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Nanostructures in Water-in-CO₂ Microemulsions

Stabilized by Double-chain Fluorocarbon Solubilizers

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Abstract

High-pressure small-angle neutron scattering (HP-SANS) studies were conducted to investigate nanostructures and interfacial properties of water-in-supercritical CO₂ (W/CO₂) 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 CO₂ even at \( W_0 \) over the solubilizing powers as determined by phase behavior studies, suggesting formation of Winsor-IV W/CO₂ microemulsions and then Winsor-II W/CO₂ 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 head group, 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 CO₂. Increasing the microemulsion water loading led the critical packing parameter to decrease to \( \sim 1.3 \) 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.

Keywords: Supercritical CO₂, Microemulsion, Fluorinated surfactant, Aqueous Core, Micelle, Small-Angle Neutron Scattering
1. Introduction

Supercritical CO\textsubscript{2} (scCO\textsubscript{2}) is seen as a promising green solvent in various fields, including organic synthesis, dry cleaning, polymerization, extraction, nanomaterial processing.\textsuperscript{1} The reasons why scCO\textsubscript{2} has attracted much attention for those applications are based on CO\textsubscript{2} and supercritical fluid properties, which are, low cost, non-flammability, environmentally benign, natural abundance, high mass transfer, and pressure/temperature-tunable solvency (or CO\textsubscript{2} density). Unfortunately, supercritical CO\textsubscript{2} can dissolve only nonpolar and small molecular mass materials, and common polar or high molecular mass materials always separate from neat scCO\textsubscript{2}. Improving the poor solubility of polar materials is important for developing applications of scCO\textsubscript{2}. One of the most promising approaches for enhancing solubility in scCO\textsubscript{2} is to form reversed micelles with high-polarity aqueous cores in the continuous scCO\textsubscript{2} phase, that is, water-in-scCO\textsubscript{2} microemulsions (W/CO\textsubscript{2} µEs).\textsuperscript{2} Since such organized fluids have the attractive characteristics of scCO\textsubscript{2}, as well as the solvation properties of water, they have potential as volatile organic compound (VOC)-free and energy-efficient solvents for nano-material synthesis, enzymatic reactions, dry-cleaning, dyeing, preparation of inorganic/organic hybrid materials, and so on.\textsuperscript{2}

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\textsubscript{2} µEs 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\textsubscript{2} µEs. Since 1990, much effort has been directed towards the development of surfactants for W/CO\textsubscript{2} µEs.\textsuperscript{3-30} Three main kinds of surfactant have been examined so far, being hydrocarbon, silicone, and fluorocarbon (FC) surfactants.

Development of CO\textsubscript{2}-philic hydrocarbon surfactants has also been conducted for economic and environmental reasons.\textsuperscript{3-9} However, most commercial and known hydrocarbon surfactants are insoluble and inactive in scCO\textsubscript{2} systems.\textsuperscript{3} In this regard, it became apparent that conventional surfactant-design theory cannot be applied to W/CO\textsubscript{2} systems directly, and that CO\textsubscript{2}-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 surfactants.

Only a few hydrocarbon surfactants have so far been reported to stabilize a W/CO2 µEs. One of these successful surfactants is the nonionic TMN-6,4-6 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, W0 of 30. Custom-made anionic surfactants with highly branched double- or triple-tails (sodium bis(3,5,5-trimethyl-1-hexyl) sulfosuccinate7 or (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate8) were also found to be soluble in scCO2 and yield transparent single phase W/CO2 µEs (Winsor-IV W/CO2 µE or IVµE) with W0 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 scCO2, hence is ineffective at stabilizing W/CO2 µEs. It has been recognized that hydrocarbon surfactants with highly branched tails, especially methyl-branches, can be considered sufficiently CO2-philic. On the other hand, ester and ether groups have been reported to increase solubility in scCO2 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 µEs, like the AOT used commonly for W/O µEs10, has not yet been found.

In the case of silicone surfactants, polydimethylsiloxanes (PDMS) have attracted attention as potential non-fluorinated CO2-philles. While they are known to be miscible with CO2, they still require greater pressures to dissolve than is generally needed for fluorocarbon surfactants.11 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 scCO2.12 A copolymer of PDMS24-b-EO22 was shown to lower the water - scCO2 interfacial tension from 20 to 0.2 mN m⁻¹, a PDMS surfactant did however form W/CO2 emulsions,13 which flocculated and coalesced, limiting the stability of these systems. New trisiloxanes ((CH3)₃SiO)₂Si(CH₃)₂(CH₂)₃(OCH₂CH₂)ₙR were reported to be effective emulsifiers, forming both W/CO2 emulsions at n < 7 and CO2/W emulsions at n ≥ 7.14 This
change in curvature is attributed to variations in hydrophilic-CO$_2$-philic balance (HCB)$^{15}$, which is accompanied by a minimum in interfacial tension between water and CO$_2$.

In earlier studies, several fluorinated surfactants were found to dissolve in CO$_2$ and have a high activity at the W/CO$_2$ interface, suggesting the feasibility of forming W/CO$_2$ µEs.$^{16,17}$ Amongst others, surfactants described below are noteworthy for generating W/CO$_2$ µEs. Early on a perfluoropolyether (PFPE) surfactant$^{16}$ was found to stabilize IVµE, 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$_2$, $W_0^c = 14$). After that, numerous reports dealing with W/CO$_2$ µEs focused on PFPEs.

Another successful class of CO$_2$-philic surfactants are the HC-F hybrid, for example sodium 1-pentadecafluoroheptyl-1-octanesulfate (F7H7, (C$_7$H$_{15}$)(C$_7$F$_{15}$)CHOSO$_3$Na): these have both a HC and a FC chain in the same molecule. As such F7H7 is able to solubilize up to $W_0^c=35$ (or $W_0^c=32$) to form stable Winsor-IV W/CO$_2$ µEs.$^{18}$ Further studies$^{19}$, with hybrid surfactants related to F7H7 but with different FC and HC chain lengths, resulted in the formation of Winsor-IV W/CO$_2$ µEs for most of the analogues, but unfortunately smaller attainable $W_0$ values than for F7H7.

Other investigations$^{20-22}$ studied a class of fluorinated AOT analogues, for example sodium bis(1$H,1H,5H$-octafluoropentyl)-2-sulfo succinate (di-HCF4), 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$^{23}$, the most favorable case stabilizing $W_0$ up to 45.$^{24}$

Berkowitz et al. and Cummings et al. studied nanostructures of W/CO$_2$ µEs with FC and HC surfactants by molecular dynamics simulations. Berkowitz 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 REF. 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$_2$ µEs. On the other hand, Cummings reported that the HC tails in scCO$_2$ had an average of 74 ± 4% trans bonds (cf. 89% in vacuum) while the FC tails had 91 ± 2% (cf.
81% in vacuum). This implies that the HC tails assume more contracted conformations in CO$_2$, indicating CO$_2$-phobic interactions while the FC tails assume more extended conformations, consistent with favourable CO$_2$-philic interactions.

Recent molecular simulation studies$^{27,28}$ 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 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 inter-micellar interactions as compared with hydrocarbon surfactant analogues.

To obtain more economic and environmentally friendly W/CO$_2$ µEs, the minimum fluorine content necessary to render a surfactant CO$_2$-philic has been identified by using double-pentyl-tail surfactants with different fluorination levels. It was found that at least two fluorinated carbons (CF$_3$CF$_2$-) are required to stabilize µEs.$^{30,31}$ An increase in fluorine level leads to a lower aqueous surface tension at CMC and a lower stabilization cloud pressure for the W/CO$_2$ µEs.

Recently, with the aim of optimizing surfactant structure of fluorinated AOT analogues for W/CO$_2$ µE, double-FC-tail anionic surfactants with various FC lengths ($n = 4, 6, 8$) and a sulfo-glutarate ($n$FG(EO)$_2$) or sulfo-succinate ($n$FS(EO)$_2$) head group were synthesized (see Table 1 for their chemical structures).$^{24,30,31}$ As the structural difference between $n$FS(EO)$_2$ and $n$FG(EO)$_2$ is only one methylene unit in the group linking the polar ionic head group 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 head group between $n$FG(EO)$_2$ and $n$FS(EO)$_2$ at the same FC length $n$.$^{31}$ However, visual observation and UV-vis spectral measurements with a hydrophilic dye methyl orange (MO) clarified that the solubilizing powers of the glutarates $n$FG(EO)$_2$ were higher than those of the succinate analogues $n$FS(EO)$_2$: the most efficient found in that study was 4FG(EO)$_2$ at 75°C (max.
$W_0=80$ in IVμEs) even though it has the shortest FC tails.\textsuperscript{11} Significantly, this is the highest $W_0$ reported to date for W/CO$_2$ μEs. Many earlier papers mentioned that fluorocarbon is one of a few CO$_2$-philic groups, with \textit{longer FC chains promoting the higher the solubilising powers}.\textsuperscript{12} 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$_2$, being capable of solubilizing water in just a few seconds, even at high $W_0$ and close to its maximum solubilizing capacity.\textsuperscript{31} 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\textsuperscript{15}, a high critical packing parameter (CPP)\textsuperscript{33}, weak interactions between tail-tail and tail-head groups\textsuperscript{34,35}, if the spherical reversed micelles supported the formation of IVμEs.

To further characterize the surfactant, and explore the origins of the super efficiency, this new study reports aggregation behavior and nanostructures of the custom-made double-FC-tail surfactants, $n$FG(EO)$_2$ (FC length $n=2, 4, 8$) and $n$FS(EO)$_2$ ($n=4, 8$) in W/CO$_2$ μEs, by High-pressure Small-Angle Neutron Scattering (HP-SANS). The significance of this study to the field of surfactant science is that optimized, super-efficient, low fluorine content surfactants are now available for stabilization of W/CO$_2$ μEs.
2. Experimental Section

2.1. Materials

The surfactants used in this study were sodium 1,5-bis[(1H,1H,2H,2H-perfluorobutyl)oxy]-1,5-dioxopentane-2-sulfonate (2FG(EO)₂), sodium 1,5-bis[(1H,1H,2H,2H-perfluorohexyl)oxy]-1,5-dioxopentane-2-sulfonate (4FG(EO)₂), sodium 1,5-bis[(1H,1H,2H,2H-perfluorodecyl)oxy]-1,5-dioxopentane-2-sulfonate (8FG(EO)₂), and sodium 1,4-bis[(1H,1H,2H,2H-perfluorohexyl)oxy]-1,4-dioxobutane-2-sulfonate (4FS(EO)₂), sodium 1,4-bis[(1H,1H,2H,2H-perfluorodecyl)oxy]-1,4-dioxobutane-2-sulfonate (8FS(EO)₂). These surfactants except 2FG(EO)₂ were synthesized and evaluated in terms of interfacial properties as described previously\(^{24,30,31}\). Two surfactants were newly synthesized to examine the FC length effect in this study, as shown in Sec. 2.2. 1H,1H,2H,2H-pentafluoro-1-butanol (SantaCruz) and dimethyl glutaconate (Aldrich) were used without further purification. Reagent grade acetone, dichloromethane, hexane, 1,4-dioxane, toluene, p-toluene sulfonic acid monohydrate, and sodium hydrogensulfite 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 scCO₂\(^{24,30,31}\). As compared to \(nFS(EO)₂\), \(nFG(EO)₂\) has an extra –CH₂– spacer between the FC chain and the sulfonate group. Ultrapure water with a resistivity of 18.2 MΩ cm, obtained from a Millipore Milli-Q Plus system, was used in the experiments. CO₂ 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 1H,1H,2H,2H-pentafluoro-1-butanol (61.0 mmol), 4.80 g dimethyl glutaconate (30.4 mmol), 1.45 g p-toluene sulfonic acid monohydrate (7.4 mmol) in 200 cm³ 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 trans-esterification reaction. After the reaction was complete, the mixture was purified by column chromatography with dichloromethane/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 %): ¹H-NMR (500MHz, CDCl₃, TMS), (δH/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 C₂F₅CH₃CH₂bCOCH₂cCHd=CHfCOOCHbCH₂cC₂F₅; IR (film) νmax/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)-2-sulfoglutarate (2FG(EO)₂)

Bis(1H,1H,2H,2H-pentafluorobutyl) glutaconate (3.29 g, 7.79 mmol) was dissolved in 1,4-dioxane (140 cm³); then, the mixture was heated to 50 °C. A solution of sodium hydrogensulfite (3.60 g, 34.4 mmol) in water (60 cm³) 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)₂ (with no regioisomers as C₂F₅CH₂CH₂OCOCH₂CH(-SO₃Na)CH₂COOCH₂CH₂C₂F₅), after vacuum drying (yield 3.11 g, 76.0 %): ¹H-NMR (500MHz, CF₃COOD, TMS), (δH/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 C₂F₅CH₃CH₂bCOCH₂cCH₂ddCHf(SO₃Na)COOCHbCH₂cC₂F₅; IR (KBr) νmax/cm⁻¹: 2977, 1736, 1600,
Elemental analysis for $\text{C}_{13}\text{H}_{13}\text{O}_7\text{F}_{10}\text{Na}$: 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. High-pressure SANS (HP-SANS) is a particularly important technique for determining surfactant aggregation structures in supercritical CO$_2$. The HP-SANS measurements of the D$_2$O/surfactant/scCO$_2$ 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 high-pressure cell (Thar). The path length was 10 mm, the neutron beam diameter was 10 mm. The measurements gave the absolute scattering cross section $I(Q)$ (cm$^{-1}$) as a function of momentum transfer $Q$ (Å$^{-1}$), which is defined as $Q = (4\pi/\lambda)\sin\theta$. The accessible $Q$ range was 0.007-0.22 Å$^{-1}$, 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.$^{20}$

Pre-determined amounts of D$_2$O and surfactant, where the molar ratio of surfactant to CO$_2$ was fixed at $8 \times 10^{-4}$ (= 17 mM at the experimental condition), were loaded into the Thar cell. Then, CO$_2$ (11.3 g), was introduced into the cell by using a high pressure pump, and the surfactant/D$_2$O/CO$_2$ 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$_2$ were calculated using the Span-Wagner equation of state (EOS)$^{36}$.

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$^{-2}$). For CO$_2$, $\rho_{\text{CO}_2} \sim 2.50 \times \text{mass density} \times 10^{10}$ cm$^{-2}$ $^{37}$; at the experimental pressure of 350 bar and temperature of 45
°C, the CO₂ density is 0.917 g cm⁻³ so that ρ_{CO₂}~ 2.29 × 10^{10} cm⁻². The scattering length density of surfactant (ρ_{surf}) and D₂O (ρ_{D₂O}) were obtained using;

\[ \rho = \sum_i b_i/V_m \]  

(1)

\( b_i \) are the nuclear scattering lengths as given in the literature 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 g/cm³ as 1.7 g/cm³ for a typical fluorinated compound and 1.0 g/cm³ for a hydrocarbon surfactant. The calculated scattering length densities for \( n_{FS(EO)} \) and \( n_{FG(EO)} \) were 3.24 × 10^{10} cm⁻² (\( n = 8 \)), 2.80 × 10^{10} cm⁻² (\( n = 4 \)), and 2.33 × 10^{10} cm⁻² (\( n = 2 \)), respectively. The scattering length density of D₂O at 45 °C was calculated to be \( \sim 6.32 \times 10^{10} \text{ cm}^{-2} \). Samples in pure CO₂ (11.3 g) were run at the constant molar ratio of surfactant to CO₂ of 8 × 10⁻⁴.

For model fitting data analysis the μE droplets were treated as spherical core-shell particles with a Schultz distribution in core radius. Full accounts of the scattering laws are given elsewhere. For polydisperse spherical droplets at volume fraction \( \phi \), radius \( R_i \), volume \( V_i \), and coherent scattering length density \( \rho_p \) dispersed in a medium of \( \rho_m \), the normalized SANS intensity \( I(Q) \) (cm⁻¹) may be written as

\[ I(Q) = \phi (\rho_p - \rho_m)^2 [\sum_i V_i P(Q, R_i) X(R_i)] S(Q, R_{hs}, \phi_{hs}) \]  

(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. \( S(Q, R_{hs}, \phi_{hs}) \) is the structure factor, and a hard-sphere model modified for polydispersity was used; the constraints were \( \phi_{hs} = \phi_i \) and \( R_{hs} = R_d^{av} \) 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.

The least-squares FISH program was used to analyze the SANS data. 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 \( R_{\text{sph}} \) the typical \( \sigma/R_{\text{cav}} \) value (0.15) reported for many common W/O \( \mu \)E systems\(^{44} \) and the estimated length of the chains (12.7 Å for \( n = 8 \), 7.5 Å for \( n = 4 \), and 4.9 Å for \( n = 2 \))\(^{32} \), respectively. The sequence of fitting parameters was as follows; firstly, at constant \( \sigma/R_{\text{cav}} \) and \( t_s \) values, the other two parameters were adjusted to the experimental data, and then suitable \( \sigma/R_{\text{cav}} \) 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/CO₂ microemulsions

Previous studies reported solubilizing powers of each surfactant listed in Table 1, which were measured by visual observation and spectroscopically with the water-soluble dye methyl orange (MO) as an indicator for the μE water pool. At $W_0$ lower than the solubilizing power, the water/surfactant/CO₂ mixtures form transparent single-phases W/CO₂ μE (IVμEs), but at higher $W_0$ values turbid W/CO₂ macroemulsions or a precipitate (liquid crystals) are observed.

To examine the shape and size of aggregates in surfactant/D₂O/CO₂ mixtures at different $W_0$, 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 can be useful in determining the shape of colloid particles. In the low $Q$ region (typically in the case of droplet microemulsions $< 0.01 \text{ Å}^{-1}$), 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 non-interacting spheres, $D$ should be zero in this low $Q$ region, whereas $D = 1$ for rods and 2 for disks. 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 ~ 0, suggesting the presence of globular (spherical) nanodomains. On the other hand, 2FG(EO)₂ shows negative slopes at $Q < 0.01$ and $W_0 \geq 25$, 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 scCO₂ 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)₂ 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)₂ is approximately 10 Å by MM2 simulations, so thickness of the bilayers could be ~20 Å if CO₂ 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 behaviour.
lamellar LCs. For lamellar LCs, the relation between \( d \) and surfactant volume fraction \( \phi_{\text{surf}} \) (\( \phi_{\text{surf}} = 1 - \phi_{\text{alv}}, \phi_{\text{alv}}: \text{solvent volume fraction} \)) could be expressed as follows:  

\[
d = \frac{\delta}{\phi_{\text{surf}}} \quad (3),
\]

where \( \delta \) is a bilayer thickness. On the assumption of absence of CO\(_2\) 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\(_2\) incorporated into the lamellar LC.

One method to approximate radii from SANS data for the spherical microemulsions is via Guinier plots 1 (log \( [I(Q) \text{ vs } Q^2] \)) 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 \( R_{\text{sph}} \) as \( R_g = (3/5)^{0.5} R_{\text{sph}} \). The values of \( R_{\text{sph}} \) 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\(_2\)O cores (\( R_{\text{cav}} \)) and reversed micelles (\( R_{\text{sv}}^\text{av} = t_s + R_{\text{cav}}^\text{av} \)), and the polydispersity width (\( \sigma/R_{\text{cav}}^\text{av} \)). These fitted parameters with \( R_{\text{sph}} \) 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 \( \sigma/R_{\text{cav}}^\text{av} \) 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. 44 Such a high polydispersity was reported for W/CO\(_2\) IV\(_\mu\)Es with the anionic fluorinated double-tail surfactant di-HCF4 and the cationic perfluoropolyether surfactant PFPE–TMMA; the \( \sigma/R_{\text{cav}}^\text{av} \) values being 0.17–0.40 at \( W_0 =5–30 \) for di-HCF4 20 and for 0.22–0.49 at \( W_0 =19.4–38.1 \) for PFPE–TMMA 45. As the fluorocarbon-hydrocarbon hybrid surfactant F7H7 19 and AOT analogue surfactants (AOK and AO-Vac) 40 were found to give typical \( \sigma/R_{\text{cav}}^\text{av} \) values (< 0.2) for W/CO\(_2\) IV\(_\mu\)Es, the origin of these high polydispersities is unlikely to be due to the use of compressed CO\(_2\) fluid (i.e. high diffusivity 49 increasing frequency of \( \mu\)E-droplet aggregation/separation) 20,48. For the surfactant/W/CO\(_2\) mixtures be thermodynamically stable
microemulsions (energy-minimum equilibrium state), longer equilibration might be necessary (> 1 hour) than employed in this study (~5 min owing to expense of SANS time), 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/CO₂ systems

Table 2 also shows that \( R_{c}^{av} \) and \( R_{s}^{av} \) increased with \( W_0 \), and \( R_{s}^{av} \) was slightly different from \( R_{sph} \) in IVµE 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 head group \( A_{h,p} \) for \( n\text{FG(EO)}_2 \) in W/CO₂ IVµE, Porod plots were generated. Figure 2 shows Porod plots for 4FGEO₂, and those of the other surfactants are displayed in supporting information (Figures SI4 and SI5). For W/O µE droplets, \( A_{h,p} \) can be estimated from high \( Q \) SANS data, by assuming a sharp interface and applying the Porod equation:

\[
\{I(Q) \cdot Q^4\}_{Q \to \infty} = 2\pi (\Delta \rho)^2 \Sigma
\]

where \( \Sigma \) is the total area per unit volume. Another requirement here is that the cmc (concentration of non-adsorbed free surfactant) in CO₂ is negligible compared with the experimental surfactant concentration; i.e. all \( N \) surfactant molecules are at the CO₂-D₂O interface; given those conditions then the area per head group, \( A_{h,p} \approx \Sigma/N \). In the Porod plots of Figure 2 at \( Q > 0.16 \text{ Å}^{-1} \), the data are essentially asymptotic, suggesting these approximations are reasonable. The \( \Delta \rho \) in eq. 4 was assumed to be \( \{(\rho_{D2O}+\rho_{surf})/2 - \rho_{CO2}\} \) because the scattering will arise from not only the D₂O core but also the surfactant shell (\( \rho_{surf} \) were \( 2.33-3.24 \times 10^{10} \text{ cm}^{-2} \) against \( \rho_{CO2} \approx 2.29 \times 10^{10} \text{ cm}^{-2} \)) and volume fractions of total surfactant molecular fragments in the W/CO₂ µE interfacial region were calculated as ~0.5 (see supporting information Fig SI6 and Tables SI1-SI2). The broken lines at each \( W_0 \) indicate asymptotes.
\[ I(Q)Q^4 \xrightarrow{Q \to \infty} \] giving \( A_h \) values as listed in Table 3. Except at \( W_0 = 60 \) which gives rise to a macroemulsion, \( A_{h,p} \) values of same surfactant are similar within an experimental uncertainty \( \pm 10 \text{Å}^2 \).

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. The Porod plots display only the first maxima, but not the first minima clearly. By using the Porod-\( Q \) first maxima the \( \mu E \) droplet radii were estimated (Table 2); in the table, \( R_{p\text{max}} \) means the radius given from the first Porod maximum. As seen in the table \( R_{c \text{av}} \) and \( R_{p\text{max}} \) were similar at same \( W_0 \), supporting the validity of these analyses.

Figure 3 shows changes in the radii obtained by the theoretical curve fitting for \( \text{D}_2\text{O} \) cores and reversed micelle shells as function of \( W_0 \). When comparing \( n\text{FS(EO)}_2 \) and \( n\text{FG(EO)}_2 \), no significant difference in \( \text{D}_2\text{O} \) core radii could be seen at constant \( W_0 \) for the IV\( \mu E \)s. Differences in FC length \( n \) did not affect the radius in the IV\( \mu E \) region, but at \( W_0 \geq 60 \) an increase of \(~10 \text{ Å} \) was seen in the radius between \( n=4 \) and 8 surfactants. This suggests the following: (1) the turbid two-phase system at high \( W_0 \) was identified as a Winsor-II \( \text{W/CO}_2\mu E \), and (2) excess water molecules (=\( W_0 \) – the solubilizing power) formed \( \text{W/CO}_2 \) “macro”-emulsion droplets, and separated from \( \text{scCO}_2 \) in the absence of stirring whilst the equilibrium reversed micelles still remain in \( \text{scCO}_2 \). This behaviour was suggested by changes in UV-vis light absorption of the surfactant/aqueous methyl orange solution/\( \text{CO}_2 \) mixtures as a function of \( W_0 \), as seen previously. In addition, the linear dependences for radii vs \( W_0 \) suggested \( \text{D}_2\text{O} \) molecules are incorporated into spherical \( \mu E \) droplets. This linear behavior for \( R_{c \text{av}} \) as a function of \( W_0 \) can be used to provide another estimate for the effective head group area using:

\[
\alpha(p)R_{c \text{av}} = \frac{3\nu_w}{A_h} W_0 + \frac{3\nu_h}{A_h}
\]

where \( \nu_w \) is the volume of a water molecule, \( p \) is the polydispersity index \( (\sigma/R_{c \text{av}}) \) 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 \( R_{c \text{av}} \) in Fig. 3 is expected to have slope which depends on the interfacial area \( A_h \) and an intercept which depends on the average head group volume \( \nu_h \) via the head group radius \( r_h \). The head
group areas calculated in this way span 117-129 Å² with an uncertainty of ± 10 Å² (Table 3), which is consistent with the previous results obtained by Porod analyses of high Q SANS data in W/CO₂ μEs. Areas per head group Aₘₚ of 4FG(EO)₂, obtained by Porod analysis were slightly larger than Aₘₙ obtained from the slope of Fig.3. The assumption in these calculations for Aₘₚ is that all surfactant molecules are at the W/CO₂ interface, which may not be the case: the computed area will be too large if the solubilities of surfactant in CO₂ and water are high. In a previous study, 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 CO₂ (i.e. number of free 4FG(EO)₂ molecules not at the W/CO₂ 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 head group of 4FG(EO)₂ should be lower than Aₘₚ, and could be similar to the Aₘₙ.

In previous work, fluorinated double-tail surfactants (di-HCF₄, di-HCF₆ and di-CF₄) having same head groups as nFG(EO)₂ and nFS(EO)₂ were investigated in a similar fashion to as described above, giving 115 ± 5 Å² for Aₘ (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 Å² for Aₘ was reported. The difference in Aₘ between W/CO₂ and W/O μEs suggests that packing density of AOT type surfactants at water surface increases in CO₂ as compared to typical hydrocarbon oil. Earlier papers reported Aₘ of AOT to be 155 Å² at a W/scCO₂ but 75 Å² at the water/air and 72 Å² at the water/alkane interface.

Although the values of radii R_{av} in Fig. 3 are approximately half those seen for AOT W/alkane μEs, this could be accounted for owing to the difference in interfacial packing and the determined Aₘ values. In Fig. 3, intercepts of linear functions of R_{av} and R_{av} vs W₀ give mean radii of the head group core and the dry reversed micelle, in other words, dimensions of head group (lₘ) and overall surfactant molecule (l_{surf}), respectively. The head groups -SO₃Na of nFG(EO)₂ and nFS(EO)₂ displayed the same
radius in dry micelle cores (~5.2 Å). The \( l_{\text{surf}} \) values obtained from Fig.3 were almost consistent with those calculated by the MM2 calculation, suggesting \( R_c^{\text{av}} \) and \( R_s^{\text{av}} \) values in Fig. 3 to be reasonable: for example, \( l_{\text{surf}} \) of 8FG(EO)\textsubscript{2} was 17.6 Å from the intercept (radius of dry reversed micelles) of Fig.3 and 18 Å obtained by MM2 calculation.

By using the intercept for \( l_h \) and eq. 5, the effective head group volume was calculated as \( v_h \approx 199-231 \text{ Å}^3 \), and assuming the head group 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 \( v_h \approx 200-236 \text{ Å}^3 \) and \( r_h = 3.8 \) Å\textsuperscript{10} and these are consistent with the values calculated here for surfactants with identical polar head groups. This suggests the head group volume is not affected by being in supercritical CO\textsubscript{2}, making it unlikely the CO\textsubscript{2} penetrates into the polar region of the micellar structure.

These parameters relating to the size of the chain and head group allow estimates of the aggregation number numbers \( N_{\text{agg}} \) and critical packing parameters (CPP)\textsuperscript{33} by using:

\[
N_{\text{agg}} = \frac{4\pi R_c^{\text{av}}}{A_h} \tag{6}
\]

\[
\text{CPP} = \frac{v_c}{A_h l_c} \tag{7}
\]

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

\[
v_c = \frac{l_c(A_h + A_c + \sqrt{A_h A_c})}{3} \tag{8}
\]

where \( A_c \) is area per hydrophobic chain terminus, obtained using \( A_c = 4\pi (R_s^{\text{av}})^2 / N_{\text{agg}} \). To calculate \( N_{\text{agg}} \) and CPP of surfactants used in this study, \( A_h \) values obtained from eq. 5 were employed here. The calculated \( N_{\text{agg}} \) and CPP are shown as a function of \( W_0 \) in Figure 4 with previous data for AOT/W/n-heptane \( \mu \)Es\textsuperscript{10}. As expected from typical behavior of W/O reversed micelle systems\textsuperscript{8,55}, \( N_{\text{agg}} \) for these W/CO\textsubscript{2} \( \mu \)Es increased with \( W_0 \). For example, \( N_{\text{agg}} \) was close to 10 at \( W_0=10 \), but it reached up to ~100 and ~200 for 4FG(EO)\textsubscript{2} at \( W_0=80 \) and 8FG(EO)\textsubscript{2} at \( W_0=66 \), respectively. When the \( N_{\text{agg}} \) data were compared at a constant \( W_0 \), significant differences were not observed between these FC surfactants. On
the other hand, \( N_{\text{agg}} \) values of the FC surfactants in \( \text{scCO}_2 \) \( \mu \)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., \( N_{\text{agg}} \approx 90 \) at \( W_0 = 10 \) and \( \approx 290 \) at \( W_0 = 20 \) in isooctane and cyclohexane\(^{54,55} \)), the difference in \( N_{\text{agg}} \) is quite large, resulting from the small \( R_S^{\text{av}} \) and large \( A_h \) for \( n\text{FG(EO)}_2 \) and \( n\text{FS(EO)}_2 \) in IV\( \mu \)Es.

The critical packing parameter (CPP)\(^{33} \) is an indicator of “bulkiness” of a given hydrophobic group compared to the head group, and dictates interfacial curvature of a surfactant assembly. Negative interfacial curvature for a W/O or W/\( \text{CO}_2 \) \( \mu \)Es is only stabilized for surfactants with CPP > 1, and if CPP \( \approx 1 \) 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 Fig. 4, the CPP values are 1.92, 1.76 and 2.57 for 4FG(EO)\(_2\), 4FS(EO)\(_2\) 8FG(EO)\(_2\), respectively. These values were found to decrease with increasing \( W_0 \), and then finally reached constant values of \( \approx 1.3 \) at \( W_0 \).
3.3 Effects of Fluorocarbon and Methylene Spacer Lengths on Solubilization

Earlier SANS data for AOT/W/n-heptane µEs\(^10\) were used to calculate CPPs, represented by closed circles in Fig. 4. The AOT-analogue glutarate in W/n-heptane µEs also had CPP values similar to the regular AOT (e.g. 1.18 at 25 °C and \(W_0 = 40\))\(^{10}\). These are always smaller than those for the FC-surfactants in scCO\(_2\) at any \(W_0\), and demonstrate that even at small CPP of ~1.15 can stabilize Winsor-IV W/O µEs, whereas such a small CPP is not possible in the W/CO\(_2\) µEs. It implies that other parameters, for example, HCB\(^{15}\), Winsor R\(^{34,51}\) and/or W/CO\(_2\) interfacial tension\(^{5,52}\) mainly affect the solubilizing power of the double-FC-tail surfactants in IVµEs.

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\(_2\) µEs, suggesting that the extra methylene in \(nFG(EO)\(_2\) did not affect CPP: i.e. 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 head group region (i.e. succinate → glutarate) has also been investigated before for hydrocarbon AOT-like surfactants\(^6\). Interestingly, the addition of just one extra –CH\(_2–\) in the head group 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 head group at CMC were 0.8 mM, < 0.1 mN/m, and < 7 Å\(^2\), respectively.\(^{56}\) However, a maximum attainable \(W_0\) ratio with the glutarate analogue in W/n-heptane µEs was higher by > 10 as compared with the normal succinate (10–40 °C).\(^{56}\) Previously studies have been made of succinate and glutarate fluoro-AOT-type analogues in hydrocarbon W/CO\(_2\) µEs, suggesting that there is a notable enhancement in stability for the glutarate\(^{21,22}\) (i.e. comparing bis(1H,1H,5Hoctafluoropentyl)-2-sulfosuccinate or di-HCF\(_4\), versus bis(1H,1H,5Hoctafluoropentyl)-2-glutarate or di-HCF\(_4\)GLU)\(^{41}\) However, that work was only limited, comparing the pressure-temperature (\(P-T\)) phase stability of the W/CO\(_2\) µEs 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)\(^{21,22}\). The higher solubilizing powers of glutarates have been often reported not only in scCO\(_2\)
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) CO₂-ester interactions instead of hydration. These possibilities could be investigated by measuring FT-IR spectra for the ester groups in the two water/scCO₂ mixtures with nFG(EO)₂ and nFS(EO)₂.

The effect of FC length n of the double-FC-tail surfactants on CPP can be seen in Fig. 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, 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 discussed the reason why 4FG(EO)₂ is the most efficient solubilizer at temperature > 65 °C, and one of the proposed reasons was 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/CO₂ mixtures at W₀ ≥ 25, raising the possibility of formation of 4FG(EO)₂ bicontinuous microemulsions. In general, a negative curvature of W/O (or W/scCO₂) µEs approaches zero with decreasing CPP and/or increasing HLB (or HCB), 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/CO₂ 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-CO₂ 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 curvature but also an extremely low W/CO₂ 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-scCO₂ microemulsions: this compound can solubilize water of $W_0$ up to 80 at 75 °C, in spite of the short C₄ 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 CO₂ 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, metal-plating, and organic or nanomaterial synthesis.

This study characterized microemulsions with the double-FC-tail solubilizers $n$FG(EO)₂ and $n$FS(EO)₂, and clarified the effects of FC tail and methylene spacer lengths on the nanostructure (radii of D₂O cores and reversed micelle shells, area per head group, 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 head group for each surfactant were almost the same based on the common –SO₃Na head group 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 ($A_{h,l}$, $N_{agg}$, and CPP) in the CO₂ IVµEs were significantly different from those in typical AOT/W/O µEs 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 CO₂.
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$_2$-type bicontinuous microemulsions, and it seems highly probable based on fact (3) mentioned above. If bicontinuous μEs form in the 4FG(EO)$_2$ mixtures, this would be first example of single-phase bicontinuous microemulsions for a ternary single-surfactant/W/CO$_2$ mixture. However, in earlier papers bicontinuous microemulsions were found but in equilibrium with separated water and CO$_2$ phases or by using mixed fluorinated surfactants (Zonyl FSH/Zonyl FSN 100 mixtures). High water content bicontinuous microemulsions could represent new generation solvents with unique properties. Further studies on 4FG(EO)$_2$ and its analogues should be continued to advance surfactant design theory for W/CO$_2$ μE and bicontinuous systems.
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Figure captions

**Figure 1.** SANS profiles for surfactant/D$_2$O/CO$_2$ mixtures with various $W_0$ at 45 °C and 350 bar (CO$_2$ density = 0.92 g/cm$^3$). 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)$_2$, (c) 4FG(EO)$_2$, (d) 4FS(EO)$_2$, (e) 8FG(EO)$_2$, and (f) 8FS(EO)$_2$. The molar ratio of the surfactant to CO$_2$ was fixed at $8 \times 10^{-4}$.

**Figure 2.** Porod plots to obtain $\mu E$ droplet radii $R_{pmax}$ and areas per head group $A_{h,p}$ in D$_2$O/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 $\{I(Q)Q^{4}\}_{Q \rightarrow \infty}$ for calculation of $A_{h,p}$.

**Figure 3.** Dependence of droplet radius for the 8FG(EO)$_2$ D$_2$O/CO$_2\mu E$s as a function of $W_0$ at 45 °C and 350 bar.

**Figure 4.** Change in aggregation number ($N_{agg}$) and critical packing parameter (CPP) of $n$FG(EO)$_2$ and $n$FS(EO)$_2$ in D$_2$O/CO$_2\mu E$s or AOT in D$_2$O/$n$-heptane $\mu E$s$^{10}$ as a function of $W_0$ at 45 °C and 350 bar.
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