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A New Class of Amphiphiles Designed for Use in Water-in-Supercritical CO₂ Microemulsions

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Abstract

Water-in-supercritical CO₂ microemulsions formed using the hybrid F-H surfactant sodium 1-oxo-1-[4-(perfluorohexyl)phenyl]hexane-2-sulfonate, FC6-HC4, have recently been shown to have the highest water solubilizing power ever reported. FC6-HC4 demonstrated the ability to not only outperform other surfactants but also other FC_m-HC_n analogues containing different fluorocarbon and hydrocarbon chain lengths [Sagisaka, M. et al. *Langmuir*, 31, 7479-7487 (2015)].

With an aim to clarify the structural key features of this surfactant, this study examined the phase behavior and water/supercritical CO₂ aggregate formation of 1-oxo-1-[4-(perfluorohexyl)phenyl]hexane (“Nohead” FC6-HC4), which is an FC6-HC4 analogue, but now interestingly, without the sulfonate headgroup. Surprisingly, Nohead FC6-HC4, which would not normally be identified as a classic surfactant, yielded transparent single-phase W/CO₂ microemulsions with polar cores able to solubilize a water-soluble dye, even at pressures and temperatures so low as to be approaching the critical point of CO₂ (e.g. ~100 bar at 35 °C). High-pressure small angle scattering (SANS) measurements revealed the transparent phases to consist of ellipsoidal nano-droplets of water. The morphology of these droplets was shown to be dependent on the pressure, Nohead FC6-HC4 concentration, and the water-to-“surfactant” molar ratio. Despite having almost the same structure, as Nohead FC6-HC4, analogues containing both shorter and longer hydrocarbons were unable to form W/CO₂ microemulsion droplets. This shows the importance of the role of the hydrocarbon chain for stabilization of W/CO₂ microemulsions. A detailed examination of the adsorption mechanism of Nohead FC6-HC4 onto the water surface suggests that the hexanoyl group protrudes into the aqueous core, allowing for association between the carbonyl group and water.

Keywords: Supercritical CO₂, Microemulsion, Fluorocarbon, Solubilizing power, Small-Angle Neutron Scattering

1. Introduction

The use of supercritical CO₂ (scCO₂) for industrial applications has received much attention due to attractive properties such as low cost, inflammability, environmentally benignity, natural abundance, high mass transfer, and pressure/temperature-tunable solvency (i.e. tunable density)¹. Unfortunately, supercritical CO₂ can only dissolve nonpolar and small molecular mass materials, with large polar materials always separating in neat scCO₂². Improving the poor solubility of polar materials is important for further developing the potential applications of scCO₂. One of the most promising approaches to increase the solubility of polar substances is to form reversed micelles with high-polarity aqueous cores in the continuous scCO₂ phase, that is, water-in-scCO₂ microemulsions (W/CO₂ μEs).² Since such organized fluids have the attractive characteristics of scCO₂ as well as the solvation properties of bulk water, they have potential to act as volatile organic compound (VOC)-free and energy-efficient solvents for nano-material synthesis, enzymatic reactions, dry-cleaning, dyeing, and preparation of inorganic/organic hybrid materials².

To be a viable green and economical technology, the amount of surfactant used for W/CO₂ μEs should be as small as possible. This low surfactant level needs to be balanced against the need for large interfacial areas when forming W/CO₂ μEs, with the appropriate levels of dispersed water needed to enhance process efficiencies. One approach to meet these requirements is to explore or develop highly efficient solubilizers for W/CO₂ μEs, and studies aiming to do this started in the 1990s.³

The development of CO₂-philic hydrocarbon surfactants for scCO₂ has been recognized as an important task for economic and environmental reasons.³⁻⁶ However, most commercial and known hydrocarbon surfactants are insoluble and inactive in scCO₂ systems³. In this regard, it has become apparent that conventional surfactant-design theory cannot be applied to W/CO₂ systems, and that CO₂-philicity is not directly comparable to oleo-philicity. Therefore, advancing molecular-design theory for CO₂-philic surfactants has required new directions and paradigms in the field of surfactant research. In the current search for CO₂-soluble compounds, highly branched hydrocarbons⁴⁻⁶, especially with methyl-branches, ester and ether groups have been reported to increase solubility in scCO₂.

Many earlier studies reported that several fluorinated surfactants, including perfluoropolyethers (PFPEs) and the double fluorinated tail surfactants, dissolve in CO₂ and exhibit high activity at the W/CO₂ interface, suggesting the feasibility of forming W/CO₂ μ Es.⁷⁻¹¹ The water-solubilizing power in CO₂ has often been discussed in terms of the water-to-surfactant molar ratio W_0 ($=[\text{water}]/[\text{surfactant}]$). Hereafter, the maximal W_0 achievable in a single-phase W/CO₂ μ E, namely W_0^{max} , is used to evaluate the solubilizing power. In the cases of PFPE and the double perfluorobutyl tail surfactants 4FG(EO)₂, the reported W_0^{max} values reached ~20 and ~80, respectively.⁷⁻¹¹

Along with the exploration and development of CO₂-philic surfactants, applied research into using W/CO₂ microemulsions for industrial chemical processes such as nanoparticle (NP) synthesis¹², enzymatic reaction¹³, dry cleaning¹⁴, and extraction¹⁵ has also been carried out. However, in these applied investigations, the use of surfactants often has disadvantages. For example, though nanoparticle synthesis¹² using W/CO₂ microemulsion with CO₂-philic fluorinated surfactants has been tried for ZnS, CdS, TiO₂, and SiO₂, unfortunately, the surfactant strongly binds to the NPs with attractive interactions between the headgroups and charged NP surfaces (mainly electrostatic in nature). Therefore, the NP products collected after releasing CO₂ usually contain surfactant residue, needing further steps to remove. As these additional steps require the use of a conventional solvent, the total processes cannot be considered net VOC-free. For extraction and dry cleaning, when using μ Es, washings and extracts are also suspected to contain surfactant residue in the same manner as NP synthesis. In the case of enzymatic reactions in W/CO₂ μ Es, it is well known that enzymes can be deactivated by ionic surfactants¹⁶. These demerits happen not only in surfactant-stabilized W/CO₂ μ Es but also in surfactant-stabilized W/O μ Es, as they are caused by the relatively strong interactions between surfactant headgroups and other materials. Keeping these limitations in mind, a promising CO₂-philic surfactant for practical applications should be designed to have nonionic and small hydrophilic groups that are CO₂-philic whilst being less polar and therefore less likely to interact unfavorably with other materials. On the other hand, there are some examples of less polar compounds for solubilizing ionic materials in dense CO₂ phase^{17,18}. For example, DeSimone et al.¹⁷ reported that dendrimers with a fluorinated shell were soluble in liquid CO₂, and could

extract an ionic dye methyl orange in the dendrimer core from water phase. Liu et al.¹⁸ found that the fluorinated compound N-Ethylperfluorooctylsulfonamide yielded ionic liquid (IL)-in-CO₂ μ Es with three ILs of 1,1,3,3-tetramethylguanidinium acetate, lactate and trifluoroacetate, and that these micelles could solubilize ionic compounds like methyl orange, CoCl₂ and HAuCl₄. These studies show that additives with non-traditional surfactant structures can potentially act as polar solubilizers and stabilizers for W/CO₂ μ Es.

Recently, a series comprising the hybrid surfactant, sodium 1-oxo-1-[4-(perfluoroalkyl)phenyl]alkane-2-sulfonates, FC m -HC n (FC length $m = 4, 6$, HC length $n = 2, 4, 5, 6$ and 8) were used to clarify the effects of FC and HC chain length on the phase stability and nanostructures of the reversed micelles formed.¹⁹ The optimal HC-tail and FC-tail length in this hybrid surfactant was found to be $n = 4$ and $m = 6$ respectively (i.e. FC6-HC4). This surfactant was able to yield microemulsions with a maximum solubilizing power, $W_0^{\max}$ of 80; a value equal to the highest performance yet reported in W/CO₂ systems³⁻¹⁵. The identification of an optimal HC-length is very interesting, since straight-chain HCs were commonly considered not to be CO₂-philic³⁻⁶ and their inclusion in FC-surfactant molecules was intentionally limited in order to retain CO₂-philicity. To evaluate the effectiveness per F-atom in the solubilization, the solubilizing power was divided by number of F-atoms in the molecule, and calculated as 6.2. This is 1.5 times larger than the most effective FC-surfactant in earlier papers¹¹. The highest effectiveness per F-atom generated by hybrid structures is also an interesting concept for developing design theory of new CO₂-philic surfactants. High pressure-small angle neutron scattering (HP-SANS) measurements¹⁹ characterized the D₂O cores of the FC6-HC n reversed micelles at $W_0 = 20$, and demonstrated shape transitions in core morphology upon increasing HC-tail length (ellipsoid for $n = 4 \rightarrow$ cylinder for $n = 5$ and $6 \rightarrow$ sphere for $n = 8$). The aspect ratio was seen to reach a maximum of 6.3 at a HC-tail length $n = 6$. Earlier papers²⁰ demonstrated the formation of reversed cylindrical micelles of hybrid surfactants; however, the role of the HC-tails in micelle elongation was unclear. Revealing the role of the HC-tail in hybrid surfactants will lead to finding optimized, super-efficient, low fluorine content

surfactants available for stabilization of W/CO₂ μ Es and formation of CO₂-philic elongated reversed micelles.

With the aim of clarifying the role of the HC-tail in hybrid surfactants, this study examined the phase and aggregation behavior of FC6-HC n analogues without the ionic headgroup, 1-oxo-1-[4-(perfluorohexyl)phenyl]alkane (Nohead FC6-HC n), in water/supercritical CO₂ mixtures by using visual observation, UV-vis absorption spectrometry (employing aqueous methyl orange (MO) solution as a dispersed water-phase), and HP-SANS measurements. The findings described here were unexpected, and very interesting, being never before reported in this field. Despite the fact that Nohead FC6-HC4 is not formally identified as a classic surfactant (no identifiable head group), W/CO₂ microemulsions were formed even at pressures and temperatures approaching the critical point of CO₂, whereas similar analogues with different HC-tail lengths did not form microemulsions.

This study also clarifies why only specific HC-lengths of the Nohead FC6-HC4 can be used for solubilization of water in scCO₂. The findings and information obtained in this study suggest new directions and strategies for developing CO₂-philic surfactants for stabilizing microemulsions and elongated reversed micelles, both of which are applicable to many practical applications.

2. Experimental Section

2.1. Materials

The family of compounds Nohead FC6-HC n ($n = 2, 4, 6$) and Nohead HC6-HC4 are the intermediates obtained before the sulfonation step used to obtain the hybrid surfactants sodium 1-oxo-1-[4-(perfluoroalkyl)phenyl]alkane-2-sulfonates, FC m -HC n (FC length $m = 6$, HC length $n = 2, 4, 6$) and the non-hybrid hydrocarbon surfactant sodium 1-oxo-1-[4-(hexyl)phenyl]-2-hexanesulfonates, HC6-HC4 as shown in Figure 1. All of these compounds were synthesized and purified as described in the earlier paper¹⁹. Data of elemental analysis, ¹H-NMR, and IR for these compounds are shown in supporting information. For synthesis, butanoyl, hexanoyl, and octanoyl chlorides and iodo-benzene were purchased from Tokyo Chemical Industries, and used without further purification. Reagent grade 1,2-dichloroethane and copper powder were commercially obtained from Wako Pure Chemical Industries and employed as received. Tridecafluorohexyl iodide and sulphur trioxide were purchased from Synquest laboratories and Nacalai tesque, respectively.

Ultrapure water with a resistivity of 18.2 M Ω cm was generated from a Millipore Milli-Q Plus system. CO₂ was of 99.99% purity (Ekika Carbon Dioxide Co., Ltd.). D₂O (99.9 atom % D) was purchased from Aldrich. The structures of the steric models and the length of one surfactant molecule in the absence of other molecules were calculated by MOPAC (Molecular Mechanics program 2) calculations (Chem 3D; CambridgeSoft Corp., Cambridge, MA).

2.2. Phase behavior and UV-visible absorption spectral measurements

A high-pressure vessel with an optical window and a moveable piston inside the vessel was used to observe phase behaviour of the hybrid compound/water/scCO₂ mixtures with varying pressure and temperature. A detailed description of the experimental apparatus and procedures for the measurements can be found elsewhere.^{11,12,19}

In order to examine the formation of aqueous cores in W/CO₂ μ Es, UV-visible absorption spectroscopy measurements were performed on a double-beam spectrophotometer (Hitachi High-Technologies, Co., U-2810) with a quartz window pressure cell (volume: 1.5 cm³) that was connected to the experimental apparatus. Methyl orange (MO) was used as a trace marker dye. The cell was made of stainless steel (SUS316) and had three quartz windows with a thickness of 8 mm. Each window had an inner diameter of 10 mm and was positioned so as to provide a perpendicular 10-mm optical path. Each window was attached to the stainless steel body of the cell using PTFE kel-F packing. The windows were fastened tightly to the steel body, thereby compressing the packing between the stainless steel parts and the quartz window, providing excellent sealing (tested up to 400 bar). The temperature of the cell was controlled by circulating water with a thermostat bath. Spectroscopic measurements were performed and the resulting absorption spectra of the cell windows were compared with those of a standard quartz cell for an aqueous MO solution at ambient pressure; it was observed that both the spectra were in good agreement with each other.

The measurements of the water/hybrid compound/scCO₂ systems were performed at temperatures of 35 – 75 °C and pressures lower than 400 bar. The densities of CO₂ were calculated using the Span-Wagner equation of state (EOS)²¹. Pre-determined amounts of the hybrid compound and CO₂ (20.0g), where the molar ratio of hybrid compound to CO₂ was fixed at 8×10^{-4} (i.e. 16.7 mM at 350 bar and 45 °C) or 2.4×10^{-3} (i.e. 50 mM at 350 bar and 45 °C) were loaded into a variable-volume high-pressure optical cell. Water or an aqueous MO solution (3 mM) was added into the optical cell through a six-port valve until the clear Winsor-IV W/CO₂ μ E (i.e. single-phase W/CO₂ μ E) transformed into a turbid macroemulsion or a precipitated hydrated compound. The hybrid compound molar concentration varied between the range 10-20 mM in case of the molar ratio of hybrid compound to CO₂ = 8×10^{-4} , as the inner volume of the cell was varied by changing experimental pressure and temperature.

During spectroscopic measurements, the scCO₂ mixtures were stirred and circulated between the optical vessel and the quartz window cell until a constant absorbance was attained. The circulation was

then discontinued; the valves between the vessel and the quartz window cell were closed, and the measurement was performed. The physical properties of the continuous phase of scCO₂ were assumed to be equivalent to those of pure CO₂.

2.3 High-Pressure Small-Angle Neutron Scattering (HP-SANS) measurements and data analysis

Due to the range of neutron wavelengths available, time-of-flight SANS is suitable for studying the shapes and sizes of colloidal systems. High-pressure SANS (HP-SANS) is a particularly important technique for determining aggregate nanostructure in supercritical CO₂. The HP-SANS measurements of the D₂O/hybrid compound/scCO₂ systems were performed at 45 °C at various pressures. The LOQ time-of-flight instrument, and the SANS2D instrument, at the Rutherford Appleton Laboratory at ISIS UK, were used in conjunction with a stirred high-pressure cell (Thar). The path length in the cell and neutron beam diameter were both 10 mm. The measurements gave absolute scattering cross sections $I(Q)$ (cm⁻¹) as a function of momentum transfer Q (Å⁻¹), which is defined as $Q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The accessible Q ranges were 0.007-0.22 Å⁻¹ for LOQ and 0.002-1 Å⁻¹ for SANS2D arising from an incident neutron wavelength, λ , of 2.2-10 Å. The data were normalized for transmission, empty cell, solvent background, and pressure induced changes in cell volume as before.^{19,20}

Pre-determined amounts of D₂O and hybrid compound, where the molar concentration of hybrid compound in CO₂ was fixed at 50 or 80 mM at the measurement conditions, were loaded into the Thar cell. Then, CO₂ (11.3g), was introduced into the cell by using a high pressure pump, and the compound/D₂O/CO₂ mixture was pressurized up to the experimental pressures at 45 °C by decreasing the inner volume of the Thar cell. With vigorous stirring, visual observation was carried out to identify the mixture as being a transparent single-phase W/CO₂ μ E or a turbid phase. Finally, the HP-SANS experiments were performed for not only the single-phase W/CO₂ μ E, but also the turbid phase formed below the cloud point phase transition pressure P_{trans} . Because these are dilute dispersions (volume

fractions typically 0.05 or less), the physical properties of the continuous phase of scCO₂ were assumed to be equivalent to those of pure CO₂.

Neutrons are scattered by short-range interactions with sample nuclei, with the “scattering power” of different components being defined by a scattering-length density (SLD), ρ (cm⁻²). For CO₂, $\rho_{\text{CO}_2} \sim 2.50 \times \text{mass density} \times 10^{10} \text{ cm}^{-2}$ ²²; at the experimental temperature of 45 °C, the CO₂ densities are 0.917 g cm⁻³ at 350 bar, 0.813 g cm⁻³ at 200 bar, and 0.561 g cm⁻³ at 105 bar, so that ρ_{CO_2} are $2.29 \times 10^{10} \text{ cm}^{-2}$, $2.03 \times 10^{10} \text{ cm}^{-2}$, and $1.40 \times 10^{10} \text{ cm}^{-2}$, respectively. The scattering length densities of hydrophilic and hydrophobic (or CO₂-philic) groups of Nohead FC6-HC4 and D₂O ($\rho_{\text{D}_2\text{O}}$) were obtained using;

$$\rho = \sum_i b_i / v_m \quad (1)$$

Where b_i is a nuclear scattering length as given in the literature²³ and v_m is the molecular volume, which can be obtained from the mass density. The scattering length density of D₂O at 45 °C was calculated to be $\sim 6.32 \times 10^{10} \text{ cm}^{-2}$. As the Nohead compounds except Nohead FC6-HC4 did not show any SANS under these conditions, the scattering length densities have been omitted. As it is assumed the aqueous cores in Nohead FC6-HC4 aggregates to contain not only D₂O molecules but also the hexanoyl groups from results and discussion in Sec 3.3, the scattering length density of the aqueous core ρ_{core} was calculated by using the following equation;

$$\rho_{\text{core}} = (v_{\text{imm}} \times \rho_{\text{imm}} + v_{\text{D}_2\text{O}} \times \rho_{\text{D}_2\text{O}} \times W_0) / (v_{\text{imm}} + v_{\text{D}_2\text{O}} \times W_0) \quad (2)$$

where $v_{\text{D}_2\text{O}}$ and v_{imm} are volumes of a D₂O molecule and the hexanoyl group ($v_{\text{imm}} = 203 \text{ \AA}^3$), respectively, and ρ_{imm} is scattering length density of the hexanoyl group ($\rho_{\text{imm}} = 2.24 \times 10^9 \text{ cm}^{-2}$). The values of v_{imm} and ρ_{imm} were assumed from the mass density of 2-hexanone (0.81 g cm⁻³ at 25 °C)²⁴ and equation (1). In the case of calculation of ρ_{core} at $W_0 = 10$, the solubilizing power of Nohead FC6-HC4 ($W_0^{\text{max}} = 9$ evaluated in Sec 3.1) was employed for the calculation instead of the W_0 value. The ρ_{core} values were decided as $3.27 \times 10^{10} \text{ cm}^{-2}$ at $W_0 = 6.7$ and $3.71 \times 10^{10} \text{ cm}^{-2}$ at $W_0 = 10$.

The shell of Nohead FC6-HC4 aggregate was estimated to be composed of the perfluorohexyl-phenylene groups, and the scattering length density, ρ_{shell} , was calculated as $2.69 \times 10^{10} \text{ cm}^{-2}$ from equation

(1) and the average value of mass densities of benzene (0.88 g cm^{-3} at 25°C) and perfluorohexane (1.67 g cm^{-3} at 25°C). As ρ_{shell} was close to ρ_{CO_2} ($2.29\text{-}2.03 \times 10^{10} \text{ cm}^{-2}$) at $P \geq 200 \text{ bar}$ and the shells are solvated with CO_2 to get both scattering length densities closer, neutron scattering from the shells was identified to be negligible. Then SANS from the $\text{D}_2\text{O}/\text{CO}_2$ microemulsions with Nohead FC6-HC4 at 45°C and $200\text{-}350 \text{ bar}$ was assumed to only be from the so-called aqueous core contrast.

For model fitting data analysis, the W/CO_2 μE droplets were treated as disk-like and ellipsoidal particles with a Schultz distribution in core radius and thickness.²⁵ The polydispersities in disk radius and thickness were fixed at 0.3 as found in spherical $\text{D}_2\text{O}/\text{CO}_2$ microemulsions with the double FC-tail surfactants (polydispersity = 0.17-0.40).^{26,27} Full accounts of the scattering laws are given elsewhere^{17,18,26}.

Data have been fit to models as described above using the SasView small-angle scattering analysis software package (<http://www.sasview.org/>).²⁸ The fitted parameters are the core radii perpendicular to the rotation axis ($R_{\text{f-ell,a}}$) and along the rotation axis ($R_{\text{f-ell,b}}$) for ellipsoidal particles, or the core radius $R_{\text{f-disk}}$ and the thickness $L_{\text{f-disk}}$ for disk-like particles; these values were initially obtained by preliminary Guinier analyses²⁹ ($L_{\text{g-disk}}$, $R_{\text{g-disk}}$, and $R_{\text{g-sph}}$).

2.4. Surface pressure measurements

Surface pressure-area isotherms were measured on a KSV minitrough (KSV 2000, KSV Instruments Ltd.) equipped with a platinum Wilhelmy plate, at 25°C . In each experiment, $10 \mu\text{L}$ of a chloroform solution of surfactant was spread on the water surface. The concentrations in each chloroform solution were 2.36 mM for Nohead FC6-HC2, 4.23 mM for FC6-HC4, 2.87 mM for Nohead FC6-HC6, and 2.63 mM for Nohead HC6-HC4. 15 min were allowed for solvent evaporation before compression. The barrier was moved at a speed of 10 mm min^{-1} .

3. Results and Discussion

3.1 Phase behavior of W/CO₂ microemulsion with Nohead FC6-HC4

To examine the solubility and microemulsion stabilization of Nohead FC6-HC4 in scCO₂, the pressures at which transparent single phases would cloud, P_{trans} , were measured for water/Nohead FC6-HC4/CO₂ mixtures at various temperatures (35 – 75 °C) and W_0 values. Figure 2 shows changes in P_{trans} as a function of temperature for Nohead FC6-HC4 at $W_0 = 9$ -15. The P_{trans} data for the hybrid surfactant FC6-HC4,¹⁹ the double fluorinated tail surfactant 4FG(EO)₂,¹¹ and the perfluoropolyether surfactant PFPECOONH₄³⁰ are also shown as a control. In the case of Nohead FC6-HC4 with $W_0 < 9$, transparent single phases always appeared even at the lowest pressures in the experimental pressure range (e.g. 83 bar at 35 °C). This suggests that for Nohead FC6-HC4 at [hybrid compound]/[CO₂] = 8×10^{-4} at $W_0 < 9$ the water can remain solubilized at any pressure and temperature (studied here). On the other hand, for W_0 values ≥ 9 , phase transitions (P_{trans}) from a transparent to a cloudy phase (photos (a)→(b) in Figure 2) occurred when decreasing the pressure at temperatures lower than 55 °C. The cloudy phase was not observed at temperatures higher than 65 °C.

These P_{trans} values are significantly lower than those of the hybrid surfactant FC6-HC4 with $W_0 = 0$ and 10, and the pressure differences were >100 bar at $W_0 = \sim 10$, demonstrating that the CO₂-phobic headgroup (SO₃Na) of FC6-HC4 generates the higher P_{trans} , i.e. the lower solubility in CO₂. Interestingly, the P_{trans} values for the Nohead systems were essentially independent of W_0 value, though those of FC6-HC4 strongly depended on W_0 . The W_0 independence on P_{trans} was probably due to a weak affinity of the Nohead FC6-HC4 with water, resulting in a low solubilizing capacity (i.e. $W_0^{\text{max}} = 9$ as discussed later), leading to formation of a Winsor-II W/CO₂ μE phase. Even when compared to the highly CO₂-soluble surfactants, PFPECOONH₄ and 4FG(EO)₂ reported in earlier papers^{11,30}, the P_{trans} of Nohead FC6-HC4 was lower by about 10-30 bar. If W/CO₂ microemulsions could be formed using Nohead FC6-HC4, it could be identified as the most effective stabilizer for microemulsion formation in scCO₂, being active at low pressures and temperatures, and even near the critical point (e.g. ~ 100 bar at 35 °C).

To confirm microemulsion formation 3 mM of aqueous methyl orange (MO) solution was loaded as a dispersed phase into the transparent single-phase CO₂ solutions with Nohead FC6-HC4, and the UV-vis adsorption spectra were measured at various W_0 values. Alone, MO does not dissolve in pure CO₂ but it does dissolve in water and is generally incorporated within the water-rich pockets of a single-phase W/CO₂ μ E, dyeing the systems red.^{11,19} The transparent single-phases of Nohead FC6-HC4 and CO₂ were initially colorless, but turned reddish after loading the MO systems. The color became deeper with further addition of the MO solution, reflecting the reversed micelles encapsulating the loaded MO solution.

With the addition of aqueous MO solution to Nohead FC6-HC4/CO₂ mixtures, clear absorption spectra were obtained at different W_0 as shown in Figure 3. A large and broad absorption peak of MO solubilized in the microemulsions was found at 360~500 nm. As the absorbance maximum λ_{max} shift to longer wavelengths when MO molecules are solubilized in more polar environments (e.g. λ_{max} in pure methanol is 421 nm but 464 nm in pure water)^{11,19}, λ_{max} can be employed as a probe of microenvironment polarity. The λ_{max} values for Nohead FC6-HC4 were 420-430 nm and were close to those in methanol as well as those observed for the hybrid surfactant FC6-HC n ¹⁹ and the other fluorinated surfactants n FG(EO)₂¹¹. Therefore, under the low W_0 values of < 9, the polar microenvironment of aqueous domains in Nohead FC6-HC4 aggregates is expected to be methanol-like, and similar to those in the previously studied surfactant reversed micelles. This implies that losing the sulfonate headgroup (FC6-HC4 $\rightarrow$ Nohead FC6-HC4) did not make any notable difference in aqueous core polarity with the low W_0 values.^{8,13,14} The absorbance peak for Nohead FC6-HC4 becomes larger with an increase in water content until W_0 reached 8.8. The addition of water over $W_0=9$ reduced the intensity of the peak suggesting that the water solubilizing power of Nohead FC6-HC4 was $W_0^{\text{max}} = 9$ and a phase transition from Winsor IV to Winsor II W/CO₂ microemulsion^{11,19} happened above this W_0 . The solubilizing power of $W_0^{\text{max}} = 9$ is similar to those for CO₂-philic hydrocarbon surfactants (e.g. TC14³¹) and is not large compared with those of the fluorinated surfactants reported^{11,19,30}. Therefore, Nohead FC6-HC4 is not an efficient solubilizer, but as solubilization occurs even at very low pressures (~100 bar) at which point the earlier surfactants are inactive, it is an effective solubilizer for stabilizing W/CO₂ microemulsions.

3.2 Nanostructure of W/CO₂ microemulsions with Nohead FC6-HC4

To examine the aggregate nanostructures of Nohead FC6-HC n /D₂O/CO₂ mixtures, SANS $I(Q)$ profiles were measured at $W_0 = 0-10$, at a concentration of 50 or 80 mM, and temperature of 45 °C. SANS data along with the fitted $I(Q)$ functions are shown in **Figures 4 and 5**. SANS profiles are useful in determining the shape of nano- and colloidal particles. At a concentration of 50 mM and $W_0 = 6.7$, Nohead FC6-HC6 and FC6-HC2 displayed no clear SANS profiles indicating absence of any aggregation (Fig. 4). On the other hand, Nohead FC6-HC4 exhibited transparent single-phases and gave measurable SANS intensities. SANS with HC numbers $n = 4$ but not $n = 2$ and 6 was also observed at higher W_0 values as shown in Fig. SI-1 and SI-2. This indicates that only the HC chain $n = 4$ stabilized microemulsions, whereas the longer or shorter HC length ($n = 2$ or 6) do not. The reason why only Nohead FC6-HC4 can form microemulsions is discussed later. Figure 5 shows SANS profiles for 80 mM Nohead FC6-HC4/D₂O/CO₂ mixtures at various pressures and W_0 values. At $W_0 = 0$ and 350 bar, since the scattering length density of the compound is almost same as for CO₂, no significant scattering was observed. However, decreasing the pressure to 105 bar produces a difference in scattering length density and a SANS profile could be obtained, implying the formation of Nohead FC6-HC4 nanoaggregates without aqueous cores. At 350 bar, loading D₂O into the systems which previously displayed no scattering produced a SANS profile: this clearly demonstrates D₂O nanodroplets dispersed in the Nohead FC6-HC4/CO₂ mixture.

In the low Q region (typically, in the case of droplet microemulsions, $Q < 0.01 \text{ \AA}^{-1}$), the scattering may scale as $I(Q) \sim Q^{-D}$, where D is a characteristic dimensionality of the dispersed colloids and the gradient of a log-log plot will be $-D$. In the case of non-interacting spheres, D should be zero in this low Q region, for cylinders, $D = 1$ and for disks, $D = 2$.^{19,26,29} The majority of Nohead FC6-HC4 SANS profiles had $D = \sim 2$, suggesting the presence of disk-like or oblate ellipsoidal D₂O nanodomains. One method to approximate the radii and disk thickness for globular and disk-like microemulsions respectively is via the use of Guinier plots^{19,26,29} ($\ln [I(Q)]$ vs Q^2 for sphere and disk radii and $\ln [I(Q) Q^2]$ vs Q^2 for disk thickness) as shown in supporting information (**Figure SI-3**). In all the plots of $\ln [I(Q)]$ vs Q^2 , linearity

was obtained over the intermediate Q range, and the gradients allowed estimation of radii of gyration, R_g (the slope = $-R_g^2/3$, where $Q R_g < 1$). This R_g may also be related to a principal sphere radius R_{g-sph} as $R_g = (3/5)^{0.5} R_{g-sph}$ and disk radius R_{g-disk} as $R_g = R_{g-disk} / (4)^{0.5}$.^{19,26,29} In other cases the $\ln [I(Q) Q^2]$ and Q^2 plots also exhibited linearity, and gradients were used to estimate disk thickness, L_{g-disk} (the slope = $L_{g-disk}^2 / 2$). The values R_{g-sph} , R_{g-disk} and L_{g-disk} were calculated, and listed in Table 1 along with R_g values.

The values of R_{g-sph} , R_{g-disk} , and L_{g-disk} were employed as the starting points for full model fit analyses using the polydisperse Schultz ellipsoid and cylinder models. The parameters obtained from fitting are the average values of radii for the ellipsoidal D₂O cores ($R_{f-ell,a}$ and $R_{f-ell,b}$) when using the ellipsoidal model, or the radius and length when using the cylinder model. When cylinder lengths are very small compared with the cylinder radius, the model can be considered to describe discs of radius R_{f-disk} and thickness L_{f-disk}). The polydispersity width was set at 0.3, which is assumed to be typical value for W/CO₂ microemulsion systems (e.g. 0.17-0.40 for double FC-tail sulfonate surfactants)²⁶. These fitted parameters and the aspect ratios of the microemulsion D₂O cores are also listed in **Table 1**.

In Figs. 4-5 and SI-2, the majority of the data for Nohead FC6-HC4 were well described by the models outlined above. All data was fitted to the ellipsoidal particle model except the sample at 80 mM, 200 bar and $W_0=10$ which was best described by the cylindrical model. Fits obtained using the ellipsoidal model produced two results with different sets of parameters. In one set, $R_{f-ell,a} < R_{f-ell,b}$ indicating an elongated prolate ellipsoid (cylinder like). However, the other possibility produced values where $R_{f-ell,a} > R_{f-ell,b}$ indicating oblate ellipsoids (disk-like). For the sample at 80 mM, 200 bar and $W_0=10$, which could only be modeled using the cylindrical model, the parameters obtained indicate disk-like D₂O cores with $L_{f-disk} = 5.2 \text{ \AA}$ and $R_{f-disk} = 31.4 \text{ \AA}$. This implies that Nohead FC6-HC4/W/CO₂ microemulsions at the other experimental conditions (where two fits could be obtained) in fact had disk-like ellipsoidal cores rather than elongated ones; the discussion hereafter is made based on the $R_{f-ell,a} > R_{f-ell,b}$ values. The SANS profile at 80 mM, 105 bar and $W_0 = 0$ gave $R_{g-sph} = 23.9 \text{ \AA}$ in the Guinier analysis, giving the aggregate size without the aqueous core.

When comparing fits from the D₂O cores at 50 mM and 200 bar, the aspect ratio decreased from 0.92 to 0.34 when increasing W_0 from 6.7 to 10, representing the ellipsoidal cores being more oblate. The aspect ratio 0.34 further decreased down to 0.08 upon increasing Nohead FC6-HC4 concentration from 50 mM to 80 mM. Focusing on the effect of pressure on core morphology, the disk-like core with the aspect ratio 0.08 was found to become more prolate (with the largest aspect ratio having 0.61) when increasing pressure by 150 bar. From the trends on core morphology mentioned above, negative aggregate curvatures of W/CO₂ microemulsions were considered to approach to zero at higher W_0 values, higher solubilizer concentrations, and at lower pressures. Similar changes of the microemulsion curvature dependent on pressure, W_0 and concentration were also reported in earlier papers^{11,19,20,26,27,30}, and the origin was identified as changes in critical packing parameter (CPP)³² and Hydrophilic/CO₂-philic balance (HCB)^{4,7}. For example, a higher pressure leads to a higher CO₂ density, and promotes CO₂-tail solvation, resulting in a larger CPP and a lower HCB and therefore larger negative curvature.^{11,19,20,26,27,30} It is interesting to note that “headgroup-free” or “less polar” Nohead FC6-HC4 exhibited W/CO₂ microemulsion aggregation behavior similar to the earlier systems with “polar” CO₂-philic surfactants. These results and findings raise an important question ‘Why does this headgroup-free compound exhibit surfactant-like properties and especially stabilize W/CO₂ microemulsions?’, and the answer will be addressed in next section.

3.3 Adsorption of Nohead FC6-HC4 at the air-water interface.

To examine the adsorption of Nohead FC6-HC4 onto a water surface, surface pressure (π)-area per molecule (A_{molec}) isotherms were measured for spread monolayers at the water/air interface at 25 °C, as shown in Figure 6. The isotherms for Nohead FC6-HC2, FC6-HC6, and HC6-HC4 are also displayed as controls in Fig. 6. These isotherms are smooth rising curves with lift off areas of 85 Å² for Nohead FC6-HC6, 70 Å² for Nohead FC6-HC4, and 25 Å² for Nohead FC6-HC2. The adsorbed films of Nohead FC6-HC4, FC6-HC6 and HC6-HC6 were found to be collapsed at 17.8, 12.6 and 7.7 mN m⁻¹ (i.e. collapse pressures π_{max}), respectively. Minimal effective area per molecule, A_{min} , values were estimated by

extrapolating the constant slope regions of the isotherms to zero surface pressure, as shown by the broken lines in Fig. 6. The $A_{\min}$ values and collapse pressures are listed in Table 2. In the case of Nohead FC6-HC2, the area per molecule obtained from the isotherm is expected to be lower than $25 \text{ \AA}^2$. However, the cross sectional area of an all-trans perfluorocarbon chain in a crystal phase is known to be $28 \text{ \AA}^2$.³³ Therefore, the small area of Nohead FC6-HC2 is likely invalid and probably arises due to some small solubility allowing some molecules of the spread monolayer to dissolve in water. Nohead FC6-HC4 gave an $A_{\min}$ smaller than that of the non-fluorinated Nohead HC6-HC4, but larger than the cross sectional area of an all-trans perfluorocarbon chain. As Nohead FC6-HC4 has a lower solubility in water the molecules probably remained at the surface and the area obtained is valid. The $A_{\min}$ of Nohead FC6-HC4 was smaller by 3/5 than Nohead FC6-HC6 and HC6-HC4, and was consistent with the cross sectional area of benzene ($42.3 \text{ \AA}^2$).³⁴ This clearly shows that Nohead FC6-HC4 adsorbs perpendicularly to the water surface and the molecular area originates from the bulkiest benzene ring, whereas the other Nohead compounds do not absorb in this way as indicated by their larger $A_{\min}$ values. With this consideration, the single polar carbonyl group would act as a hydrophilic group even though it is usually not identified as a headgroup in the field of surfactant chemistry, and the less hydrophobic hexanoyl group (when compared with the fluorocarbon + aromatic ring) was probably immersed in the water layer as shown in Figure SI-4 (supporting information). The solubility of alkanones²⁴, corresponding to the hydrophilic parts of the compound, are listed in Table 2. The solubility of 2-hexanone for Nohead FC6-HC4 is ~15 times larger than that of 2-octanone for Nohead FC6-HC6. In addition to that, the carbonyl group is recognized as a π -electron-withdrawing group, polarization $[\text{Ph-C}]^{\delta+}-[\text{O}]^{\delta-}$ is stabilized by a resonance effect with the phenylene group (Ph). Then, hydrophilicity of the hexanoyl group can be considered high compared with 2-hexanone or a hexanoyl group unconnected to a Ph group. These discussions support the idea that the hexanoyl group can be thought of as a hydrophilic group, and tends to immerse in aqueous cores of water nanodroplets. From the view points of the high solubility of butanone in water and the Ph-stabilized polarity of the carbonyl group, the butanoyl group of Nohead FC6-HC2 is also likely to be the more hydrophilic moiety and to aid in the solubilization of water. However, the fact that no W/CO_2

microemulsions were formed with Nohead FC6-HC2 implies that alkyl chains also play an important role in the aggregation. One possible role for alkyl chains could be to generate a driving force for aggregation, resulting from its CO₂-phobicity (CO₂-phobic interaction between alkyl chains), and this is enhanced with increased chain length.³⁵⁻³⁷ Nohead FC6-HC2 may be too CO₂-philic, and lack molecular CO₂-phobicity to aggregate, in other words, a very high aggregation concentration in CO₂ (> the experimental concentration 50 mM).

To investigate adsorbed Nohead FC6-HC4 layers at the water/scCO₂ interface, the aggregation number (N_{agg}) and occupied area per molecule at the Winsor-IV W/CO₂ microemulsion surface ($A_{\text{C/W}}$) with $W_0 = 6.7$ were calculated by following equations¹⁹.

$$N_{\text{agg}} = C_s / C_{\text{agg}} \quad (3)$$

$$C_{\text{agg}} = C_s (\nu_{\text{D2O}} W_0 N_A + \nu_{\text{imm}} N_A) / (\nu_{\text{core}} N_A) = C_s (\nu_{\text{D2O}} W_0 + \nu_{\text{imm}}) / \nu_{\text{core}} \quad (4)$$

$$A_{\text{C/W}} = s_{\text{core}} / N_{\text{agg}} \quad (5)$$

where N_A is Avogadro's number, C_s and C_{agg} are molar concentrations of solubilizer and aggregate respectively, ν_{D2O} , ν_{core} and ν_{imm} are volumes of a D₂O molecule, D₂O core, and the immersed part of the Nohead FC6-HC4 molecule in water (e.g. $\nu_{\text{imm}} = 203 \text{ \AA}^3$ for the C₅H₁₁(C=O)- group estimated from the density of 2-hexanone 0.812 g cm^{-3} at $25 \text{ }^\circ\text{C}$)²⁴, respectively. For the $A_{\text{C/W}}$ calculation, s_{core} is surface area per D₂O core, and calculated from the fitted micellar shape parameters ($R_{\text{f-ell,a}}$ and $R_{\text{f-ell,b}}$) as well as the calculation of ν_{core} for C_{micelle} . The N_{agg} and $A_{\text{C/W}}$ calculated for both cases of the flattened and elongated ellipsoidal D₂O cores were summarized in Table 3.

The $A_{\text{C/W}}$ values for Nohead FC6-HC4 were almost the same as those obtained by surface pressure measurements and are again comparable to the cross sectional area of benzene. In addition to this, if the calculation employs $\nu_{\text{imm}} = 305 \text{ \AA}^3$ for the C₅H₁₁(C=O)-C₆H₄- group estimated from the density of hexanophenone 0.958 g cm^{-3} at $25 \text{ }^\circ\text{C}$ ²⁴, the $A_{\text{C/W}}$ values become larger by $\sim 11 \text{ \AA}^2$ ($55.0 \text{ \AA}^2$) than the case of the hexanoyl group immersed in water, and is inconsistent with the A_{min} value obtained from the surface pressure. This suggests that Nohead FC6-HC4 molecules adsorb at W/CO₂ interfaces vertically with the

hexanoyl group of Nohead FC6-HC4 located in the aqueous core phase enabling the carbonyl group to associate with water, and the phenylene group remains in the external scCO₂ phase as shown in Fig.SI-4. According to critical packing parameter (CPP) theory³², the CPP can be also obtained by

$$CPP = v_{\text{tail}} / (A_{C/W} l_{\text{tail}}) \quad (6)$$

where v_{tail} and l_{tail} are hydrophobic tail volume and length, respectively. If the hydrophobic part is assumed to be a truncated core, the volume should be^{19,26}

$$v_{\text{tail}} = l_{\text{tail}} \{ A_{C/W} + A_{\text{tail}} + (A_{C/W} A_{\text{tail}})^{0.5} \} / 3 \quad (7)$$

where A_{tail} is area per hydrophobic tail terminus, respectively. Then eq. (6) can be simply expressed as

$$CPP = \{ s_{\text{agg}} + s_{\text{core}} + (s_{\text{agg}} s_{\text{core}})^{0.5} \} / (3s_{\text{core}}) \quad (8)$$

where s_{agg} is surface area per aggregate. In this study, the values of s_{agg} were calculated from the shape parameters ($R_{\text{f-ell,a}}$, $R_{\text{f-ell,b}}$) and tail length l_{tail} assumed to be 12.0 Å (the length between the terminal F-atom and the C-atom in the phenylene group connected to the hexanoyl group).¹⁹

The CPP value of Nohead FC6-HC4 was calculated as 1.49 as listed in Table 3. In the case of 50 mM AOT/W/heptane microemulsion²⁶, CPP = 1.48 and $N_{\text{agg}} = 79$ were reported at $W_0 = 10$, 25 °C and atmospheric pressure. On the other hand, double fluorinated tail anionic surfactants $n\text{FG}(\text{EO})_2$ and $n\text{FS}(\text{EO})_2$ showed CPP values larger than 1.76 and $N_{\text{agg}} = 10\text{-}14$ in W/CO₂ μE with $W_0 = 10$ at 45 °C and 350 bar.²⁶ When compared with the CPP and N_{agg} values reported for double tail surfactants, Nohead FC6-HC4 is very interesting in that it has similar CPP value in spite of being a single tail type. This could be as a result of the hexanoyl group acting as a nonionic headgroup where the weak steric and electrostatic repulsions between intermolecular hexanoyl groups results in smaller headgroup areas, as compared with those arising from typical ionic and nonionic headgroups in standard surfactants. Therefore, these weak repulsive interactions produce the very small $A_{W/C}$ as well as the significantly large N_{agg} value of over a hundred.

Earlier papers^{19,38-41} have reported on the unique properties of the hybrid surfactant FC6-HC4 in aqueous solution, octane/water and water/CO₂ mixtures, and again the expected typical property trends associated with changing HC chain length of a surfactant were not observed. For example, the 10 wt%

FC6-HC4/water mixture exhibited anomalous viscoelasticity, whereas the other FC6-HC4 analogues did not.³⁸⁻⁴⁰ At air/water and octane/water interfaces, FC6-HC4 was reported to have the largest area per molecule in FC6-HC n family with $n = 2, 4$, and 6 .⁴¹ In addition, FC6-HC4 showed the highest water solubilizing power in scCO₂ compared with the other FC6-HC n surfactants.¹⁹ Based on the results and discussion for Nohead FC6-HC n in this study, the unusual properties of FC6-HC4 may come from the difference in the hydrophilicity of the alkanoyl groups that then induces a different orientation of the group in the water and nonpolar phases. Namely, the HC-tail with $n \leq 4$ of FC6-HC n allows the alkanoyl group to be in water alongside the sulfonate headgroup, whereas the longer HC-tails are likely to point towards the nonpolar environments (oil, scCO₂, and internal micelle core in water). This has not been discussed in earlier papers^{19,38-41} reporting on the unusual properties of FC6-HC4 and may well be the origin of these interesting characteristics.

4. Conclusions

W/CO₂ microemulsions are promising universal green-solvents for applications such as extraction, dyeing, dry cleaning, metal-plating, and organic or nanomaterial synthesis. However, in any chemical processes using scCO₂, surfactants are likely to remain in extracts, washings, and products due to the strong interactions between headgroups and other materials.¹²⁻¹⁵ As a result, additional processes are needed to remove the remaining surfactants and this typically involves standard solvents. Therefore, if a headgroup-free water-solubilizer, having a high solubility in scCO₂ and a weak interaction with products can be developed, processes utilizing scCO₂ will produce cleaner extracts, washings, and products.

This study successfully found the headgroup-free solubilizer Nohead FC6-HC4 to yield W/CO₂ μ Es with W_0 up to 9, as demonstrated by SANS and the solubilization of aqueous methyl orange solutions. In addition, this study also clarified new findings [1]-[5] as shown below.

[1] Nohead FC6-HC4 can stabilize W/CO₂ μ Es even at considerably low pressures (e.g. $\sim$ 100 bar at $W_0 = 9$, 35 °C and [Nohead FC6-HC4]/[CO₂] = 8×10^{-4}), independent of the water loading W_0 .

[2] Aqueous cores in Nohead FC6-HC4 aggregates can solubilize a water-soluble compound like methyl orange, and the micro-environmental polarity is similar to those seen from W/CO₂ μ Es prepared with ionic surfactants.^{8,13,14}

[3] The aqueous cores were mostly non-spherical (prolate or oblate ellipsoids), and the core morphology strongly depended on W_0 , pressure and the compound concentration. Namely, the aspect ratios deviated further from unity (i.e. spherical) at lower pressures, higher Nohead FC6-HC4 concentrations and at higher W_0 values.

[4] The hexanoyl group of Nohead FC6-HC4 appears to be immersed in the aqueous cores, enabling the carbonyl group to strongly associate with water. Since the other short and long alkanoyl groups (i.e. Nohead FC6-HC2 and FC6-HC6) were unable to do this, the HC length seems to play an important role in solubilizing the aqueous cores.

[5] The CPP of Nohead FC6-HC4 was found to be similar to those of double FC-tail surfactants in W/CO₂ μ Es and the double HC-tail surfactant AOT in a W/heptane μ E at similar W_0 conditions²⁶. The

double-tail surfactant-like CPP of the single-tail Nohead FC6-HC4 was dominated by the small cross-sectional area of the hydrophilic hexanoyl group, lacking any distinct repulsive interactions. This resulted in the large N_{agg} and the small areas occupied by the molecules at W/air and W/scCO₂ interfaces.

Most of the HC-surfactants tested before were insoluble in scCO₂ because of a combination of the poor CO₂-philicity of HC-tails and CO₂-phobicity of conventional headgroups.^{3-11,19} The increase in HC length acts to increase the tail-bulkiness (i.e. CPP)³² and lowers the hydrophilic/lipophilic balance, HLB (not hydrophilic/CO₂-philic balance or HCB)^{4,7} making the surfactant more suitable for reversed micelle formation. However, the larger molecular weight is also detrimental, that is the larger the molecular weight, the lower solubility in scCO₂.⁴² Therefore, balancing these two factors to obtain an optimum CPP/HLB for reversed micelles and to increase CO₂-philicity of surfactant has been an issue in the design of an effective CO₂-philic HC-surfactants, and different studies³⁻⁶ have focused on the optimization of the HC-tail structure. Over the years, highly methylated HC-tails were found to yield a high CPP as well as a high CO₂-philicity, and these groups have been a staple for CO₂ surfactant design.³⁻⁶ On the other hand, different headgroups for CO₂-philic HC-surfactants have not been so well studied and only a few variations of headgroups like sulfate, sulfonate, carboxylate, phosphate and polyoxyethylene are commonly employed.^{3-15,19,20,26,30} These headgroups are usually CO₂-phobic and have a large volume, and this disadvantage often leads to CO₂ inactivity in the designed HC-surfactant. Considering this, the findings in this study that carbonyl can act as a hydrophilic group is a surprising result, because it is not commonly identified as a hydrophilic group in surfactant science. Therefore, these findings can offer a new approach to employ in surfactant design by utilizing small, hydrophilic and less CO₂-phobic carbonyl groups able to generate a large CPP even in a low molecular weight, single HC-tail surfactant.

Additional suggestions for the development of surfactant science arising from this study can be proposed from the unique interfacial properties of hybrid, FC m -HC n , surfactants in water, W/O and W/CO₂.^{19,38-41} It appears certain characteristics may originate from the HC-tail orientation, depending on whether the tails point towards the water or nonpolar solvent. As mentioned above, it appears that the hexanoyl group can be sufficiently hydrophilic, and partition into the water phase along with the

headgroup, whereas a longer alkanoyl cannot, due to its increased hydrophobicity. This can lead to large differences in CPP and HLB (or HCB) even with only a small change of HC-tail length of one or two methylene units. These large differences may also occur for other hybrid surfactants which show unusual trends when varying HC-tail length. If this can be demonstrated, molecular design strategy for developing hybrid surfactant will be greatly advanced.

5. ASSOCIATED CONTENT

Supporting Information. Data of elemental analysis, ¹H-NMR, and IR for Nohead FC6-HC_n and Nohead HC6-HC4. SANS profiles for 50mM Nohead FC6-HC6/D₂O/CO₂ mixtures with different W_0 values at 45 °C and 200 bar. SANS profiles for 50mM Nohead FC6-HC_n ($n = 2, 4, 6$)/D₂O/CO₂ mixtures with $W_0 = 10$ at 45 °C and 200 bar, and theoretical curves with the ellipsoidal form factor model fitted to the experimental data. Guinier plots ($\ln [I(Q)]$ vs Q^2 and $\ln [I(Q) Q^2]$ vs Q^2) for Nohead FC6-HC4/D₂O/CO₂ mixtures at $W_0 = 0, 6.7$ and 10, pressures of 105, 200 and 350 bar, and 45 °C. Schematic representation of Nohead FC6-HC4 molecule adsorbed at a W/CO₂ microemulsion droplet surface. This material is available free of charge via the Internet at “<http://pubs.acs.org>.”

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Notes. The authors declare no competing financial interest.

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Figure captions

Figure 1. Structure of hybrid surfactants FC6-HC n , headgroup-free compounds Nohead FC6-HC n and HC6-HC4.

Figure 2. Changes in P_{trans} for W/CO₂ mixtures with CO₂-philic surfactants and Nohead FC6-HC4 at $W_0 = 0-15$ as a function of temperature. The molar ratio of the surfactant (or Nohead FC6-HC4) to CO₂ was fixed at 8×10^{-4} . Transparent (upper right) and turbid (bottom right) phases were found at higher and lower pressures than P_{trans} curves, respectively.

Figure 3. Absorbance spectra of MO in 80 mM Nohead FC6-HC4/W/CO₂ mixtures with different W_0 values at 350 bar. The MO concentration in water was 3 mM. Molar ratio of Nohead FC6-HC4-to-CO₂ was fixed at 2.4×10^{-3} .

Figure 4. SANS profiles for 50 mM Nohead FC6-HC n ($n = 2, 4, 6$)/D₂O/CO₂ mixtures with $W_0 = 6.7$ at 45 °C and 200 bar. Fitted curves were based on a model incorporating a Schultz distribution of polydisperse ellipsoidal particles.

Figure 5. SANS profiles for 80 mM Nohead FC6-HC4/D₂O/CO₂ mixtures with $W_0 = 0$ and 10 at 45 °C and pressures of 105, 200 and 350 bar. Fitted curves were based on a model incorporating a Schultz distribution of polydisperse ellipsoid or disk particles.

Figure 6. Surface pressure (π) vs area per molecule (A) isotherms for adsorbed films of Nohead FC6-HC n ($n = 2, 4, 6$) or HC6-HC4 at the air/water interface of 25 °C.

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