Delta$ log(CMC) values for the linking group were $-2.9 \times 10^{-2}$ to $-1.6 \times 10^{-1}$ in the cases of di-SC$_6$SS (or di-C6SS) $\rightarrow$ di-SC$_6$SG (or di-C6GLU), di-BC$_6$SS $\rightarrow$ di-BC$_6$SG, and di-BC$_8$SS (or AOT1) $\rightarrow$ di-BC$_8$SG (or AOTGLU), whereas $-2.9 \times 10^{-1}$ and $-2.2 \times 10^{-1}$ for the tails calculated from $B$ values of di-SC$_n$SS and di-BC$_n$SS, respectively. Such a very small hydrophobic effect of the additional methylene spacer in the linking group on CMC was also observed in studies of Gemini surfactants; for a typical Gemini C$_n$H$_{2n+1}$N-(CH$_3$)$_2$Br$-$(CH$_2$)$_m-$C$_n$H$_{2n+1}$N(CH$_3$)$_2$Br, the CMCs stay in a range of $0.28 \times 10^{-3}$–$1.12 \times 10^{-3}$ M even if the spacer length $m$ increased from 3 to 12 at $n =$ 12, whereas $B$ values for the Geminis are 0.22 and 0.23 at $m =$ 3 and 6, respectively.[21–23]

The value of log(CMC) of mono-BC$_{12}$SS is closer to the fitted line for the single-tail surfactant than the lines for the double-tail surfactants, suggesting that the methyl ester group in the mono-BC$_{12}$SS molecule has only minimal effect on the aggregation tendency. When comparing di-BC$_{12}$SS with 6FS(EO)$_2$, the CMC of the branched hydrocarbon surfactant is similar to the fluorocarbon analogue ($4.5 \times 10^{-5}$ M),[13] suggesting the hydrophobicity of both double tails are almost the same, also consistent with the similar $T_K$ values. Unfortunately, the hyperbranched HC-surfactant di-BC$_{12}$SS has a slightly higher $\gamma_{CMC}$ than that of the FC-surfactant

6FS(EO)$_2$ (22 mN m$^{-1}$),[13] but this is still low when compared with a straight-HC-chain surfactant, as discussed later.

**3.3. Surface Properties of Low Solubility C$_{18}$ Surfactants.** The BC$_{18}$ surfactants have high $T_K$ values and therefore a reliable surface tension curve in water at 35 °C could not be obtained due to the poor solubility (<CMC). To obtain $A_{min}$ and/or $\gamma_{min}$ of the BC$_{18}$ surfactants, surface pressure ($\pi$)−area per molecule ($A_{molec}$) isotherms were measured of spread monolayers at the water/air interface at 35 °C as shown in Figure 3. The isotherm for di-SC$_{14}$SS is also displayed as a
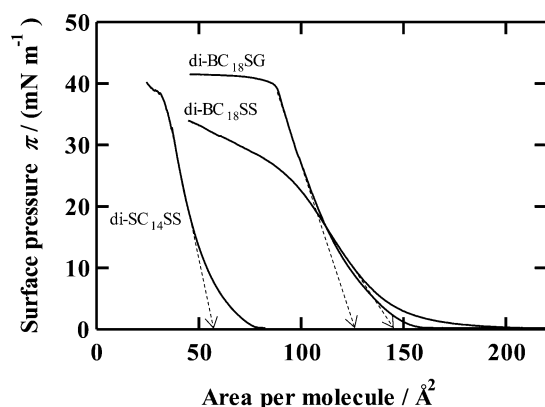


**Figure 4.** Variation of $A_{min}$ with branching factor for the double-tail surfactants. Data for AOT1−AOT6, AOTGLU di-C6GLU, and di-C$_n$SS[15,16] are also displayed with those of surfactants synthesized here.



**Figure 3.** Surface pressure ($\pi$) vs area per molecule ($A$) isotherms for adsorbed films of high-$T_K$ surfactants (di-BC$_{18}$SS, di-BC$_{18}$SG, and di-SC$_{14}$SS) at the air/water interface of 35 °C.

control in Figure 3. These isotherms are smooth rising curves with lift off areas of 190 Å$^2$ for di-BC$_{18}$SS, 160 Å$^2$ for di-BC$_{18}$SG, and 80 Å$^2$ for di-SC$_{14}$SS. The surfactant films of di-BC$_{18}$SG and di-SC$_{14}$SS were found to be collapsed at about 40.0 and 38.5 mN m$^{-1}$ (i.e., collapse pressures $\pi_{max}$), respectively. Surface pressures of di-BC$_{18}$SS reached >30 mN m$^{-1}$ but did not show a kink identified as film collapse even at the area of <50 Å$^2$. The $A_{min}$ values were estimated as 146 Å$^2$ for di-BC$_{18}$SS, 127 Å$^2$ for di-BC$_{18}$SG, and 58 Å$^2$ for di-SC$_{14}$SS by extrapolating the constant slope regions of the isotherms to zero surface pressure, as shown by broken lines and arrows in Figure 3. The $\gamma_{CMC}$ values were also calculated by the equation $\gamma = \gamma_{water} - \pi_{max}$, where $\gamma_{water}$ is a surface tension of pure water (70.4 mN m$^{-1}$ at 35 °C) and listed with the $A_{min}$ in Table 1.

**3.4. Links between Lowering Surface Tension and Surfactant Film Density.** This study is to develop HC surfactants yielding surface tensions as low as can be obtained for fluorinated surfactants, and to achieve this a dense surfactant film is needed. The area $A_{min}$ directly affects the effective mass density of the surfactant film and has been found to depend on branching position and length of tail, in other words, branching factor.[11,15] This empirical factor accounts for contributions from both the extent and position of a branch relative to the headgroup. For instance, the branching factor of the BC$_{18}$ tail was calculated as follows: from the headgroup there are 2 methyls in position 2, 1 methyl in position 4, and 7 methyls in position 7 on a C$_8$ linear chain, i.e., $[(2 \times 2) + (1 \times 4) + (7 \times 7)]/8 = 7.12$. Branching factors calculated in this way are listed in Table 2. Then $A_{min}$ values for the surfactants used in this study and from the literature (AOT1−6, di-SC$n$SS, AOTGLU, and di-C6GLU)[15,16] are plotted as a function of branching factor as shown in Figure 4. Thus, this figure clearly shows the dependence of $A_{min}$ on structure of the hydrophobic group: increasing the branch length and/or branching closer to
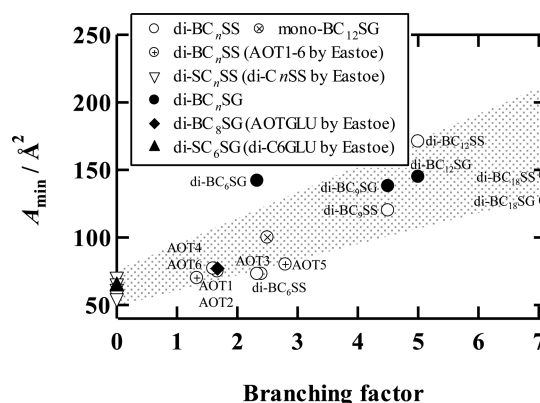
the headgroup increases $A_{min}$, as one would expect owing to geometrical constraints. Such trends, although not expressed in terms of a branching factor, have been reported for a series of linear and branched alkylpyridinium halides.[24] As the $A_{min}$ value of di-BC$_6$SG was far from those of the AOT series and di-BC$_6$SS in spite of similar branching factors, the double tails of di-BC$_6$SG might be more open than the tails in the sulfosuccinates, as a result of the extra methylene spacer of SG, a weak hydrophobicity, and a weak tail−tail interaction of BC$_6$ tails.

To confirm the relationship between $\gamma_{CMC}$ and the density of the surfactant HC-tail layer on water surface $\rho_{layer}$, the apparent mass densities of surface films were estimated by using the equation $\rho_{layer} = m/(A_{min} \times L)$, where $m$ is molecular weight of surfactant double tail and $L$ is length of surfactant tail (obtained by $L = 1.5 + 1.265x$, where $x$ is the carbon number of the longest alkyl chain in tail).[25] In addition, changes in $\gamma_{CMC}$ as a function of temperature have been reported:[26] for example, the $\gamma_{CMC}$ of C$_n$H$_{2n+1}$SO$_3$Na ($n$ = 10, 12) at an air/water interface decreased by 1.8−2.0 mN m$^{-1}$ with increasing temperature from 25 to 40 °C. To the $\gamma_{CMC}$ values for AOT1−6, di-C$n$SS, C6GLU, and AOTGLU reported in earlier papers at 25 °C,[15,16] 1.4 mN m$^{-1}$ was added, thus estimating the values at 35 °C and allowing for comparison with the $\gamma_{CMC}$ data of di-BC$_n$SS and di-BC$_n$SG in this study. Figure 5 is the relationship between $\gamma_{CMC}$ and $\rho_{layer}$ for surfactants displayed in Figure 4. As expected in the design of low surface energy surfactant layers, $\rho_{layer}$ is identified as an important property for affecting $\gamma_{CMC}$ with a higher $\rho_{layer}$ leading to a lower $\gamma_{CMC}$. The lowest $\gamma_{CMC}$ of 23.8 mN m$^{-1}$ is obtained at the highest $\rho_{layer}$ = 0.73 g cm$^{-3}$ for di-BC$_6$SS: it is interesting to compare this record low value with the surface tension of 23.7 mN m$^{-1}$ for pure liquid $n$-decane at 20 °C and a density 0.73 g cm$^{-3}$.[27]

Another important question for obtaining low surface energy HC surfactants is, "what is the optimal thickness of a surfactant layer (i.e., the best length of surfactant tail) to attain very low surface tensions?". This is very interesting to know as too long a surfactant HC tail causes a high $T_K$ (a poor solubility in water) and a stronger tail−tail interaction increases $\gamma_{CMC}$ as surface tension of pure $n$-alkanes increases with chain length:[27] on the other hand, a too short tail is insufficiently hydrophobic. The answer could be obtained from examining the data for di-SC$_n$SS, di-BC$_6$SS, and di-BC$_6$SG. In the case of di-SC$_n$SS, a longer tail length $n$ drives $A_{min}$ smaller with increasing tail−tail interactions, resulting in a higher $\rho_{layer}$. On the other hand, $\gamma_{CMC}$
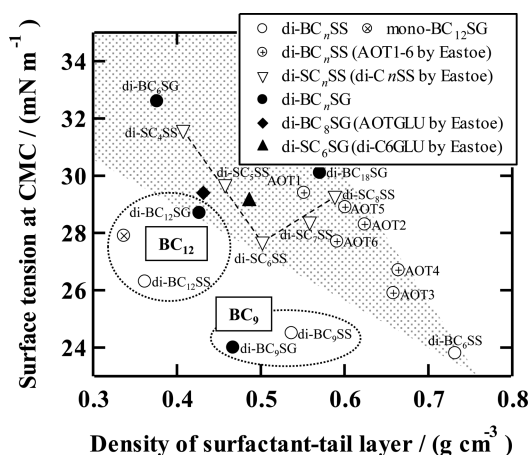
**Figure 5.** Relationship between $\gamma_{CMC}$ and density of the surfactant-tail layer calculated with $A_{min}$ and tail length at 35 °C. Tail lengths of each surfactant were calculated using the Tanford equation.[25] The $\gamma_{CMC}$ values of AOT1−AOT6, AOTGLU di-C6GLU, and di-C$_n$SS at 35 °C[15,16] were estimated from the data at 25 °C and plotted to clarify the trend of $\gamma_{CMC}$ vs the density.

decreased with increasing $\rho_{layer}$ from $n$ 4 to 6 but then becomes higher with $n \geq 6$ in spite of an increase in $\rho_{layer}$. This suggests that an effective carbon number $n = 6$ is the best length for the double-straight-HC-tail surfactants for obtaining a low $\gamma_{CMC}$. On the other hand, focusing on the shortest-double-tail surfactants di-BC$_6$SS and di-BC$_6$SG, di-BC$_6$SG has a much higher $\gamma_{CMC}$ than the mono-BC$_{12}$SG and di-BC$_{12}$SS with similar $\rho_{layer}$ values. Furthermore, the $\gamma_{CMC}$ is a little higher than that of the straight-double-tail surfactant di-SC$_4$SS, although a methyl group was reported to be more effective in lowering $\gamma_{CMC}$ than methylene.[28] These results imply that the longest C$_3$-chain in BC$_6$ tail is little too short for diminishing water surface energy efficiently. If this is true and the tails of di-BC$_6$SS and di-BC$_6$SG could be manipulated to be longer, the $\gamma_{CMC}$ may be lower as found in the straight-tail di-SC$_n$SS, even in the case of di-BC$_6$SS yielding the lowest $\gamma_{CMC}$ of 23.8 mN m$^{-1}$.

Unfortunately, $\gamma_{CMC}$ of branched-tail surfactants are still far from ideal values as typical alkanes ($n$-hexane, 18.4 mN m$^{-1}$ at density of ~0.65 g cm$^{-3}$ and 20 °C). However, the $\gamma_{CMC}$ values of di-BC$_6$SS, di-BC$_9$SS, and diBC$_9$SG are close to that obtained by short FC-tail surfactants (e.g., 22.0 mN m$^{-1}$ for the sulfosuccinate-type FC-surfactant with R = F-(CF$_2$)$_6$CH$_2$CH$_2$−).[13] Interestingly, in comparison, the hedge-hog BC$_9$ and BC$_{12}$ tails gave much lower $\gamma_{CMC}$, even at low $\rho_{layer}$ values of <0.55 g cm$^{-3}$, with the $\gamma_{CMC}$ of 24.0 mN m$^{-1}$ at 0.467 g cm$^{-3}$, with di-BC$_9$SG being the most effective case. Why do these hedgehog tails effectively act to lower $\gamma_{CMC}$ compared with the others? One conceivable reason is the difference in order parameter,[29] which quantifies the degree of parallel ordering of anisotropic molecules along their longitudinal axes. For example, the low surface energies of pure liquid alkanes are generated with order parameter ~0, and it drastically increases when the state changes to solids (crystals) with order parameters of ~1.[29] When incorporating order parameter theory into the design of low surface energy surfactant tails, the order parameter in the layer should be as close to 0 as possible. In this study, the order parameter in the layer is defined as the degree of the average of 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 order parameter ~0 could be

obtained by isotropic C−C bond ordering such as for the neopentyl ((CH$_3$)$_3$CCH$_2$−) tail. The BC$_9$ tail is composed of symmetric isobutyl units, and the symmetric structure and the four methyl branches are likely to produce a high isotropy in C−C bond ordering. On the other hand, the BC$_{12}$ tail has nearly symmetric isobutyl and heptyl units and five methyl branches lowering the order parameter close to zero. In this case, such a very small order parameters of BC$_9$ and BC$_{12}$ tails may generate a surface tension lowering ability, even at low packing density <0.55 g cm$^{-3}$.

Therefore, BC$_9$ and BC$_{12}$ tails are promising hedgehog groups for the design of very low surface energy systems which could be realized if $\rho_{layer}$ could be increased to values exhibited by di-BC$_6$SS. One way to increase the $\rho_{layer}$ of these tails is the molecular design of triple-tail hedgehog surfactants, and this hypothesis will be tested in a future study.

## 4. CONCLUSIONS

This study has aimed at developing hydrocarbon (HC) surfactants able to generate low surface energy interfaces, as effective as those observed for fluorocarbon (FC) surfactants. The approach taken here attempted to mimic the high densities of pure liquid alkanes (0.6−0.7 g cm$^{-3}$). To achieve these high-density layers, hyperbranched alkyl (hedgehog groups) with C$_6$, C$_9$, C$_{12}$, and C$_{18}$ were employed in AOT-analogue, double-tail surfactants (sulfosuccinate and sulfogultarate types). Here, were confirmed not only structure−property correlations ([1] and [3] described below) as reported in earlier papers[15−19] but also new findings and hypotheses ([2] and [4]−[6]) for advancing this field.

[1] The CMCs of the hedgehog surfactants were correlated with the total carbon number of the double tails, and [2] $B$-values for the Klevens equation were found to be smaller ($B = 0.20−0.25$) than those for the double-straight-tail analogue ($B = 0.29$).[15] [3] The minimum areas per surfactant molecule, $A_{min}$, derived from analyses of surface tension and pressure isotherms, increased with branching factor due to the greater bulkiness of the tail, as found in earlier papers.[15] The effective densities of the surfactant tail layers in films were calculated by using surface tension derived $A_{min}$ values and tail lengths from the Tanford equation[25] and were used to examine any relationship between the film density and surface tension at the CMC ($\gamma_{CMC}$). [4] As expected, a higher density tends to yield lower surface tensions: for example, one of the hedgehog surfactants formed layers with the highest density of 0.73 g cm$^{-3}$ and gave the lowest $\gamma_{CMC}$ of 23.8 mN m$^{-1}$. It is interesting to note that now the surfactant films have properties similar to those for liquid, long-chain alkanes.[27] If making a high density layer is the best way of lowering surface energy, this challenge would be achieved by generating $\gamma_{CMC}$ and surfactant-tail layer densities comparable to those of neat liquid alkanes. [5] On the other hand, even at a low density of <0.55 g cm$^{-3}$, the highly branched nonyl (BC$_9$) tail exhibited quite low $\gamma_{CMC}$ close to the lowest value obtained at the highest density studied here. [6] From these results, two options have been suggested as key to advance hedgehog surfactant design further. These are a suitable surfactant-tail length which gives an appropriate layer thickness and an order parameter[29] of ~0 similar to a liquid alkane, expected to be ~C$_6$ for straight-chain surfactants.[15]

Further studies will consider both key parameters to explore if values of $\gamma_{CMC}$ lower than 22 mN m$^{-1}$ can be attained. Other work will also evaluate of low surface energy hedgehog surfactants for stabilizing water-in-CO$_2$ microemulsions and

reveal branching structure—solubilizing property correlations to advance surfactant design for an efficient and effective $CO_2$-philes. These further studies will allow for the achievement of hedgehog surfactants able to generate FC-like low surface energies which could lead new applications such as dry-cleaning, agrochemicals, enhanced oil recovery, treatment of oil spills, and so on.[1−5,30]

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Surfactant synthesis for eight hedgehog surfactants and characterization by ^{1}H NMR, FT-IR, and elemental analysis; Klevens plots for Gemini surfactants $C_nH_{2n+1}N(CH_3)_2Br−(CH_2)_m−C_nH_{2n+1}N(CH_3)_2Br$. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail sagisaka@cc.hirosaki-u.ac.jp; Ph +81-172-39-3579 (M.S.).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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