

# Nanostructures in Water-in-CO<sub>2</sub> Microemulsions Stabilized by Double-Chain Fluorocarbon Solubilizers

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**S** Supporting Information



**ABSTRACT:** High-pressure small-angle neutron scattering (HP-SANS) studies were conducted to investigate nanostructures and interfacial properties of water-in-supercritical  $CO_2$  (W/CO<sub>2</sub>) microemulsions with double-fluorocarbon-tail anionic surfactants, having different fluorocarbon chain lengths and linking groups (glutarate or succinate). At constant pressure and temperature, the microemulsion aqueous cores were found to swell with an increase in water-to-surfactant ratio,  $W_0$ , until their solubilizing capacities were reached. Surfactants with fluorocarbon chain lengths of n = 4, 6, and 8 formed spherical reversed micelles in supercritical  $CO_2$  even at  $W_0$  over the solubilizing powers as determined by phase behavior studies, suggesting formation of Winsor-IV W/CO<sub>2</sub> microemulsions and then Winsor-II W/CO<sub>2</sub> microemulsions. On the other hand, a short C2 chain fluorocarbon surfactant analogue displayed a transition from Winsor-IV microemulsions to lamellar liquid crystals at  $W_0 =$ 25. Critical packing parameters and aggregation numbers were calculated by using area per headgroup, shell thickness, the core/ shell radii determined from SANS data analysis: these parameters were used to help understand differences in aggregation behavior and solubilizing power in  $CO_2$ . Increasing the microemulsion water loading led the critical packing parameter to decrease to ~1.3 and the aggregation number to increase to >90. Although these parameters were comparable between glutarate and succinate surfactants with the same fluorocarbon chain, decreasing the fluorocarbon chain length *n* reduced the critical packing parameter. At the same time, reducing chain length to 2 reduced negative interfacial curvature, favoring planar structures, as demonstrated by generation of lamellar liquid crystal phases.

# 1. INTRODUCTION

Supercritical  $CO_2$  (sc $CO_2$ ) is seen as a promising green solvent in various fields, including organic synthesis, dry cleaning, polymerization, extraction, and nanomaterial processing.<sup>1</sup> The reasons why sc $CO_2$  has attracted much attention for those applications are based on  $CO_2$  and supercritical fluid properties, which are low cost, nonflammability, environmentally benign, natural abundance, high mass transfer, and pressure/temperature-tunable solvency (or  $CO_2$  density). Unfortunately, supercritical  $CO_2$  can dissolve only nonpolar and small molecular mass materials, and common polar or high molecular mass materials always separate from neat  $scCO_2^2$ . Improving

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the poor solubility of polar materials is important for developing applications of scCO<sub>2</sub>. One of the most promising approaches for enhancing solubility in scCO<sub>2</sub> is to form reversed micelles with high-polarity aqueous cores in the continuous scCO<sub>2</sub> phase, that is, water-in-scCO<sub>2</sub> micro-emulsions (W/CO<sub>2</sub>  $\mu$ Es).<sup>2</sup> Since such organized fluids have the attractive characteristics of scCO<sub>2</sub>, as well as the solvation properties of water, they have potential as volatile organic compound (VOC)-free and energy-efficient solvents for nanomaterial synthesis, enzymatic reactions, dry-cleaning, dyeing, preparation of inorganic/organic hybrid materials, and so on.<sup>2</sup>

To be a viable green technology, the amount of surfactant used should be as small as possible, and this needs to be balanced against the need for large interfacial areas in W/CO<sub>2</sub>  $\mu$ Es and appropriate levels of dispersed water for enhanced process efficiencies. One approach to meet these requirements is to explore or develop a highly efficient solubilizers for W/CO<sub>2</sub>  $\mu$ Es. Since 1990, much effort has been directed toward the development of surfactants for W/CO<sub>2</sub>  $\mu$ Es.<sup>3–30</sup> Three main kinds of surfactant have been examined so far, being hydrocarbon, silicone, and fluorocarbon (FC) surfactants.

Development of  $\rm CO_2$ -philic hydrocarbon surfactants has also been conducted for economic and environmental reasons.<sup>3–9</sup> However, most commercial and known hydrocarbon surfactants are insoluble and inactive in scCO<sub>2</sub> systems.<sup>3</sup> In this regard, it became apparent that conventional surfactant-design theory cannot be applied to W/CO<sub>2</sub> systems directly and that CO<sub>2</sub>-philicity is not directly comparable to oleo-philicity. Therefore, advancing molecular-design theory for CO<sub>2</sub>-philic surfactants has required new directions and paradigms in the field of surfactants.

Only a few hydrocarbon surfactants have so far been reported to stabilize a W/CO<sub>2</sub>  $\mu$ Es. One of these successful surfactants is the nonionic TMN-6,<sup>4-6</sup> which has highly branched alkyl tails and ~8 oxyethylene units: TMN-6 was reported to solubilize water up to a water-to-surfactant molar ratio,  $W_0$  of 30. Custom-made anionic surfactants with highly branched double- or triple-tails (sodium bis(3,5,5-trimethyl-1hexyl) sulfosuccinate<sup>7</sup> or (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate<sup>8</sup>) were also found to be soluble in scCO<sub>2</sub> and yield transparent single phase W/CO<sub>2</sub>  $\mu$ Es (Winsor-IV W/CO<sub>2</sub>  $\mu$ E or IV $\mu$ E) with  $W_0$ less than 15. Note that the commercial analogue of these surfactants, Aerosol-OT (sodium bis-(2-ethyl-1-hexyl) sulfosuccinate, AOT) is inactive and insoluble in scCO<sub>2</sub> and hence is ineffective at stabilizing W/CO<sub>2</sub>  $\mu$ Es. It has been recognized that hydrocarbon surfactants with highly branched tails, especially methyl branches, can be considered sufficiently CO<sub>2</sub>-philic. On the other hand, ester and ether groups have been reported to increase solubility in  $scCO_2$  as well as methyl branches, and highly CO2-philic, and W/CO2-interfacially active copolymers with these groups have been developed and used for emulsification and polymerization.9 Unfortunately, an efficient and cost-effective hydrocarbon stabilizer for W/ CO2  $\mu \text{Es},$  like the AOT used commonly for W/O  $\mu \text{Es},^{10}$  has not yet been found.

In the case of silicone surfactants, polydimethylsiloxanes (PDMS) have attracted attention as potential nonfluorinated  $CO_2$ -philes. While they are known to be miscible with  $CO_2$ , they still require greater pressures to dissolve than is generally needed for fluorocarbon surfactants.<sup>11</sup> The majority of siloxane surfactants tested were only found to be soluble at low

concentration (~ 0.1 wt %), and none were observed to form microemulsions or generate micellar structures in scCO<sub>2</sub>.<sup>12</sup> A copolymer of PDMS<sub>24</sub>-*b*-EO<sub>22</sub> was shown to lower the water– scCO<sub>2</sub> interfacial tension from 20 to 0.2 mN m<sup>-1</sup>; a PDMS surfactant did however form W/CO<sub>2</sub> emulsions,<sup>13</sup> which flocculated and coalesced, limiting the stability of these systems. New trisiloxanes ((CH<sub>3</sub>)<sub>3</sub>SiO)<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>R were reported to be effective emulsifiers, forming both W/CO<sub>2</sub> emulsions at n < 7 and CO<sub>2</sub>/W emulsions at  $n \ge 7$ .<sup>14</sup> This change in curvature is attributed to variations in hydrophilic-CO<sub>2</sub>-philic balance (HCB),<sup>15</sup> which is accompanied by a minimum in interfacial tension between water and CO<sub>2</sub>.

In earlier studies, several fluorinated surfactants were found to dissolve in CO<sub>2</sub> and have a high activity at the W/CO<sub>2</sub> interface, suggesting the feasibility of forming W/CO<sub>2</sub>  $\mu$ Es.<sup>16,17</sup> Among others, surfactants described below are noteworthy for generating W/CO<sub>2</sub>  $\mu$ Es. Early on a perfluoropolyether (PFPE) surfactant<sup>16</sup> was found to stabilize IV $\mu$ E, but with only a low  $W_0$ = 21 (also expressed as a corrected water-to-surfactant molar ratio by subtracting the low background water solubility in CO<sub>2</sub>,  $W_0^c$  = 14). After that, numerous reports dealing with W/ CO<sub>2</sub>  $\mu$ Es focused on PFPEs.

Another successful class of CO<sub>2</sub>-philic surfactants are the hydrocarbon–fluorocarbon (HC-FC) hybrids, for example, sodium 1-pentadecafluoroheptyl-1-octanesulfate (F7H7,  $(C_7H_{15})(C_7F_{15})$ CHOSO<sub>3</sub>Na): these have both a HC and a FC chain in the same molecule. As such F7H7 is able to solubilize up to  $W_0 = 35$  (or  $W_0^c = 32$ ) to form stable Winsor-IV W/CO<sub>2</sub>  $\mu$ Es.<sup>18</sup> Further studies,<sup>19</sup> with hybrid surfactants related to F7H7 but with different FC and HC chain lengths, resulted in the formation of Winsor-IV W/CO<sub>2</sub>  $\mu$ Es for most of the analogues, but unfortunately smaller attainable  $W_0$  values than for F7H7.

Other investigations<sup>20–22</sup> studied a class of fluorinated AOT analogues, for example sodium bis(1*H*,1*H*,5*H*-octafluoropen-tyl)-2-sulfosuccinate (di-HCF<sub>4</sub>), which yield Winsor IVµEs with  $W_0 = 30$  ( $W_0^c \sim 20$ ). In addition, double-FC-tail phosphate surfactants were also found to be efficient µE stabilizers,<sup>23</sup> the most favorable case stabilizing  $W_0$  up to 45.<sup>24</sup>

Lu and Berkowitz<sup>25</sup> and Cummings et al.<sup>26</sup> studied nanostructures of W/CO<sub>2</sub>  $\mu$ Es with FC and HC surfactants by molecular dynamics simulations. Lu and Berkowitz<sup>25</sup> observed a quick self-assembly of the PFPE surfactant spherical reverse micelles over time periods of 5 ns, irrespective of initial conditions. In most cases, the self-assembled PFPE reverse micelles have a spherical shape and properties consistent with SANS results.<sup>17,25</sup> When the FC surfactant is replaced by a HC analogue, the HC assembly contains a region of direct contact between water and carbon dioxide, indicating that HC surfactants are likely to be inappropriate for formation of W/  $CO_2 \mu Es$ . On the other hand, Cummings et al.<sup>26</sup> reported that the HC tails in scCO<sub>2</sub> had an average of  $74 \pm 4\%$  trans bonds (cf. 89% in vacuum), while the FC tails had  $91 \pm 2\%$  (cf. 81% in vacuum). This implies that the HC tails assume more contracted conformations in CO<sub>2</sub>, indicating CO<sub>2</sub>-phobic interactions while the FC tails assume more extended conformations, consistent with favorable CO2-philic interactions.

Recent molecular simulation studies<sup>27,28</sup> have elucidated the reasons why FC surfactants can act as efficient  $W/CO_2$  solubilizers; as compared with HC chains, FC groups have (1) a stronger interactions with  $CO_2$  via quadrupolar and

Table 1. Properties of  $nFS(EO)_2$  (m = 1) and  $nFG(EO)_2$  (m = 2) in Water at 1 bar or  $scCO_2$  at 350 bar<sup>24,28,29</sup>

Surfactant structure	n/m	Krafft point / °C	CMC <sup>a/</sup> (10 <sup>-4</sup> mol L <sup>-1</sup> )	<sup>7</sup> смс <sup>b/</sup> (mN m <sup>-1</sup> )	A <sub>h,st</sub> <sup>c</sup> / Å <sup>2</sup>	Solu power @45 °C	bilizing in scCO2 <sup>d</sup> @75 °C
	2/2	< 0	_	-	-	20	_
0	4/1	< 0	4.3 at 35 °C	17	96	45	50
$F(CF_2)_nCH_2CH_2O-C-(CH_2)_m$	4/2	< 0	2.6 at 35 °C	18	94	45	80
$F(CF_2)_nCH_2CH_2O-C-CHSO_3Na$	8/1	73	2.7 at 75 °C	20	118	42	48
0	8/2	-	5.0 at 75 °C	14	118	62	60

<sup>*a*</sup>Critical micelle concentration in water. <sup>*b*</sup>Surface tension at CMC. <sup>*c*</sup>Area per surfactant headgroup at CMC obtained by using the Gibbs adsorption equation. Values of Krafft point, CMC,  $\gamma_{CMC}$  and  $A_{h,st}$  in aqueous surfactant solutions were obtained from literature.<sup>24,28,29</sup> <sup>*d*</sup>Solubilizing powers expressed as  $W_0$  for Winsor-IV W/CO<sub>2</sub>  $\mu$ Es at 350 bar, which were reported in earlier studies.<sup>24,28,29</sup> The uncertainties are ±3 in  $W_0$ . The solubilizing power of 2FG(EO)<sub>2</sub> at 45 °C was measured by visual observation.

dispersion interactions, and (2) weaker FC-FC chain-chain interactions which are down to a weak repulsion, electrostatic in origin. These properties conspire together to give FC surfactant reversed micelles better solvation by  $CO_2$ , and this causes lower surfactant interfacial packing densities, and weaker attractive intermicellar interactions as compared with hydrocarbon surfactant analogues.

To obtain more economic and environmentally friendly W/ CO<sub>2</sub>  $\mu$ Es, the minimum fluorine content necessary to render a surfactant CO<sub>2</sub>-philic has been identified by using doublepentyl-tail surfactants with different fluorination levels. It was found that at least two fluorinated carbons (CF<sub>3</sub>CF<sub>2</sub>-) are required to stabilize  $\mu$ Es.<sup>29</sup> An increase in fluorine level leads to a lower aqueous surface tension at CMC and a lower stabilization cloud pressure for the W/CO<sub>2</sub>  $\mu$ Es.

Recently, with the aim of optimizing surfactant structure of fluorinated AOT analogues for W/CO2 µE, double-FC-tail anionic surfactants with various FC lengths (n = 4, 6, 8) and a sulfo-glutarate  $(nFG(EO)_2)$  or sulfo-succinate  $(nFS(EO)_2)$ headgroup were synthesized (see Table 1 for their chemical structures).<sup>24,30,31</sup> As the structural difference between *n*FS- $(EO)_2$  and  $nFG(EO)_2$  is only one methylene unit in the group linking the polar ionic headgroup to the pendant FC tails, these surfactants examined the effect of not only FC length but also the additional methylene spacer. From surface tension measurements on aqueous surfactant solutions, no significant differences were found in CMC, surface tension at CMC, and area per headgroup between  $nFG(EO)_2$  and  $nFS(EO)_2$  at the same FC length n.<sup>31</sup> However, visual observation and UV-vis spectral measurements with a hydrophilic dye methyl orange (MO) clarified that the solubilizing powers of the glutarates  $nFG(EO)_2$  were higher than those of the succinate analogues  $nFS(EO)_2$ : the most efficient found in that study was  $4FG(EO)_2$  at 75 °C (max.  $W_0 = 80$  in IV $\mu$ E) even though it has the shortest FC tails.<sup>31</sup> Significantly, this is the highest  $W_0$ reported to date for W/CO<sub>2</sub>  $\mu$ Es. Many earlier papers mentioned that fluorocarbon is one of a few CO2-philic groups, with longer FC chains promoting the higher the solubilizing powers.<sup>32</sup> This is an exciting result leading to new approach to equip a fluorine-light surfactant with high solubilizing power. As well as the high solubilizing power,  $4FG(EO)_2$  was found to give the fastest dissolution into scCO<sub>2</sub>, being capable of solubilizing water in just a few seconds, even at high  $W_0$  and close to its maximum solubilizing capacity.<sup>31</sup> Such a fast solubilization rate is very rare in this field.

It is very interesting to consider how the beneficial properties of  $4FG(EO)_2$  are related to the molecular structure, especially for advancing surfactant design theory. These excellent solubilizing properties could be related to a low HCB,<sup>15</sup> a high critical packing parameter (CPP),<sup>33</sup> and weak interactions between tail-tail and tail-head groups,<sup>34,35</sup> if the spherical reversed micelles supported the formation of IVµEs.

To further characterize the surfactant and explore the origins of the superefficiency, this new study has examined aggregation behavior and nanostructures of the custom-made double-FCtail surfactants,  $nFG(EO)_2$  (FC lengths n = 2, 4, 8) and  $nFS(EO)_2$  (n = 4, 8) in W/CO<sub>2</sub> µEs, by high-pressure smallangle neutron scattering (HP-SANS). The significance of this study to the field of surfactant science is that optimized, superefficient, low fluorine content surfactants are now available for stabilization of  $W/CO_2 \mu Es$ . In addition, although surfactant structure–aggregation property correlations in  $W/CO_2$  systems have been reported, <sup>19–22,29,31</sup> as mentioned above, changes in CPP (or curvature) and aggregation number as a function of microemulsion composition through  $W_0$ , and surfactant chemical structure in terms of FC and methylene spacer lengths have not been examined in such detail as here. The extensive HP-SANS experiments described here as a function of these variables show that very different interfacial curvatures can be obtained, being negative curvature in the droplet microemulsions and "planar" in the lamellar phase systems. As such this paper describes a new approach for controlling interfacial curvature in CO2 self-assembly systems by using a simple composition parameter and also a more sophisticated surfactant molecular structure design. These approaches hold promise for tuning of and control over scCO<sub>2</sub> physicochemcial properties which will be needed for future applications.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** The surfactants used in this study were sodium 1,5bis[(1H,1H,2H,2H-perfluorobuty])oxy]-1,5-dioxopentane-2-sulfonate (2FG(EO)<sub>2</sub>), sodium 1,5-bis[(1H,1H,2H,2H-perfluorohexy])oxy]-1,5dioxopentane-2-sulfonate (4FG(EO)<sub>2</sub>), sodium 1,5-bis-[(1H,1H,2H,2H-perfluorodecy])oxy]-1,5-dioxopentane-2-sulfonate (8FG(EO)<sub>2</sub>), sodium 1,4-bis[(1H,1H,2H,2H-perfluorohexy])oxy]-1,4dioxobutane-2-sulfonate (4FS(EO)<sub>2</sub>), and sodium 1,4-bis-[(1H,1H,2H,2H-perfluorodecy])oxy]-1,4-dioxobutane-2-sulfonate (8FS(EO)<sub>2</sub>). These surfactants except 2FG(EO)<sub>2</sub> were synthesized and evaluated in terms of interfacial properties as described previously.<sup>24,30,31</sup> 2FG(EO)<sub>2</sub> was newly synthesized to examine the FC length effect in this study, as shown in Section 2.2. 1H,1H,2H,2H-Pentafluoro-1-butanol (SantaCruz) and dimethyl glutaconate (AI- drich) were used without further purification. Reagent grade acetone, dichloromethane, hexane, 1,4-dioxane, toluene, *p*-toluene sulfonic acid monohydrate, and sodium hydrogen sulfite were obtained from Wako Pure Chemical Industries and employed as received. Surfactant structures are shown in Table 1 with interfacial properties of aqueous solutions obtained by standard measurements and solubilizing powers in scCO<sub>2</sub>.<sup>24,30,31</sup> As compared to  $nFS(EO)_2$ ,  $nFG(EO)_2$  has an extra  $-CH_2-$  spacer between the FC chain and the sulfonate group. Ultrapure water with a resistivity of 18.2 M $\Omega$  cm, obtained from a Millipore Milli-Q Plus system, was used in the experiments. CO<sub>2</sub> of 99.99% purity (Ekika Carbon Dioxide Co., Ltd.) was used. The structures of these steric models and the length of one surfactant molecule in the absence of other molecules were obtained using MM2 (Molecular Mechanics program 2) calculations (Chem 3D; CambridgeSoft Corp., Cambridge, MA).

2.2. Synthesis. 2.2.1. Synthesis of Bis(1H,1H,2H,2H-pentafluorobutyl) Glutaconate. A mixture of 9.79 g of 1H,1H,2H,2Hpentafluoro-1-butanol (61.0 mmol), 4.80 g of dimethyl glutaconate (30.4 mmol), and 1.45 g of *p*-toluene sulfonic acid monohydrate (7.4 mmol) in 200 cm<sup>3</sup> toluene was refluxed under stirring at 130 °C for 40 h. During the reaction, the methanol liberated was removed azeotropically from the reaction system to shift the equilibrium of the transesterification reaction. After the reaction was complete, the mixture was purified by column chromatography with dichloromethane/n-hexane (3:1) as a developing solvent and silica gel. Finally, transparent sticky liquid, bis(1H,1H,2H,2H-pentafluorobutyl) glutaconate was obtained (yield 3.69 g, 28.8%): <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ , TMS), ( $\delta_H$ /ppm): 2.40–2.51 (a, m, 4H), 3.28 (c, dd, 2H, J = 1.5, 7.2 Hz), 4.41(b, t, 2H, J = 5.6 Hz), 4.44 (b', t, 2H, J = 5.6 Hz), 5.96 (e, dt, 1H, J = 1.6, 15.7 Hz), 7.02 (d, dt, 1H, J = 7.2, 15.7 Hz) for C<sub>2</sub>F<sub>5</sub>CH<sub>2</sub><sup>a</sup>CH<sub>2</sub><sup>b</sup>OCOCH<sub>2</sub><sup>c</sup>CH<sup>d</sup>=CH<sup>e</sup>COOCH<sub>2</sub><sup>b'</sup>CH<sub>2</sub><sup>a</sup>C<sub>2</sub>F<sub>5</sub>; IR (film)  $\nu_{\rm max}/{\rm cm}^{-1}$ : 2979, 1749, 1663, 1464, 1348, 1277, 1195, 1159, 1080, 987, 720, 694.

2.2.2. Synthesis of Sodium Bis(1H,1H,2H,2H-pentafluorobutyl)-2sulfoglutarate (2FG(EO)<sub>2</sub>). Bis(1H,1H,2H,2H-pentafluorobutyl) glutaconate (3.29 g, 7.79 mmol) was dissolved in 1,4-dioxane (140 cm<sup>3</sup>); then, the mixture was heated to 50 °C. A solution of sodium hydrogensulfite (3.60 g, 34.4 mmol) in water (60 cm<sup>3</sup>) was added to this mixture. The reaction mixture was stirred under reflux for 24 h. After, solvents were evaporated, leaving a white solid residue, which was washed with 1,4-dioxane to remove the unreacted diester. The product was Soxhlet extracted with dry acetone to remove excess NaHSO3 and recrystallized from acetone. It afforded a white powder, 2FG(EO)<sub>2</sub> (with no regio-isomers as C<sub>2</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>OCOCH<sub>2</sub>CH- $(-SO_3Na)CH_2COOCH_2CH_2C_2F_5)$ , after vacuum drying (yield 3.11 g, 76.0%); <sup>1</sup>H NMR (500 MHz, CF<sub>3</sub>COOD, TMS), ( $\delta_{\rm H}$ /ppm): 2.73– 2.59 (a, m, 4H), 3.07 (d, dd, 2H, J = 6.0, 17.0 Hz), 3.36 (c, dd, 2H, J = 7.5, 17.0 Hz), 4.34–4.44 (e, m, 1H), 4.69 (b, t, 4H, J = 6.5 Hz) for C<sub>2</sub>F<sub>5</sub>CH<sub>2</sub><sup>a</sup>CH<sub>2</sub><sup>b</sup>OCOCH<sub>2</sub><sup>c</sup>CH<sub>2</sub><sup>d</sup>CH<sup>e</sup>(SO<sub>3</sub>Na)COOCH<sub>2</sub><sup>b</sup>CH<sub>2</sub><sup>a</sup>C<sub>2</sub>F<sub>5</sub>; IR (KBr)  $\nu_{\rm max}/{\rm cm}^{-1}$ : 2977, 1736, 1600, 1408, 1348, 1311, 1197, 1080, 800, 720. Elemental analysis for C13H13O7F10Na: found C, 29.1; H, 2.5; S, 7.0. Calcd C, 29.7; H, 2.5.; S, 6.1.

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. HP-SANS is a particularly important technique for determining surfactant aggregation structures in supercritical CO2. The HP-SANS measurements of the D<sub>2</sub>O/surfactant/scCO<sub>2</sub> systems were performed at 45 °C and 350 bar. The LOQ time-of-flight instrument, at the Rutherford Appleton Laboratory at ISIS UK, was used in conjunction with a stirred highpressure cell (Thar). The path length was 10 mm, and the neutron beam diameter was 10 mm. The measurements gave the absolute scattering cross section I(Q) (cm<sup>-1</sup>) as a function of momentum transfer  $\tilde{Q}$  (Å<sup>-1</sup>), which is defined as  $Q = (4\pi/\lambda)\sin\theta$ . The accessible Q range was 0.007-0.22 Å<sup>-1</sup>, arising from an incident neutron wavelength of 2.2-10 Å. The data were normalized for transmission, empty cell, solvent background, and pressure induced changes in cell volume as before.<sup>20</sup>

Predetermined amounts of D<sub>2</sub>O and surfactant, where the molar ratio of surfactant to CO<sub>2</sub> was fixed at  $8 \times 10^{-4}$  (= 17 mM at the experimental condition), were loaded into the Thar cell. Then, CO<sub>2</sub> (11.3 g) was introduced into the cell by using a high pressure pump, and the surfactant/D<sub>2</sub>O/CO<sub>2</sub> mixture was pressurized up to 350 bar at 45 °C by decreasing inner volume of the Thar cell. With vigorous stirring, visual observation was carried out to identify the mixture to be a transparent single IVµE or the other turbid phases. Finally, HP-SANS measurements were conducted for not only IVµEs but also turbid phases. The densities of CO<sub>2</sub> were calculated using the Span–Wagner equation of state (EOS).<sup>36</sup>

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),  $\rho$  (cm<sup>-2</sup>). For CO<sub>2</sub>,  $\rho_{CO_2} \sim 2.50 \times$  mass density  $\times 10^{10}$  cm<sup>-2</sup>;<sup>37</sup> at the experimental pressure of 350 bar and temperature of 45 °C, the CO<sub>2</sub> density is 0.917 g cm<sup>-3</sup> so that  $\rho_{CO_2} \sim 2.29 \times 10^{10}$  cm<sup>-2</sup>. The scattering length densities of surfactant ( $\rho_{surf}$ ) and D<sub>2</sub>O ( $\rho_{D_2O}$ ) were obtained using

$$\rho = \sum_{i} b_i / V_m \tag{1}$$

 $b_i$  are the nuclear scattering lengths as given in the literature,<sup>38</sup> and  $V_m$  is the molecular volume, which can be obtained from the mass density. Mass densities of surfactants were assumed to be  $1.0-1.7 \text{ g/cm}^3$  as  $1.7 \text{ g/cm}^3$  for a typical fluorinated compound<sup>17</sup> and 1.0 g/cm<sup>3</sup> for a hydrocarbon surfactant. The calculated scattering length densities for  $n\text{FS}(\text{EO})_2$  and  $n\text{FG}(\text{EO})_2$  were  $3.24 \times 10^{10} \text{ cm}^{-2}$  (n = 8),  $2.80 \times 10^{10} \text{ cm}^{-2}$  (n = 4), and  $2.33 \times 10^{10} \text{ cm}^{-2}$  (n = 2), respectively. The scattering length density of D<sub>2</sub>O at 45 °C was calculated to be ~6.32 ×  $10^{10} \text{ cm}^{-2}$ . Samples in pure CO<sub>2</sub> (11.3 g) were run at the constant molar ratio of surfactant to CO<sub>2</sub> of  $8 \times 10^{-4}$ .

For model fitting data analysis the  $\mu$ E droplets were treated as spherical core–shell particles with a Schultz distribution in the core radius.<sup>39</sup> Full accounts of the scattering laws are given elsewhere.<sup>39–43</sup> For polydisperse spherical droplets at volume fraction  $\phi$ , radius  $R_{i}$ , volume  $V_{i}$  and coherent scattering length density  $\rho_{\rm p}$  dispersed in a medium of  $\rho_{\rm m}$ , the normalized SANS intensity I(Q) (cm<sup>-1</sup>) may be written as

$$I(Q) = \Theta(\rho_{\rm p} - \rho_{\rm m})^2 \left[\sum_{i} V_i P(Q, R_i) X(R_i)\right] \times S(Q, R_{\rm hs}, \Theta_{\rm hs})$$
(2)

 $P(Q, R_i)$  is the single-particle form factor. The Schultz distribution  $X(R_i)$  defines the polydispersity using an average radius,  $R^{av}$ , and a root-mean-squared deviation,  $\sigma = R^{av}/(Z + 1)^{0.5}$ , Z being a width parameter.  $S(Q, R_{\rm hs}, \phi_{\rm hs})$  is the structure factor, and a hard-sphere model modified for polydispersity was used:<sup>39,42</sup> the constraints were  $\phi_{\rm hs} = \phi_{\rm d}$  and  $R_{\rm hs} = R_{\rm d}^{av}$  together with the known  $\rho$  values for solvents. (The subscripts "d" and "hs" denote the droplet and hard-sphere, respectively). Using the approach of Ottewill et al., eq 2 can be modified to allow for sharp-step shells built onto a spherical core.<sup>43</sup>

The least-squares FISH program was used to analyze the SANS data.<sup>19-21,40,41</sup> The fitted parameters are the volume fraction  $\phi$ , the core radius  $R_c^{av}$ , polydispersity index  $\sigma/R_c^{av}$ , and shell thickness  $t_s$ ; these were initially set at physically reasonable values, radii obtained by preliminary Guinier analyses  $R_{sph}$ , the typical  $\sigma/R_c^{av}$  value (0.15) reported for many common W/O  $\mu$ E systems,<sup>44</sup> and the estimated length of the chains (12.7 Å for n = 8, 7.5 Å for n = 4, and 4.9 Å for n = 2),<sup>32</sup> respectively. The sequence of fitting parameters was a follows; first, at constant  $\sigma/R_c^{av}$  and  $t_s$  values, the other two parameters were adjusted to the experimental data, and then suitable  $\sigma/R_c^{av}$  and  $t_s$  were obtained by floating for the best fit (to minimize sum of weighted squared residuals).

#### 3. RESULTS AND DISCUSSION

**3.1. Characterization of Structure in W/CO<sub>2</sub> Microemulsions.** Previous studies reported solubilizing powers of each surfactant listed in Table 1,  $^{24,30,31}$  which were measured by visual observation and spectroscopically with the water-soluble dye methyl orange (MO) as an indicator for the  $\mu$ E water pool. At  $W_0$  lower than the solubilizing power, the water/surfactant/ CO<sub>2</sub> mixtures form transparent single-phases W/CO<sub>2</sub>  $\mu$ E (IV $\mu$ Es), but at higher  $W_0$  values turbid W/CO<sub>2</sub> macroemulsions or a precipitate (liquid crystals) are observed.<sup>24,30–32</sup>

To examine the shape and size of aggregates in surfactant/  $D_2O/CO_2$  mixtures at different  $W_{0\nu}$  SANS I(Q) profiles were measured as a function of  $W_0$  at 45 °C and 350 bar, as shown in Figure 1, with the fitted I(Q) functions added. SANS profiles



**Figure 1.** SANS profiles for surfactant/ $D_2O/CO_2$  mixtures with various  $W_0$  at 45 °C and 350 bar (CO<sub>2</sub> density = 0.92 g/cm<sup>3</sup>). Fitted curves were based on a model incorporating a Schultz distribution of polydisperse spheres with a core/shell structure. These SANS profiles are for (a-b) 2FG(EO)<sub>2</sub>, (c) 4FG(EO)<sub>2</sub>, (d) 4FS(EO)<sub>2</sub>, (e) 8FG(EO)<sub>2</sub> and (f) 8FS(EO)<sub>2</sub>. The molar ratio of the surfactant to CO<sub>2</sub> was fixed at  $8 \times 10^{-4}$ .

can be useful in determining the shape of colloid particles. In the low Q region (typically in the case of droplet microemulsions <0.01 Å<sup>-1</sup>), the scattering may scale as  $I(Q) \sim Q^{-D}$ , where *D* is a characteristic "fractal dimension" for the colloids; hence, the gradient of a log–log plot will be -D. In the case of noninteracting spheres, D should be zero in this low Q region, whereas D = 1 for rods and 2 for disks.<sup>30,40-43</sup> For all SANS, profiles except for  $2FG(EO)_2$  at  $W_0 \leq 20$ , the gradients in the low Q region of log–log plots were found to be  $\sim$ 0, suggesting the presence of globular (spherical) nanodomains. On the other hand,  $2FG(EO)_2$  shows negative slopes at Q < 0.01 and  $W_0 \ge 25$  and shoulders and peaks at Q of 0.02–0.2. These were ascribed to Bragg peaks, suggesting formation of liquid crystal (LC) phases. Earlier lamellar LCs of  $nFS(EO)_2$  in water and/or  $scCO_2^{32}$  and peaks from Miller indices (001), (002), and (003) observed in SANS profiles were identified as lamellar LC

phases. Using  $d = 2\pi/Q$  the Q max value (001) allows to estimate a layer spacing (d) comprising one 2FG(EO)<sub>2</sub> bilayer and an aqueous layer. The calculated d was 62.5 Å at  $W_0 = 30$ , increasing to 110.2 Å at  $W_0 = 60$ . The molecular length of 2FG(EO)<sub>2</sub> is approximately 10 Å by MM2 simulations, so thickness of the bilayers could be ~20 Å if CO<sub>2</sub> was not incorporated into the interior, and then thickness of the aqueous layer would be ~43 Å at  $W_0 = 30$  and ~90 Å at  $W_0 =$ 60. It is noticed that doubling the  $W_0$  ratio yielded almost double the aqueous layer thickness, according to a typical swelling behavior<sup>45,46</sup> for lamellar LCs. For lamellar LCs, the relation between d and surfactant volume fraction  $\phi_{\text{surf}} = (\phi_{\text{solv}}, \phi_{\text{solv}}; \text{ solvent volume fraction})$  could be expressed as follows:<sup>46</sup>

$$d = \frac{\delta}{\phi_{\text{surf}}} \tag{3}$$

where  $\delta$  is a bilayer thickness. On the assumption of absence of CO<sub>2</sub> layer in the lamellar LC, *d* values calculated by eq 3 were 50 Å at  $W_0 = 30$  ( $\phi_{\text{surf}} = 0.40$ ) and 80 Å at  $W_0 = 60$  ( $\phi_{\text{surf}} = 0.25$ ). The differences of *d* values from Bragg peak and eq 3 are 10–30 Å, implying the presence of CO<sub>2</sub> incorporated into the lamellar LC.

One method to approximate radii from SANS data for the spherical microemulsions is via Guinier plots<sup>47</sup> (log [I(Q) vs  $Q^{2}$ ]) as shown in Supporting Information (Figures SI1-SI3). In the all plots, linearity was obtained in the appropriate low  $Q^2$ region, and the gradients allowed estimation of a radius of gyration,  $R_g$  (the slope =  $-R_g^2/3$ ). This  $R_g$  may also be related to a principal sphere radius  $R_{\rm sph}$  as  $R_g = (3/5)^{0.5}R_{\rm sph}$ .<sup>47</sup> The values of  $R_{\rm sph}$  were calculated and then employed as the starting points for model fit analyses using the full polydisperse Schultz sphere model. The parameter outputs are the average radii for the D<sub>2</sub>O cores ( $R_c^{av}$ ) and reversed micelles ( $R_s^{av} = t_s + R_c^{av}$ ) and the polydispersity width  $(\sigma/R_c^{av})$ . These fitted parameters with  $R_{\rm sph}$  are shown in Table 2. As  $W_0$  increases, the change in intensity at low Q, and crossover at high Q, are characteristic of an increase in droplet size, which is also clear from the fitted radii. The polydispersities  $\sigma/R_c^{av}$  of IV $\mu$ Es at  $W_0 \leq 40$  ranged from 0.24 to 0.39, which was 1.2-2.0 times larger than typical values for reversed microemulsions.<sup>44</sup> Such a high polydispersity was reported for  $W/CO_2$  IVµEs with the anionic fluorinated double-tail surfactant di-HCF4 and the cationic perfluoropolyether surfactant PFPE-TMMA; the  $\sigma/R_c^{av}$  values being 0.17–0.40 at  $W_0 = 5-30$  for di-HCF4<sup>20</sup> and for 0.22– 0.49 at  $W_0 = 19.4 - 38.1$  for PFPE-TMMA.<sup>48</sup> As the fluorocarbon-hydrocarbon hybrid surfactant F7H7<sup>19</sup> and AOT analogue surfactants (AOK and AO-Vac)<sup>40</sup> were found to give typical  $\sigma/R_c^{av}$  values (<0.2) for W/CO<sub>2</sub> IVµEs, the origin of these high polydispersities is unlikely to be due to the use of compressed  $\dot{CO}_2$  fluid (i.e., high diffusivity<sup>49</sup> increasing frequency of  $\mu$ E-droplet aggregation/separation).<sup>20,48</sup> For the surfactant/W/CO2 mixtures be thermodynamically stable microemulsions (energy-minimum equilibrium state), longer equilibration might be necessary (>1 h) than employed in this study ( $\sim$ 5 min owing to expense of SANS time),<sup>24</sup> even though clear single phases have already appeared. The limited equilibration time in this experiment may be one reason for the higher polydispersity.

3.2. Adsorption and Aggregation Properties of the Double-Chain Fluorocarbon Solubilizers in W/CO<sub>2</sub> Systems. Table 2 also shows that  $R_c^{av}$  and  $R_s^{av}$  increased with

Table 2. Radii <sup><i>a</i></sup> for Water-in-CO <sub>2</sub> M	Microemulsions at 45 °C and 350 bar
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	$W_0$	$R_{\rm c}^{\rm av}/{ m \AA}$	$R_{\rm s}^{\rm av}/{ m \AA}$	$\sigma R_{ m c}^{ m av}$	$R_{\rm sph}/{\rm \AA}$	$R_{\rm pmax}/{\rm \AA}$		$W_0$	$R_{\rm c}^{\rm av}/{ m \AA}$	$R_{\rm s}^{\rm av}/{ m \AA}$	$\sigma R_{ m c}^{ m av}$	$R_{\rm sph}/{ m \AA}$	$R_{\rm pmax}/{\rm \AA}$
$4FG(EO_2)$	10	11.9	19.5	0.32	21.1		$8FG(EO_2)$	22	18.6	31.0	0.39	38.0	31.5
	20	17.9	25.4	0.17	24.4			44	30.8	43.2	0.28	47.7	40.8
	30	24.6	32.1	0.24	34.9			60	41.4	53.8	0.32	63.6	54.6
	40	25.1	32.6	0.27	36.2	29.9		$66^b$	44.2	56.4	0.27	64.0	56.9
	$60^b$	27.2	34.7	0.32	42.8	34.6		80 <sup>b</sup>	40.4	52.8	0.32	63.0	54.7
	80 <sup>b</sup>	31.4	38.9	0.42	60.8	44.0	$8FS(EO_2)$	10	10.9	23.4	0.39	23.0	
$4FS(EO_2)$	0				15.1			22	18.9	31.3	0.38	37.2	31.3
	10	10.2	17.7	0.25	17.1			40	29.2	41.6	0.35	50.3	40.0
	20	18.1	25.6	0.38	33.2	28.5		$60^{b}$	39.0	51.4	0.32	60.9	52.2
	40	28.6	36.1	0.25	39.5	32.5		80 <sup>b</sup>	39.0	51.4	0.32	60.6	52.6
	$60^b$	29.2	36.7	0.32	44.5	37.0	$2FG(EO_2)$	10	10.5	15.5	0.35	18.1	
								20	247	20.6	0.25	25 4	

<sup>*a*</sup>Radii of aqueous core and shell of reversed micelles ( $R_c^{av}$  and  $R_s^{av}$ ) and polydispersity index  $\sigma R_c^{av}$  were obtained by fitting of theoretical curve of polydispersed core/shell-structured sphere to experimental values.  $R_{sph}$  and  $R_{pmax}$  were obtained from the slopes of Guinier plots and first maxima in Porod plots, respectively. <sup>*b*</sup>Turbid phase.

 $W_0$  and  $R_s^{av}$  was slightly different from  $R_{sph}$  in IV $\mu$ E phases, namely, at  $W_0$  below the maximum solubilizing powers listed in Table 1. To confirm the reliability of the radii obtained by fitting and to estimate an effective area per headgroup  $A_{h,p}$  for  $nFG(EO)_2$  in W/CO<sub>2</sub> IV $\mu$ E, Porod plots were generated. Figure 2 shows Porod plots for 4FGEO<sub>2</sub>, and those of the other



**Figure 2.** Porod plots to obtain  $\mu$ E droplet radii  $R_{pmax}$  and areas per headgroup  $A_{h,p}$  in  $D_2O/CO_2$  mixtures with  $4FG(EO)_2$  for several  $W_0$  values at 45 °C and 350 bar. Each arrow shows the first maximum used for calculating  $R_{pmax}$ . Broken lines display  $\{I(Q)Q^4\}_{Q\to\infty}$  for the calculation of  $A_{h,p}$ .

surfactants are displayed in Supporting Information (Figures SI4 and SI5). For W/O  $\mu$ E droplets,  $A_{h,p}$  can be estimated from high Q SANS data, by assuming a sharp interface and applying the Porod equation:<sup>50</sup>

$$\{I(Q) \times Q^4\}_{Q \to \infty} = 2\pi (\Delta \rho)^2 \Sigma \tag{4}$$

where  $\Sigma$  is the total area per unit volume. Another requirement here is that the cmc (concentration of nonadsorbed free surfactant) in CO<sub>2</sub> is negligible compared with the experimental surfactant concentration; that is, all N surfactant molecules are at the CO<sub>2</sub>-D<sub>2</sub>O interface; given those conditions then the area per headgroup,  $A_{\rm h,p} \approx \tilde{\Sigma}/N$ . In the Porod plots of Figure 2 at Q > 0.16 Å<sup>-1</sup>, the data are essentially asymptotic, suggesting these approximations are reasonable. The  $\Delta \rho$  in eq 4 was assumed to be  $\{(\rho_{D,O} + \rho_{surf})/2 - \rho_{CO_2}\}$ because the scattering will arise from not only the D<sub>2</sub>O core but also the surfactant shell ( $\rho_{surf}$  were 2.33–3.24 × 10<sup>10</sup> cm<sup>-2</sup> against  $\rho_{CO_2} \sim 2.29 \times 10^{10}$  cm<sup>-2</sup>) and volume fractions of total surfactant molecular fragments in the W/CO<sub>2</sub>  $\mu$ E interfacial region were calculated as ~0.5 (see Supporting Information, Figure SI6 and Tables SI1–SI2). The broken lines at each  $W_0$ indicate asymptotes  $\{I(Q) \cdot Q^4\}_{O \to \infty}$  giving  $A_h$  values as listed in Table 3. Except at  $W_0 = 60$  gives rise to a macroemulsion,  $A_{h,p}$ values of same surfactant are similar within an experimental uncertainty  $\pm 10$  Å<sup>2</sup>.

For Porod plots of spherical particles, with these characteristic polydispersities, the position of the first maximum and first minimum typically occurs at ~2.7/R and ~4.5/R in Q, respectively.<sup>50</sup> The Porod plots display only the first maxima, but not the first minima clearly. By using the first maxima the  $\mu$ E droplet radii were estimated (Table 2); in the table,  $R_{\rm pmax}$ means the radius given from the first Porod maximum. As seen in the table  $R_{\rm s}^{\rm av}$  and  $R_{\rm pmax}$  were similar at same  $W_0$ , supporting the validity of these analyses.

Table 3. Area  $(A_{h,p} \text{ and } A_{h,l})$ , Volume  $(\nu_{h,l})$ , and Radius  $(r_{h,l})$  of Head Group and Chain Length  $(l_c)$  of  $nFG(EO)_2$  in  $D_2O/CO_2$ IV $\mu$ E at 45 °C and 350 bar

			$A_{ m h}$	$_{\rm p}^{a}/{\rm \AA}^2$						
	W <sub>0</sub>	10	20	30	40	60	$A_{\mathrm{h},1}{}^{b}/\mathrm{\AA}^2$	$\nu_{\mathrm{h},1}{}^{b}/\mathrm{\AA}^{3}$	$r_{\rm h,1}{}^b/{\rm \AA}$	$l_{\rm c}{}^c/{\rm \AA}$
$4FG(EO_2)$		131	140	136	146	151 <sup>f</sup>	128	231	3.8	7.7
$4FS(EO_2)$					129	$123^{f}$	129	213	3.7	7.6
$4FG(EO_2)$			114 <sup>d</sup>		116 <sup>e</sup>	167	125	215	3.7	12.4
$4FS(EO_2)$			$108^d$		111	129 <sup>f</sup>	117	199	3.6	12.5

<sup>*a*</sup>Calculated by Porod plot on the assumption of  $\Delta \rho = (\rho_{D_2O} + \rho_{surfactant})/2 - \rho_{CO_2}$ . The uncertainties are ±10 Å<sup>2</sup>. <sup>*b*</sup>Obtained from a linear function of  $R_c^{av}$  vs  $W_0$  as shown in Figure 2. The uncertainties of  $A_h$  are ±5 Å<sup>2</sup>. <sup>*c*</sup>Yielded by subtracting intercept of a linear function of  $R_c^{av}$  vs  $W_0$  from that of  $R_s^{av}$  vs  $W_0$ , in other words,  $l_c = l_{surf} - l_{h\nu}$  as shown in Figure 2. <sup>*d*</sup>At  $W_0 = 22$ . <sup>*e*</sup>At  $W_0 = 44$ . <sup>*f*</sup>Turbid phase.

Figure 3 shows changes in the radii obtained by the theoretical curve fitting for  $D_2O$  cores and reversed micelle



**Figure 3.** Dependence of droplet radius for the  $8FG(EO)_2 D_2O/CO_2 \mu Es$  as a function of  $W_0$  at 45 °C and 350 bar.

shells as a function of  $W_0$ . When comparing  $nFS(EO)_2$  and  $nFG(EO)_{21}$  no significant difference in D<sub>2</sub>O core radii could be seen at constant  $W_0$  for the IVµEs. Differences in FC length n did not affect the radius in the IV $\mu$ E region, but at  $W_0 \ge 60$  an increase of ~10 Å was seen in the radius between n = 4 and 8 surfactants. This suggests the following: (1) the turbid twophase system at high  $W_0$  was identified as a Winsor-II W/  $CO_2\mu E$ , and (2) excess water molecules (=  $W_0$  – the solubilizing power) formed W/CO<sub>2</sub> "macro"-emulsion droplets and separated from  $scCO_2$  in the absence of stirring while the equilibrium reversed micelles still remain in scCO<sub>2</sub>. This behavior was suggested by changes in UV-vis light absorption of the surfactant/aqueous methyl orange solution/CO<sub>2</sub> mixtures as a function of  $W_0$ , as seen previously.<sup>51</sup> In addition, the linear dependences for radii vs  $W_0$  suggested that  $D_2O$ molecules are incorporated into spherical  $\mu E$  droplets. This linear behavior for  $R_c^{av}$  as a function of  $W_0$  can be used to provide another estimate for the effective headgroup area using<sup>10</sup>

$$\alpha(p)R_{\rm c}^{\rm av} = \frac{3v_{\rm w}}{A_{\rm h}}w_0 + \frac{3v_{\rm h}}{A_{\rm h}} \tag{5}$$

where  $v_{\rm w}$  is the volume of a water molecule, p is the polydispersity index  $(\sigma/R_c^{av})$ , and  $\alpha(p)$  depends on the Schultz distribution  $\alpha(p) = 1 + 2p^2$ . Therefore, assuming the polydispersity to be independent of  $W_0$ , the broken line for  $R_{\rm c}^{\rm av}$  in Figure 3 is expected to have a slope which depends on the interfacial area  $A_{\rm h}$  and an intercept which depends on the average headgroup volume  $v_{\rm h}$  via the headgroup radius  $r_{\rm h}$ . The headgroup areas calculated in this way span 117-129 Å<sup>2</sup> with an uncertainty of  $\pm 10$  Å<sup>2</sup> (Table 3), which is consistent with the previous results obtained by Porod analyses of high Q SANS data in W/CO<sub>2</sub>  $\mu$ Es. Areas per headgroup  $A_{\rm h,p}$  of  $4FG(EO)_2$  obtained by Porod analysis were slightly larger than  $A_{\rm hl}$  obtained from the slope of Figure 3. The assumption in these calculations for  $A_{\rm h,p}$  is that all surfactant molecules are at the  $W/CO_2$  interface, which may not be the case: the computed area will be too large if the solubilities of surfactant in  $\overline{CO}_2$  and water are high. In a previous study,<sup>31</sup> the dissolution pressures of 0.08 mol % surfactant in scCO2 were found to decrease at shorter FC chain lengths for  $nFG(EO)_2$ and  $nFS(EO)_2$ , suggesting the solubility of  $4FG(EO)_2$  in pure  $CO_2$  (i.e., number of free  $4FG(EO)_2$  molecules not at the W/  $CO_2$  interface) is larger than those of longer FC surfactants. In

addition, the Kraft temperature shown in Table 1 shows that  $4FG(EO)_2$  seems to be more soluble in water, meaning the actual area per headgroup of  $4FG(EO)_2$  should be lower than  $A_{h,P}$  and could be similar to the  $A_{h,P}$ .

In a previous work,<sup>21</sup> fluorinated double-tail surfactants (di-HCF4, di-HCF6, and di-CF4) having the same head groups as  $nFG(EO)_2$  and  $nFS(EO)_2$  were investigated in a similar fashion to as described above, giving  $115 \pm 5$  Å<sup>2</sup> for  $A_h$  (15 °C and 500 bar). Interestingly, and importantly, that value is almost similar as found here, not only for the sulfosuccinate  $nFS(EO)_2$  but also the analogous glutarate surfactant  $nFG(EO_2)$ , on account of difference of 30 °C in experimental temperature. For AOT in a range of *n*-alkanes from propane to decane, a mean value of 72 Å<sup>2</sup> for  $A_h$  was reported.<sup>41</sup> The difference in  $A_h$  between W/CO<sub>2</sub> and W/O  $\mu$ Es suggests that packing density of AOT type surfactants at water surface increases in CO<sub>2</sub> as compared to typical hydrocarbon oil. Earlier papers reported  $A_h$  of AOT to be 155 Å<sup>2</sup> at a W/scCO<sub>2</sub><sup>52</sup> but 75 Å<sup>2</sup> at the water/air<sup>53</sup> and 72 Å<sup>2</sup>

Although the values of radii  $R_c^{av}$  in Figure 3 are approximately half those seen for AOT W/alkane  $\mu$ Es,<sup>10</sup> this could be accounted for owing to the difference in interfacial packing and the determined  $A_h$  values. In Figure 3, intercepts of linear functions of  $R_c^{av}$  and  $R_s^{av}$  vs  $W_0$  give mean radii of the headgroup core and the dry reversed micelle, in other words, dimensions of headgroup ( $l_h$ ) and overall surfactant molecule ( $l_{surf}$ ), respectively. The head groups  $-SO_3Na$  of  $nFG(EO)_2$  and  $nFS(EO)_2$  displayed the same radius in dry micelle cores (~5.2 Å). The  $l_{surf}$  values obtained from Figure 3 were almost consistent with those calculated by the MM2 calculation, suggesting  $R_c^{av}$  and  $R_s^{av}$  values in Figure 3 to be reasonable: for example,  $l_{surf}$  of  $8FG(EO)_2$  was 17.6 Å from the intercept (radius of dry reversed micelles) of Figure 3 and 18 Å obtained by MM2 calculation.

By using the intercept for  $l_h$  and eq 5, the effective headgroup volume was calculated as  $v_h = 199-231$  Å<sup>3</sup>, and assuming the headgroup to be spherical, the radius  $(r_h)$  would be 3.6–3.8 Å, as summarized in Table 3. AOT analogues in W/O  $\mu$ Es were found to have  $v_h = 200-236$  Å<sup>3</sup> and  $r_h = 3.8$  Å,<sup>10</sup> and these are consistent with the values calculated here for surfactants with identical polar head groups. This suggests the headgroup volume is not affected by being in supercritical CO<sub>2</sub>, making it unlikely the CO<sub>2</sub> penetrates into the polar region of the micellar structure.

These parameters relating to the size of the chain and headgroup allow estimates of the aggregation number numbers  $N_{\rm agg}$  and critical packing parameters (CPP)<sup>33</sup> by using

$$N_{\rm agg} = \frac{4\pi (R_{\rm c}^{\rm av})^2}{A_{\rm h}}$$
(6)

$$CPP = \frac{\nu_c}{A_h l_c}$$
(7)

where  $v_c$  is the hydrophobic chain volume. If the hydrophobic part is assumed to be a truncated core, the volume should be;

$$v_{\rm c} = \frac{l_{\rm c}(A_{\rm h} + A_{\rm c} + \sqrt{A_{\rm h}A_{\rm c}})}{3}$$
(8)

where  $A_c$  is area per hydrophobic chain terminus, obtained using  $A_c = 4\pi (R_s^{av})^2 / N_{agg}$ . To calculate  $N_{agg}$  and CPP of surfactants used in this study,  $A_h$  values obtained from eq 5 were employed here. The calculated  $N_{agg}$  and CPP are shown as a function of  $W_0$  in Figure 4 with previous data for AOT/W/*n*-heptane  $\mu$ Es.<sup>10</sup> As expected from typical behavior of W/O



**Figure 4.** Change in aggregation number  $(N_{agg})$  and critical packing parameter (CPP) of nFG(EO)<sub>2</sub> and nFS(EO)<sub>2</sub> in D<sub>2</sub>O/CO<sub>2</sub> $\mu$ Es or AOT in D<sub>2</sub>O/*n*-heptane  $\mu$ Es<sup>10</sup> as a function of  $W_0$  at 45 °C and 350 bar.

reversed micelle systems, <sup>54,55</sup>  $N_{agg}$  for these W/CO<sub>2</sub>  $\mu$ Es increased with  $W_0$ . For example,  $N_{agg}$  was close to 10 at  $W_0 =$  10, but it reached up to ~100 and ~200 for 4FG(EO)<sub>2</sub> at  $W_0 =$  80 and 8FG(EO)<sub>2</sub> at  $W_0 =$  66, respectively. When the  $N_{agg}$  data were compared at a constant  $W_0$ , significant differences were not observed between these FC surfactants. On the other hand,  $N_{agg}$  values of the FC surfactants in scCO<sub>2</sub>  $\mu$ Es were found to be quite small, one-fifth to one-sixth of those of AOT/W/*n*-heptane  $\mu$ Es. Even if compared with AOT in the other organic solvents (e.g.,  $N_{agg} = \sim$ 90 at  $W_0 =$  10 and ~290 at  $W_0 =$  20 in isooctane and cyclohexane <sup>54,55</sup>), the difference in  $N_{agg}$  is quite large, resulting from the small  $R_s^{av}$  and large  $A_h$  for nFG(EO)<sub>2</sub> and nFS(EO)<sub>2</sub> in IV $\mu$ Es.

The critical packing parameter (CPP)<sup>33</sup> is an indicator of "bulkiness" of a given hydrophobic group compared to the headgroup, and dictates interfacial curvature of a surfactant assembly. Negative interfacial curvature for a W/O or W/CO<sub>2</sub>  $\mu$ Es is only stabilized for surfactants with CPP > 1, and if CPP ~1 the interfacial curvature is planar: in other words, the reversed curvature  $\mu$ E droplets would tend to more planar macroemulsions. At  $W_0 = 10$  in Figure 4, the CPP values are 1.92, 1.76, and 2.57 for 4FG(EO)<sub>2</sub>, 4FS(EO)<sub>2</sub>, and 8FG(EO)<sub>2</sub>, respectively. These values were found to decrease with increasing  $W_0$  and then finally reached constant values of ~1.3 at  $W_0$ .

**3.3. Effects of Fluorocarbon and Methylene Spacer Lengths on Solubilization.** Earlier SANS data for AOT/W/ *n*-heptane  $\mu$ Es<sup>10</sup> were used to calculate CPPs, represented by closed circles in Figure 4. The AOT-analogue glutarate in W/*n*heptane  $\mu$ Es also had CPP values similar to the regular AOT (e.g., 1.18 at 25 °C and  $W_0 = 40$ ).<sup>56</sup> These are always smaller than those for the FC-surfactants in scCO<sub>2</sub> at any  $W_0$  and demonstrate that even at small CPP of ~1.15 can stabilize Winsor-IV W/O  $\mu$ Es, whereas such a small CPP is not possible in the W/CO<sub>2</sub>  $\mu$ Es. It implies that other parameters, for example, HCB,<sup>15</sup> Winsor R,<sup>34,35</sup> and/or W/CO<sub>2</sub> interfacial tension<sup>5,52</sup> mainly affect the solubilizing power of the double-FC-tail surfactants in  $IV\mu Es$ .

On the other hand, CPPs of the sulfosuccinate  $(8FS(EO)_2 and 4FS(EO)_2)$  and the glutarate  $(8FG(EO)_2 and 4FG(EO)_2)$  were found to be similar at same chain lengths *n* in the W/CO<sub>2</sub>  $\mu$ Es, suggesting that the extra methylene in *n*FG(EO)<sub>2</sub> did not affect CPP: that is, CPP is not the main parameter explaining differences in solubilizing power. Then, the question "Why can the glutarate surfactants solubilize a higher  $W_0$  than the succinate surfactants can?" still remains unsolved.

The subtle structural change in the headgroup region (i.e., succinate  $\rightarrow$  glutarate) has also been investigated before for hydrocarbon AOT-like surfactants.<sup>56</sup> Interestingly, the addition of just one extra  $-CH_2$  – in the headgroup had little noticeable effect on most interfacial properties at both air/water and oil/ water interfaces; for example, in aqueous systems, the differences in CMC, surface tension, and area per headgroup at CMC were 0.8 mM, <0.1 mN/m, and <7  $Å^2$ , respectively.<sup>5</sup> However, a maximum attainable  $W_0$  ratio with the glutarate analogue in W/*n*-heptane  $\mu$ Es was higher by >10 as compared with the normal succinate (10-40 °C).<sup>56</sup> Previously studies have been made of succinate and glutarate fluoro-AOT-type analogues in hydrocarbon W/CO<sub>2</sub>  $\mu$ Es, suggesting that there is a notable enhancement in stability for the glutarate $^{21,22}$  (i.e., comparing bis(1H,1H,5H-octafuoropentyl)-2-sulfosuccinate or di-HCF4, versus bis(1H,1H,5H-octafuoropentyl)-2-glutarate or di-HCF4GLU). However, that work was only limited, comparing the pressure-temperature (P-T) phase stability of the W/CO<sub>2</sub>  $\mu$ Es at one fixed  $W_0$  = 10: at 25 °C the phase transition pressure  $P_{\text{trans}}$  was ~12 bar lower for the glutarate analogue (181 vs 193 bar).<sup>21,22</sup> The higher solubilizing powers of glutarates have been often reported not only in scCO<sub>2</sub> but also in typical organic solvents. Without a hypothesis based on CPP for the enhanced solubilizing power, there are another two possibilities: the extra methylene spacer results in (1) an increase in structural disorder by lowering molecular symmetry leading to a weaker molecular packing, and (2) a decrease in HCB by increasing hydrophobicity of linking group promoting (possible) CO<sub>2</sub>-ester interactions<sup>57</sup> instead of hydration. These possibilities could be investigated by measuring FT-IR spectra for the ester groups in the two water/scCO<sub>2</sub> mixtures with  $nFG(EO)_2$  and  $nFS(EO)_2$ .<sup>58</sup>

The effect of FC length n of the double-FC-tail surfactants on CPP can be seen in Figure 4: longer chains result in larger CPP values (longer surfactants have larger shells in spite of the core radius being similar, independent of FC length). As listed in Table 1, the solubilizing power of  $nFG(EO)_2$  at 45 °C increases with an increase in  $n_i$  and this trend would be accelerated by the higher CPP at larger n values. On the other hand, the solubilizing power of  $4FG(EO)_2$  at 75 °C was the highest. An earlier paper<sup>30,31</sup> discussed the reason why  $4FG(EO)_2$  is the most efficient solubilizer at temperature >65 °C, and one of the proposed reasons was the formation of bicontinuous microemulsions at high temperatures. Unfortunately, the HP-SANS cell used is restricted and cannot be used at high temperature, so that bicontinuous microemulsions could not be directly confirmed. However, lamellar LCs were observed in  $2FG(EO)_2/W/CO_2$  mixtures at  $W_0 \ge 25$ , raising the possibility of formation of  $4FG(EO)_2$  bicontinuous microemulsions. In general, a negative curvature of W/O (or W/scCO<sub>2</sub>)  $\mu$ Es approaches zero with decreasing CPP<sup>33</sup> and/or increasing HLB (or HCB),<sup>15</sup> and the microemulsion often

turns into a lamellar LC or a bicontinuous system bearing net zero interfacial curvature. In the case of  $4FG(EO)_2$ , the CPP and HCB values should be close to those of  $2FG(EO)_2$ , which prefers zero interfacial curvature, but the ability to lower W/CO<sub>2</sub> interfacial tension could be higher than that of  $2FG(EO)_2$  owing to the longer FC chains. In addition, affinities of  $4FG(EO)_2$  tail-to-CO<sub>2</sub> and head-to-water would be enhanced at higher temperature, which would in turn enhance the ability to lower interfacial tension. The discussion about CPP and HCB suggests that the  $4FG(EO)_2$  bicontinuous microemulsions, which should require not only zero interfacial tension <1 mN/m, are highly probable.

# 4. CONCLUSIONS

A previous study found the glutarate headgroup compound  $4FG(EO)_2$  to be an effective and efficient double-FC-tail surfactant for water-in-scCO<sub>2</sub> microemulsions: this compound can solubilize water of  $W_0$  up to 80 at 75 °C, in spite of the short  $C_4$  FC tails. At high temperature >65 °C, the solubilizing power was the highest in for  $FG(EO)_2$  analogues with different FC tail lengths (n = 2, 4, 6, and 8). Microemulsions in CO<sub>2</sub> are promising solvents for green chemistry and therefore should be prepared with low levels of surfactant, being also inexpensive and environmentally benign. Therefore, finding short FC-tail surfactants, which generate high solubilizing power, is key to designing useful CO2-philic surfactants. Further surfactant structure-performance studies are needed to develop CO2 as an "environmentally-benign" and "energy-saving" solvent, for applications such as extraction, dyeing, dry cleaning, metalplating, and organic or nanomaterial synthesis.

This study characterized microemulsions with the double-FC-tail solubilizers  $nFG(EO)_2$  and  $nFS(EO)_2$ , and clarified the effects of FC tail and methylene spacer lengths on the nanostructure (radii of D<sub>2</sub>O cores and reversed micelle shells, area per headgroup, aggregation number, and critical packing parameter CPP) of the microemulsions. Through SANS experiments and data analyses, relationships between nanostructure and the surfactant chain length or composition  $W_0$ were revealed: (1) the core and shell radii and aggregation number increased with  $W_0$ , but these were almost independent of addition of extra methylene spacer at same FC length and  $W_{0}$ ; (2) values of area per headgroup for each surfactant were almost the same based on the common -SO<sub>3</sub>Na headgroup employed, and (3) the CPPs of FC surfactants decreased for the shorter FC lengths and larger  $W_0$  values. These changes account for the observed transition of microemulsions into lamellar LCs as a function of surfactant structure and microemulsion composition. It was also interesting to note that the nanostructures (core radius) and surfactant properties  $(A_{\rm h,l}, N_{\rm agg})$  and CPP) in the CO<sub>2</sub> IVµEs were significantly different from those in typical AOT/W/O  $\mu$ Es at same  $W_0$ , in spite of similar surfactant structure and concentration. Those differences could be down to significant effects of intermolecular interactions between hydrocarbon chains and hydrocarbon solvents, as compared with fluorocarbon chains and  $CO_2$ .

Although the reason why  $4FG(EO)_2$  displays the highest solubilizing power (maximum  $W_0 = 80$ ) at the high temperatures is still unclear, one conceivable reason is formation of W/CO<sub>2</sub>-type bicontinuous microemulsions, and it seems highly probable based on fact (3) mentioned above. If bicontinuous  $\mu$ Es form in the  $4FG(EO)_2$  mixtures, this would be first example of single-phase bicontinuous microemulsions for a ternary single-surfactant/W/CO<sub>2</sub> mixture. However, in earlier papers bicontinuous microemulsions were found but in equilibrium with separated water and CO<sub>2</sub> phases<sup>59</sup> or by using mixed fluorinated surfactants (Zonyl FSH/Zonyl FSN 100 mixtures<sup>60</sup>). High water content bicontinuous microemulsions could represent new generation solvents with unique properties. Further studies on 4FG(EO)<sub>2</sub> and its analogues should be continued to advance surfactant design theory for W/CO<sub>2</sub> µE and bicontinuous systems.

## ASSOCIATED CONTENT

#### **S** Supporting Information

Guinier and Porod plots for W/CO<sub>2</sub>  $\mu$ Es with *n*FG(EO)<sub>2</sub> and *n*FS(EO)<sub>2</sub> (Figures SI1–5). Calculation of the volume fraction of total surfactant molecular fragments in the W/CO<sub>2</sub>  $\mu$ E interfacial region,  $\Phi_{surf}$  (Tables SI1–2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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