Nanostructures in Water-in-CO_2 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 CO_2 (W/CO_2) 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_2 microemulsions and then Winsor-II W/CO_2 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 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.

Keywords: Supercritical CO_2, Microemulsion, Fluorinated surfactant, Aqueous Core, Micelle, Small-Angle Neutron Scattering

1. Introduction

Supercritical CO_2 ($scCO_2$) is seen as a promising green solvent in various fields, including organic synthesis, dry cleaning, polymerization, extraction, nanomaterial processing.[1] The reasons why $scCO_2$ has attracted much attention for those applications are based on CO_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_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 the poor solubility of polar materials is important for developing applications of $scCO_2$. One of the most promising approaches for enhancing solubility in scCO is to form reversed micelles with high-polarity aqueous cores in the continuous $scCO_2$ phase, that is, water-in-$scCO_2$ microemulsions (W/CO_2 μEs).[2] Since such organized fluids have the attractive characteristics of $scCO_2$, 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[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_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_2 μEs. Since 1990, much effort has been directed towards the development of surfactants for W/CO_2 μEs.[3-30] Three main kinds of surfactant have been examined so far, being hydrocarbon, silicone, and fluorocarbon (FC) surfactants.

Development of CO_2-philic hydrocarbon surfactants has also been conducted for economic and environmental reasons.[3-9] However, most commercial and known hydrocarbon surfactants are insoluble and inactive in $scCO_2$ systems[3]. In this regard, it became apparent that conventional surfactant-design theory cannot be applied to W/CO_2 systems directly, and that CO_2-philicity is not directly comparable to oleo-philicity. Therefore, advancing molecular-design theory for CO_2-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_2 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, W_0 of 30. Custom-made anionic surfactants with highly branched double- or triple-tails (sodium bis(3,5,5-trimethyl-1-hexyl) sulfosuccinate[7] or (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate[8]) were also found to be soluble in scCO_2 and yield transparent single phase W/CO_2 μEs (Winsor-IV W/CO_2 μE or **IVμE**) 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 scCO_2, hence is ineffective at stabilizing W/CO_2 μEs. It has been recognized that hydrocarbon surfactants with highly branched tails, especially methyl-branches, can be considered sufficiently CO_2-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 CO_2-philic, and W/CO_2-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/CO_2 μEs, like the AOT used commonly for W/O μEs[10], has not yet been found.

In the case of silicone surfactants, polydimethylsiloxanes (PDMS) have attracted attention as potential non-fluorinated CO_2-philles. While they are known to be miscible with CO_2, 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 scCO_2.[12] A copolymer of $PDMS_{24}$-b-EO_{22} was shown to lower the water - scCO_2 interfacial tension from 20 to 0.2 mN m^{-1}, a PDMS surfactant did however form W/CO_2 emulsions,[13] which flocculated and coalesced, limiting the stability of these systems. New trisiloxanes $((CH_3)_3SiO)_2Si(CH_3)_2(CH_2)_3(OCH_2CH_2)_nR$ were reported to be effective emulsifiers, forming both W/CO_2 emulsions at $n < 7$ and CO_2/W emulsions at $n \geq 7$.[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-FC hybrids, for example sodium 1-pentadecafluoroheptyl-1-octanesulfate (F7H7, $(C_7H_{15})(C_7F_{15})CHOSO_3Na$): 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_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*,1*H*,5*H*-octafluoropentyl)-2-sulfosuccinate (di-HCF4), which yield Winsor IVμEs with W_0 = 30 (W_0^c ~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_3CF_2-) are required to stabilize μEs.[29] 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 (nFG(EO)$_2$) or sulfo-succinate (nFS(EO)$_2$) head group were synthesized (see **Table 1** for their chemical structures).[24,30,31] As the structural difference between nFS(EO)$_2$ and nFG(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 nFG(EO)$_2$ and nFS(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 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 IVμE) even though it has the shortest FC tails.[31] 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 longer FC chains promoting the higher the solubilising powers.[32] 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.[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[15], a high critical packing parameter (CPP)[33], weak interactions between tail-tail and tail-head groups[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[(1*H*,1*H*,2*H*,2*H*-perfluorobutyl)oxy]-1,5-dioxopentane-2-sulfonate (2FG(EO)$_2$), sodium 1,5-bis[(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)oxy]-1,5-dioxopentane-2-sulfonate (4FG(EO)$_2$), sodium 1,5-bis[(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)oxy]-1,5-dioxopentane-2-sulfonate (8FG(EO)$_2$), and sodium 1,4-bis[(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)oxy]-1,4-dioxobutane-2-sulfonate (4FS(EO)$_2$), sodium 1,4-bis[(1*H*,1*H*,2*H*,2*H*-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**. 1*H*,1*H*,2*H*,2*H*-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 scCO_2.[24,30,31] As compared to *n*FS(EO)$_2$, *n*FG(EO)$_2$ has an extra –CH_2– 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. CO_2 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(1*H*,1*H*,2*H*,2*H*-pentafluorobutyl) glutaconate

A mixture of 9.79 g 1*H*,1*H*,2*H*,2*H*-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 cm^3 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/*n*-hexane (3:1) as a developing solvent and silica gel. Finally, transparent sticky liquid, bis(1*H*,1*H*,2*H*,2*H*-pentafluorobutyl) glutaconate was obtained (yield 3.69 g, 28.8 %): ^{1}H-NMR (500MHz, $CDCl_3$, TMS), (δ_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 $C_2F_5CH_2{}^aCH_2{}^bOCOCH_2{}^cCH^d{=}CH^eCOOCH_2{}^{b'}CH_2{}^aC_2F_5$; IR (film) ν_{max}/cm^{-1}: 2979, 1749, 1663, 1464, 1348, 1277, 1195, 1159, 1080, 987, 720, 694.

2.2.2 Synthesis of sodium bis(1*H*,1*H*,2*H*,2*H*-pentafluorobutyl)-2-sulfoglutarate (2FG(EO)$_2$)

Bis(1*H*,1*H*,2*H*,2*H*-pentafluorobutyl) glutaconate (3.29 g, 7.79 mmol) was dissolved in 1,4-dioxane (140 cm^3); then, the mixture was heated to 50 °C. A solution of sodium hydrogensulfite (3.60 g, 34.4 mmol) in water (60 cm^3) 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 $NaHSO_3$ and recrystallized from acetone. It afforded a white powder, 2FG(EO)$_2$ (with no regio-isomers as $C_2F_5CH_2CH_2OCOCH_2CH(\text{-}SO_3Na)CH_2COOCH_2CH_2C_2F_5$), after vacuum drying (yield 3.11 g, 76.0 %); ^{1}H-NMR (500MHz, CF_3COOD, TMS), (δ_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 $C_2F_5CH_2{}^aCH_2{}^bOCOCH_2{}^cCH_2{}^dCH^e(SO_3Na)COOCH_2{}^bCH_2{}^aC_2F_5$; IR (KBr) ν_{max}/cm^{-1}: 2977, 1736, 1600, 1408, 1348, 1311, 1197, 1080, 800, 720; Elemental analysis for $C_{13}H_{13}O_7F_{10}Na$: 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_2O/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_2O and surfactant, where the molar ratio of surfactant to CO_2 was fixed at 8×10^{-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_2O/CO_2 mixture was pressurized up to 350 bar at 45 ºC 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), ρ (cm^{-2}). For CO_2, ρ_{CO2}~ 2.50 × mass density × 10^{10} cm^{-2} [37]; at the experimental pressure of 350 bar and temperature of 45

°C, the CO_2 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 D_2O (ρ_{D2O}) were obtained using;

$$\rho = \sum_i b_i / V_m \tag{1}$$

b_i are the nuclear scattering lengths as given in the literature[38] 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/cm^3 as 1.7 g/cm^3 for a typical fluorinated compound[17] and 1.0 g/cm^3 for a hydrocarbon surfactant. The calculated scattering length densities for nFS(EO)$_2$ and nFG(EO)$_2$ 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 D_2O at 45 °C was calculated to be ~ 6.32 × 10^{10} cm^{-2}. Samples in pure CO_2 (11.3 g) were run at the constant molar ratio of surfactant to CO_2 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.[39] Full accounts of the scattering laws are given elsewhere[39-43]. For polydisperse spherical droplets at volume fraction ϕ, radius R_i, volume V_i, and coherent scattering length density ρ_p dispersed in a medium of ρ_m, the normalized SANS intensity $I(Q)$ (cm^{-1}) may be written as

$$I(Q) = \emptyset\,(\rho_p - \rho_m)^2 [\textstyle\sum_i V_i P(Q, R_i)\, X(R_i)]\, S(Q, R_{hs}, \emptyset_{hs}) \tag{2}$$

$P(Q, R_i)$ is the single-particle form factor. The Schultz distribution $X(Ri)$ 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:[39,42] the constraints were $\phi_{hs} = \phi_d$ and $R_{hs} = R_d^{av}$ together with the known ρ 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.[43]

The least-squares FISH program was used to analyze the SANS data.[19-21,40,41] The fitted parameters are the volume fraction ϕ, the core radius R_c^{av}, polydispersity index σ/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 σ/R_c^{av} value (0.15) reported for many common W/O μE 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 a follows; firstly, at constant σ/R_c^{av} and t_s values, the other two parameters were adjusted to the experimental data, and then suitable σ/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_2 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 μE water pool. At W_0 lower than the solubilizing power, the water/surfactant/CO_2 mixtures form transparent single-phases W/CO_2 μE (IVμEs), but at higher W_0 values turbid W/CO_2 macroemulsions or a precipitate (liquid crystals) are observed.[24,30-32]

To examine the shape and size of aggregates in surfactant/D_2O/CO_2 mixtures at different W_0, SANS $I(Q)$ profiles were measured as a function of W_0 at 45 ºC 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 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.[30,40-43] 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 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$(EO)_2$ 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 CO_2 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[45,46] for lamellar LCs. For lamellar LCs, the relation between d and surfactant volume fraction ϕ_{surf} (ϕ_{surf} = 1 – ϕ_{solv}, ϕ_{solv}: solvent volume fraction) could be expressed as follows:[46]

$$d = \frac{\delta}{\phi_{surf}} \qquad (3),$$

where δ 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 (ϕ_{surf}=0.40) and 80 Å at W_0=60 (ϕ_{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[47] (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_{sph} as $R_g = (3/5)^{0.5} R_{sph}$.[47] The values of R_{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_2O cores (R_c^{av}) and reversed micelles ($R_s^{av} = t_s + R_c^{av}$), and the polydispersity width (σ/R_c^{av}). These fitted parameters with R_{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 σ/R_c^{av} of **IVμEs** 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 **IVμEs** with the anionic fluorinated double-tail surfactant di-HCF4 and the cationic perfluoropolyether surfactant PFPE–TMMA; the σ/R_c^{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[48]. As the fluorocarbon-hydrocarbon hybrid surfactant F7H7 [19] and AOT analogue surfactants (AOK and AO-Vac)[40] were found to give typical σ/R_c^{av} values (< 0.2) for W/CO_2 **IVμEs**, 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 μE-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)[24], 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_2 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*FG(EO)$_2$ in W/CO_2 **IVμE**, Porod plots were generated. **Figure 2** shows Porod plots for 4FGEO$_2$, 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[50]:

$$\{I(Q) \cdot Q^4\}_{Q \to \infty} = 2\pi\,(\Delta\rho)^2\Sigma \qquad (4)$$

where Σ is the total area per unit volume. Another requirement here is that the cmc (concentration of non-adsorbed free surfactant) in CO_2 is negligible compared with the experimental surfactant concentration; i.e. all N surfactant molecules are at the CO_2-D_2O 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 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 D_2O core but also the surfactant shell (ρ_{surf} were 2.33−3.24 × 10^{10} cm^{-2} against ρ_{CO2}~ 2.29 × 10^{10} cm^{-2}) and volume fractions of total surfactant molecular fragments in the W/CO_2 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

$\{I(Q)\cdot Q^4\}_{Q\to\infty}$ 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 ±10Å^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.[50] The Porod plots display only the first maxima, but not the first minima clearly. By using the ~~Porod Q~~ first maxima the μE droplet radii were estimated (**Table 2**); in the table, R_{pmax} means the radius given from the first Porod maximum. As seen in the table R_s^{av} and R_{pmax} 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 D_2O cores and reversed micelle shells as function of W_0. When comparing nFS(EO)$_2$ and nFG(EO)$_2$, no significant difference in D_2O core radii could be seen at constant W_0 for the IVμEs. Differences in FC length n did not affect the radius in the IVμE region, but at $W_0 \geq 60$ an increase of ~ 10 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 W/CO_2μE, and (2) excess water molecules (=W_0 − the solubilizing power) formed W/CO_2 "macro"-emulsion droplets, and separated from scCO_2 in the absence of stirring whilst the equilibrium reversed micelles still remain in scCO_2. This behaviour was suggested by changes in UV-vis light absorption of the surfactant/aqueous methyl orange solution/CO_2 mixtures as a function of W_0, as seen previously[51]. In addition, the linear dependences for radii vs W_0 suggested D_2O molecules are incorporated into spherical μE droplets. This linear behavior for R_c^{av} as a function of W_0 can be used to provide another estimate for the effective head group area using[10];

$$\alpha(p)R_c^{av} = \frac{3v_w}{A_h}w_0 + \frac{3v_h}{A_h} \quad (5)$$

where v_w is the volume of a water molecule, p is the polydispersity index (σ/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_c^{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 v_h via the head group radius r_h. The head group areas calculated in this way span 117-129 Å^2 with an uncertainty of ± 10 Å^2 (**Table 3)**, which is consistent with the previous results obtained by Porod analyses of high Q SANS data in W/CO_2 μEs. Areas per head group $A_{h,p}$ of 4FG(EO)$_2$, obtained by Porod analysis were slightly larger than $A_{h,l}$ obtained from the slope of **Fig.3**. The assumption in these calculations for $A_{h,p}$ ~~us~~ 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 CO_2 and water are high. In a previous study[31], the dissolution pressures of 0.08 mol% surfactant in scCO_2 were found to decrease at shorter FC chain lengths for *n*FG(EO)$_2$ and *n*FS(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 head group of 4FG(EO)$_2$ should be lower than $A_{h,P}$, and could be similar to the $A_{h,l}$.

In previous work[21], fluorinated double-tail surfactants (di-HCF4, di-HCF6 and di-CF4) having same head groups as *n*FG(EO)$_2$ and *n*FS(EO)$_2$ were investigated in a similar fashion to as described above, giving 115 ± 5 Å^2 for A_h (15 ºC and 500 bar). Interestingly, and importantly, that value is almost similar as found here, not only for the sulfosuccinate *n*FS(EO)$_2$ but also the analogous glutarate surfactant *n*FG(EO$_2$), on account of difference of 30 ºC in experimental temperature. For AOT in a range of *n*-alkanes from propane to decane, a mean value of 72 Å^2 for A_h was reported.[41] The difference in A_h between W/CO_2 and W/O μEs suggests that packing density of AOT type surfactants at water surface increases in CO_2 as compared to typical hydrocarbon oil. Earlier papers reported A_h of AOT to be 155 Å^2 at a W/scCO_2[52] but 75 Å^2 at the water/air[53] and 72 Å^2 at the water/alkane interface.[41]

Although the values of radii R_c^{av} in **Fig. 3** are approximately half those seen for AOT W/alkane μEs,[10] this could be accounted for owing to the difference in interfacial packing and the determined A_h values. In **Fig. 3**, intercepts of linear functions of R_c^{av} and R_s^{av} vs W_0 give mean radii of the head group core and the dry reversed micelle, in other words, dimensions of head group (l_h) and overall surfactant molecule (l_{surf}), respectively. The head groups -SO_3Na of *n*FG(EO)$_2$ and *n*FS(EO)$_2$ displayed the same radius in dry micelle cores (~5.2 Å). The l_{surf} values obtained from **Fig.3** were almost consistent with those calculated by the MM2 calculation, suggesting R_c^{av} and R_s^{av} values in **Fig. 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 **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= 199-231 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 μEs were found to have v_h= 200–236 Å^3 and r_h =3.8 Å,[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_2, making it unlikely the CO_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_{agg} and critical packing parameters (CPP)[33] by using;

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

$$\mathrm{CPP} = \frac{v_{\mathrm{c}}}{A_{\mathrm{h}} \cdot l_{\mathrm{c}}} \qquad (7)$$

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

$$v_c = \frac{l_c(A_h + A_c + \sqrt{A_h \cdot A_c})}{3} \qquad (8)$$

where A_c is area per hydrophobic chain terminus, obtained using $A_{\mathrm{c}} = 4\pi(R_{\mathrm{s}}^{\mathrm{av}})^2/N_{\mathrm{agg}}$. 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 μEs[10]. As expected from typical behavior of W/O reversed micelle systems[54,55], N_{agg} for these W/CO_2 μEs 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)$_2$ at W_0=80 and 8FG(EO)$_2$ 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 $scCO_2$ μEs were found to be quite small, one fifth to one sixth of those of AOT/W/*n*-heptane μEs. Even if compared with AOT in the other organic solvents (eg, N_{agg} = ~90 at W_0 = 10 and ~290 at W_0 = 20 in isooctane and cyclohexane[54,55]), the difference in N_{agg} is quite large, resulting from the small R_s^{av} and large A_h for *n*FG(EO)$_2$ and *n*FS(EO)$_2$ in **IVμEs**.

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/CO_2 μEs is only stabilized for surfactants with CPP > 1, and if CPP ~1 the interfacial curvature is planar: in other words, the reversed curvature μE 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 ~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 ºC and W_0 = 40)[56]. 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[34,35] 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 *n*FG$(EO)_2$ 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[56]. 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 ºC).[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,5Hoctafuoropentyl)-2-sulfosuccinate or di-HCF4, versus bis(1H,1H,5Hoctafuoropentyl)-2-glutarate or di-HCF4GLU). 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_{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) CO_2-ester interactions[57] instead of hydration. These possibilities could be investigated by measuring FT-IR spectra for the ester groups in the two water/scCO_2 mixtures with *n*FG$(EO)_2$ and *n*FS$(EO)_2$.[58]

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 *n*FG$(EO)_2$ at 45 ºC 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 ºC was the highest. An earlier paper[30,31] discussed the reason why 4FG$(EO)_2$ is the most efficient solubilizer at temperature > 65 ºC, 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/CO_2 mixtures at $W_0 \geq 25$, raising the possibility of formation of 4FG$(EO)_2$ bicontinuous microemulsions. In general, a negative curvature of W/O (or W/scCO_2) μEs approaches zero with decreasing CPP[33] and/or increasing HLB (or HCB)[15], 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_2 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_2 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/CO_2 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_2 microemulsions: this compound can solubilize water of W_0 up to 80 at 75 ºC, in spite of the short C_4 FC tails. At high temperature > 65 ºC, 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_2 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 CO_2-philic surfactants. Further surfactant structure-performance studies are needed to develop CO_2 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 D_2O 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 –SO_3Na 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 CO_2 **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 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_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[59] or by using mixed fluorinated surfactants (Zonyl FSH/Zonyl FSN 100 mixtures[60]). High water content bicontinous 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.

Acknowledgments

MS thanks the Japan Society for the Promotion of Science (JSPS) for a 1-year fellowship (Excellent Young Researcher Overseas Visit Program) and Hirosaki University. SC thanks the EPSRC for a PhD scholarship under the Next Generation Facility User scheme (EP/F020686). AM thanks the Ministry of Higher Education of Malaysia and Universiti Pendidikan Sultan Idris for the provision of a PhD studentship. We also acknowledge STFC for the allocation of beam time, travel, and consumables grants at ISIS.

This project was supported by JSPS [KAKENHI, Grant-in-Aid for Young Scientists (A), No. 23685034], JST [A-STEP, No. AS231Z02302D], and Leading Research Organizations, namely NSERC, ANR, DFG, RFBR, RCUK and NSF as Partner Organizations under the G8 Research Councils Initiative for Multilateral Research Funding, the Noguchi Institute Foundation, and Nissan Chemical Industries. The EPSRC is thanked for funding under grants EP/C523105/1, EP/F020686 and EP/K020676/1.

Figure captions

Figure 1. SANS profiles for surfactant/D_2O/CO_2 mixtures with various W_0 at 45 ºC 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 8×10^{-4}.

Figure 2. Porod plots to obtain μE droplet radii R_{pmax} and areas per head group $A_{h,p}$ in D_2O/CO_2 mixtures with 4FG(EO)$_2$ for several W_0 values at 45 ºC 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_2O/CO_2μEs as a function of W_0 at 45 ºC 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_2O/CO_2μEs or AOT in D_2O/*n*-heptane μEs[10] as a function of W_0 at 45 ºC and 350 bar.

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