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Water-in-CO$_2$ microemulsions stabilized by fluorinated cation-anion surfactant pairs

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Abstract

High water-content water-in-supercritical CO₂ (W/CO₂) microemulsions are considered to be green, universal solvents, having both polar and nonpolar domains. Unfortunately, these systems generally require environmentally-unacceptable stabilizers like long and/or multi fluorocarbon-tail surfactants. Here, a series of catanionic surfactants having environmentally-friendly fluorinated C₄-C₆-tails have been studied in terms of interfacial properties, aggregation behavior and solubilizing power in water and/or CO₂. The lowest surface tension and the critical micelle concentration of these catanionic surfactants are respectively lower by ~9 mN/m and 100 times than the constituent single FC-tail surfactants. Disk-like micelles in water were observed above the respective critical micelle concentrations, implying the catanionic surfactants to have a high critical packing parameter (CPP), which should also be suitable to form reverse micelles. Based on visual observation of phase behavior, FT-IR spectroscopic and small-angle neutron scattering (SANS) studies, one of the three catanionic surfactants tested was found to form transparent single-phase W/CO₂ microemulsions with a water-to-surfactant molar ratio up to ~50. This is the first successful demonstration of the formation of W/CO₂ microemulsion by synergistic ion-pairing of anionic and cationic single-tail surfactants. It indicates that catanionic surfactants offer a promising approach to generate high water-content W/CO₂ microemulsions.

Keywords: Supercritical CO₂, Microemulsion, catanionic surfactant, Solubilizing power, Small-Angle Neutron Scattering
1. Introduction

Above its critical point (31.1 °C and 73.8 bar) supercritical fluid CO$_2$ (scCO$_2$) has multifarious practical applications for replacing volatile organic compounds (VOCs) and freons$^1$. Furthermore, scCO$_2$ has other attractive properties for industrial applications such as like its low cost inexpensiveness, inflammability, natural abundance, high mass transfer, and pressure/temperature CO$_2$ density-tunable solvency (or CO$_2$ density)$^1$. On the other hand, recovery of CO$_2$ from power plants and utilizing it as a green solvent in chemical industries has some potential to abate the greenhouse effect. In fact, the green solvent scCO$_2$ is currently used as a green solvent employed for organic synthesis reactions, dry cleaning, polymerization, extraction, nanomaterial processing amongst others$^1$. Unfortunately, scCO$_2$ can realistically dissolve only nonpolar and small low molecular weight (MW) materials compounds, and more often than not polar and/or high MW solutes are incompatible with scCO$_2$$^2$. Hence, enhancing the poor solubility of polar and/or high-MW materials compounds is important a key target for developing potential applications of scCO$_2$. One of the most promising useful approaches to increase the solubility is to form molecular assemblies having hydrocarbon cores or polar cores able to solubilize those CO$_2$-insoluble materials. In the latter case, it would be reverse micelles with aqueous or ionic liquid (IL) cores nanodroplets in the continuous scCO$_2$ phase, these are water-in-scCO$_2$ microemulsions (W/CO$_2$ µEs) or IL-in-scCO$_2$ µEs.$^{2,3}$ Since such organized fluids thermodynamically-stable nano-dispersions have exhibit the attractive advantageous characteristics of scCO$_2$, as well as the solvation properties of bulk water and ILs, they have potential as volatile organic compound (VOC)-free and energy-efficient solvents for nano-material synthesis, enzymatic reactions, dry-cleaning, dyeing, and enhanced oil recovery, preparation of inorganic/organic nanocomposites production hybrid materials.$^{2,3}$, amongst other applications.

To be fulfill a viable practical In order to be considered a green and economical technology, the level of surfactants present for stabilizing µEs should be as low decreased as far as possible, and this needs to be balanced against the need that required for appropriate levels of dispersed water and/or interfacial areas in µEs for individual applications. One approach to meet satisfy these requirements is to develop
highly super-efficient surfactant stabilizers and solubilizers for the µEs. The water-to-surfactant molar ratio $W_0 = [\text{water}] / [\text{surfactant}]$ is an important indicator for evaluating the solubilizing efficiency, namely, the maximal highest $W_0$ achievable attainable in a single-phase W/CO$_2$ µE ($W_0^{\text{max}}$) can be identified called the water-solubilizing power of the surfactant. (As such $W_0^{\text{max}}$ represents the maximum number of water molecules which can be solubilized by one surfactant molecule). The studies aiming to find efficient CO$_2$-philic solubilizers started in the 1990s$^4$, and continue nowadays$^5$-$^{15}$.

Therefore, development of exploring CO$_2$-philic hydrocarbon (HC) surfactants for scCO$_2$ has been recognized known as remains an important task.$^4$-$^7$ However, most commercial and known popular HC surfactants are insoluble and inactive unusable in the scCO$_2$ solvent medium.$^3$ For example, although the common HC-surfactant Aerosol-OT (sodium bis-(2-ethyl-1-hexyl) sulfosuccinate, AOT, Figure S1 in supporting information) is well-known to exhibit very high $W_0^{\text{max}}$ values in water-in-oil µEs (e.g. $W_0^{\text{max}} = \sim 80$ in $n$-heptane at 25 °C$^8$, $W_0^{\text{max}}$ was found to be zero in dense scCO$_2$. In this regard, it has become apparent realized that conventional surfactant-design theory cannot be applied is inapplicable to W/CO$_2$ systems, and that CO$_2$-philicity is not directly comparable to replaced by oleo-philicity. Therefore, advancing molecular-design theory for CO$_2$-philic surfactants has required has to be advanced with new directions and paradigms in the field of surfactant research chemistry. In the search looking for CO$_2$-soluble compounds, highly branched hydrocarbons HC$^4$-$^7$, especially with methyl-branches and ester groups have been reported to increase solubility found to exhibit high solubility in scCO$_2$. Unfortunately However, an efficient and cost-effective HC solubilizer for W/CO$_2$ µEs, like the AOT used commonly utilized widely for W/O µEs$^4$-$^9$ has not yet been found developed.

In contrast with the poor solubilizing power of HC surfactants, some anionic fluorinated surfactants having perfluoropolyether (PFPE), double fluorocarbon (FC) and FC-HC hybrid tail-structures were reported to have a high solubility be highly soluble in CO$_2$ and high activity surface-active at the W/CO$_2$ interface, suggesting the feasibility of promising forming formation of W/CO$_2$ µEs.$^9$-$^{15}$ In the cases of the PFPE surfactant (PFPECOONH$_4$), the hybrid surfactant FC6-HC4 and the double
perfluoroctyl tail surfactant 8FG(EO)$_2$ (Figure S1 in supporting information), the reported $W_{\text{max}}$ values were found to be reached ~20, ~80 and ~60, respectively.$^{9,14,15}$

Along with the efforts to explore and develop exploration and development of CO$_2$-philic surfactants, applied research into using W/CO$_2$ µEs has also been conducted for chemical processes such as nanoparticle (NP) synthesis$^{16}$, enzymatic reactions$^{17}$, dry cleaning$^{18}$, and extraction$^{19}$ has also been conducted. However, in these applications, the use of employing ionic surfactants often has leads to disadvantages. For example, in NP synthesis$^{16}$ of ZnS, CdS, and TiO$_2$ using W/CO$_2$ µEs, the anionic FC surfactant 8FG(EO)$_2$ strongly binds to the NPs owing to via (electrostatic) attractive interactions between the headgroups and charged NP surfaces. Therefore, the NP products collected after releasing removing CO$_2$ usually contain include surfactant residues, requiring further purification and removal steps processes. Since these additional steps extra processes require the use of conventional additional solvents, overall the processes cannot be considered identified as truly VOC-free environmentally friendly. For extraction and dry cleaning using µEs, washings and extracts are also suspected to contain have surfactant residue in the same manner as for NP synthesis production. In the case of For enzymatic reactions in W/CO$_2$ µEs, it is well known that enzymes can be are known to be deactivated/denatured by ionic surfactants$^{20}$. These problems will always crop up in applications using ionic surfactant-stabilized µEs. Keeping these limitations in mind, a promising an efficient and cost-effective CO$_2$-philic surfactant for practical applications could be designed tailored to have contain nonionic and small hydrophilic groups headgroups (i.e. not a conventional poly(ethylene oxide) (PEO) group with a high MW) that are CO$_2$-philic, whilst being less polar and therefore less likely to interact bind unfavorably with other materials.

On the other hand, there are some examples reports of less polar low-polarity compounds for solubilizing ionic materials substances in dense liquid or supercritical CO$_2$ phase$^{3,21}$. For example, DeSimone et al.$^{21}$ reported demonstrated that dendrimers with having a fluorinated FC shells were soluble dissolved in liquid CO$_2$, and could extract solubilized an ionic dye methyl orange in the dendrimer cores. from separated water phase. Liu et al.$^3$ found reported that the fluorinated compound N-ethylperfluoroctylsulfonamide could stabilize generated IL/CO$_2$ µEs with three ILs of 1,1,3,3-
tetramethylguanidinium acetate, lactate and trifluoroacetate, and that these micelles could solubilize solubilized ionic compounds like methyl orange, CoCl₂ and HAuCl₄. These findings show that additives with non-traditional surfactant structures architectures can potentially act as play the roles of polar solubilizers and stabilizers for W/CO₂ µEs microemulsifiers in scCO₂. Recently, a FC-HC compound without a headgroup (Nohead FC6-HC₄, Figure S1 in supporting information) as an analogue of the superefficient surfactant FC6-HC₄ was found to stabilize W/CO₂ µEs. Despite the fact that Nohead FC6-HC₄ is not formally identified as recognized as a classic traditional surfactant (no identifiable head group), W/CO₂ µEs were formed even under mild a pressure and temperature conditions (approaching the critical point of CO₂), whereas similar analogues with different HC-tail lengths did not form µEs. Those nonionic solubilizers introduced above are likely to adhere to target materials in the applications of W/CO₂ µEs. Unfortunately, these solubilizers were inefficient (W₀²₀ < 10), expensive, and therefore not really much use for applications with high water-content W/CO₂ µEs.

One of the effective ways to enhance surfactant performance is through ion-pairing of cationic and anionic surfactants, that is formation of catanionic surfactants. Compared with the parent surfactant ions, catanionic surfactants exhibit many useful and novel properties in water and/or oil like enhanced surface activity and adsorption and much lower critical aggregation concentrations, a cloud temperature phenomenon, and formation of vesicles (or reverse vesicles) and shape-anisotropic micelles (or shape-anisotropic reverse micelles). These unique, or improved, surfactant properties mainly come from an increased critical packing parameter (CPP) and a decreased hydrophilic-lipophilic balance (HLB) based on the strong electrostatic interactions between anionic and cationic headgroups. With increasing CPP and decreasing HLB reverse micelles become more stable, hence catanionic surfactants could be advantageous for stabilizing reverse micelles and W/CO₂ µEs.

Another advantage of catanionic surfactants is the nonionic surfactant-like feature (e.g. cloud temperature not Krafft temperature for an ionic surfactant) even though they formally bear ionic groups. For example, the reverse micelles in ternary system of the catanionic surfactant octylammoniumoctanoate, octane and water were reported to grow uniaxially as W₀ and surfactant concentration increased or the
temperature decreased. The variation of spontaneous curvature with temperature seen to be the same as for other nonionic surfactants. Ion-pairing of the parent surfactant anion and cation probably affects the charge of the W/O µE interface, and hence has an effect on the spontaneous curvature/structure. For this reason catanionic surfactants may interact more weakly with target materials, and overcome the issues of strong surface binding and complexation encountered with formal ionic surfactants. Some earlier studies also tested inorganic and enzymatic reactions in catanionic surfactant reverse micelles, and yielded inorganic nanomaterials with unique shapes (e.g. nanowires and nanobelts) and a high enzymatic activity compared with in those of the parent cationic surfactants. Till now catanionic surfactants have not been investigated for stabilizing W/CO \( \mu \)Es.

This study has evaluated three different catanionic surfactants to examine efficiency and effectiveness of surfactant structure and the synergistic effects of ion-pairing for the formation of W/CO \( \mu \)Es. These catanionic surfactants (Table 1) have environmentally-acceptable C\(_4\)-C\(_6\) FC tails, and have been investigated in terms of surface tension lowering and micelle formation in water, water solubilizing power in scCO\(_2\) and properties of the µE droplets. The results help identify important design criteria for inexpensive and environmental-friendly catanionic surfactants to stabilize W/CO \( \mu \)Es as green and universal solvents for potential applications.
2. Experimental Section

2.1. Materials

The catanionic surfactants used in this study were surfactant cation-anion pairs of [C₆F₁₃mim][(CF₃)₃S], [C₆F₁₃mim][C₆F₁₃S] and [C₅F₁₁mim][C₅F₁₁S] (Table 1), respectively. The synthesis and purification of surfactants [C₆F₁₃mim][C₆F₁₃S] and [C₅F₁₁mim][C₅F₁₁S] were reported in a previous study.³⁵ [C₆F₁₃mim][(CF₃)₃S] was newly synthesized as described in supporting information (Scheme S1). The individual single FC-tail surfactants with Na⁺ or CH₃SO₃⁻ (MeS: methyl sulfonate) counterions, namely Na[C₆F₁₃S], Na[(CF₃)₃S] and MeS[C₆F₁₃mim] were also employed as a control.

Ultrapure water with a resistivity of 18.2 MΩ cm was generated produced by from a Millipore Milli-Q Plus system. CO₂ was of 99.99% purity was purchased from (Ekika Carbon Dioxide Co., Ltd.). The structures of the steric models and the lengths of surfactant compounds surfactant ions in the absence of other molecules were calculated estimated by MM2 (Molecular Mechanics program 2) calculations (Chem 3D; CambridgeSoft Corp., Cambridge, MA).

2.2. Phase behavior observation and FT-IR spectral measurements for surfactant/scCO₂ mixtures

A high-pressure (HP) vessel cell with a optical metal-to-glass sealed glass window (KP-308-3, Nihon Klingage co., ltd) and a moveable piston inside the vessel cell was used employed to observe examine phase behaviour of surfactant/water/scCO₂ mixtures by varying operating pressure and temperature. A detailed description of the experimental apparatus and procedures for the measurements can be found was introduced in earlier papers elsewhere.⁹,¹⁴-¹⁶

Formation of aqueous nanodroplets in W/CO₂ µEs was examined investigated by FT-IR spectroscopy with a pressure cell (volume: 1.5 cm³) having zinc sulfide windows (thickness: 8 mm, inner diameter: 10 mm), connected to the experimental HP-apparatus mentioned above. The FT-IR spectra spectral measurements were performed measured with a FT-IR spectrometer (JASCO Co., FT/IR-4700). The cells were made of stainless steel (SUS316) and had three zinc sulfide windows (thickness: 8 mm,
inner diameter: 10 mm). Each window was positioned to provide a perpendicular 10-mm optical path. The windows were attached and fastened tightly to the stainless-steel body of the cell with PTFE kel-F packings, thereby compressing the packings between the stainless steel parts and the windows and providing efficient sealing (tested up to 400 bar). The cell temperature of the cell was controlled by circulating water with a thermostat bath.

The measurements Visual observation of the water/surfactant/scCO$_2$ systems were performed was carried out at temperatures of 35 – 75 °C and pressures of lower than < 400 bar. The densities of CO$_2$ were calculated estimated using the Span-Wagner equation of state (EOS) $^{41}$. Pre-determined amounts of surfactant and CO$_2$ (20.0g), where the molar ratio of surfactant to CO$_2$ was fixed at $8 \times 10^{-4}$, were loaded into the variable-volume high-pressure optical HP-cell. Then, water was added loaded into the optical cell through a six-port valve with a 20 μL sample loop until the clear Winsor-IV W/CO$_2$ μE (i.e. single-phase W/CO$_2$ μE) solution became a turbid macroemulsion or a precipitated hydrated surfactant. Surfactant molar concentration was in the range 10-20 mM, for example 16.7 mM at 45 °C and 350 bar, as the inner volume of the cell was varied by changing experimental pressure and temperature.

During the spectroscopic measurements, the scCO$_2$ mixture was stirred and circulated between the optical vessel and the window cell until a constant absorbance was attained. The circulation was then discontinued; the valves between the vessel and the window cell were closed, and the measurement FT-IR spectrum was measured. The physical properties of the continuous phase of scCO$_2$ were assumed to be equivalent to those of pure CO$_2$.

**2.3 High-Pressure and ambient pressure small-angle neutron scattering (SANS) measurements and data analysis**

Due to the range of neutron wavelengths available, time-of-flight SANS is suitable for studying the shapes and sizes of colloidal systems. High-pressure SANS (HP-SANS) is a particularly important technique for determining aggregate nanostructure in supercritical CO$_2$. The HP-SANS measurements of
the D$_2$O/surfactant/scCO$_2$ systems were performed at 45 °C at various pressures. The SANS2D 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 in the cell and neutron beam diameter were both 10 mm. The measurements gave absolute scattering cross sections $I(Q)$ (cm$^{-1}$) as a function of momentum transfer $Q$ (Å$^{-1}$), which is defined as $Q = (4\pi/\lambda)\sin(\theta/2)$, where $\theta$ is the scattering angle. The accessible $Q$ range was 0.002-1 Å$^{-1}$ on SANS2D arising from an incident neutron wavelength, $\lambda$, of 2.2-10 Å. The data were normalized for transmission, empty cell, solvent background, and pressure induced changes in cell volume as before$^{15,22}$.

Pre-determined amounts of D$_2$O and surfactant, where the molar ratio of surfactant to CO$_2$ was fixed at 8.0 × 10$^{-4}$ (= 16.7 mM at the appropriate 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 to 350 bar at 45 °C by decreasing the inner volume of the Thar cell. With vigorous stirring, visual observation was carried out to identify the mixture as being a transparent single-phase (W/CO$_2$ μE) or a turbid phase. Finally, the HP-SANS experiments were performed for not only single-phase W/CO$_2$μEs, but also the turbid phases formed below the cloud point phase transition pressure $P_{\text{trans}}$. Due to the systems being dilute dispersions (volume fractions typically 0.012 or less), the physical properties of the continuous phase of scCO$_2$ were assumed to be equivalent to those of pure CO$_2$. Scattering length densities of reversed micelle shells ($\rho_{\text{shell}}$), aqueous cores ($\rho_{\text{core}}$), and CO$_2$ ($\rho_{\text{CO}_2}$) in the D$_2$O/CO$_2$ μE were calculated as $\rho_{\text{shell}} = 2.28 \times 10^{10}$ cm$^{-2}$, $\rho_{\text{core}} = 4.92 \times 10^{10}$ cm$^{-2}$, and $\rho_{\text{CO}_2} = 2.29 \times 10^{10}$ cm$^{-2}$ as shown in supporting information (see S4). As $\rho_{\text{shell}}$ was close to $\rho_{\text{CO}_2}$ and the shells are solvated with CO$_2$ to get both scattering length densities closer, neutron scattering from the shells was identified to be negligible. Therefore, SANS from the D$_2$O/CO$_2$ μEs was assumed to only be from the so-called aqueous core contrast. For model fitting data analysis, the W/CO$_2$ μE droplets were treated as spherical or ellipsoidal particles with a Schultz distribution in core radii $^{42}$. The polydispersities in spherical and ellipsoid radii were fixed at 0.3 as found in spherical D$_2$O/CO$_2$ μEs with the double FC-
tail surfactants (polydispersity = 0.17-0.40)\textsuperscript{43}. Full accounts of the scattering laws are given elsewhere\textsuperscript{15,22,43}. Data have been fitted to the models described above using the SasView small-angle scattering analysis software package (http://www.sasview.org/\textsuperscript{44}). The fitted parameters are the core radii perpendicular to the rotation axis ($R_{\text{f-ell,a}}$) and along the rotation axis ($R_{\text{f-ell,b}}$) for ellipsoidal particles, or the core radius $R_{\text{sph}}$ for spherical particles; these values were initially obtained by preliminary Guinier analysis ($R_{\text{g-sph}}$\textsuperscript{45}).

Cationic surfactant micelles in water were also characterized by ambient pressure SANS measurement and the data analysis. The SANS measurements were performed on D33 SANS instrument at the Institut Laue-Langevin (ILL, Grenoble, France), with a wavelength of $\lambda = 6$ Å and two sample detector positions (2 and 7.5 m) providing an accessible $Q$ range of 0.005-0.2 Å$^{-1}$. All samples were made in D$_2$O using 2 mm path length rectangular quartz cells at 25 °C. Raw SANS data were reduced by subtracting the scattering of the empty cell and D$_2$O background to an appropriate standard using the instrument-specific software. The SANS data analysis for cationic surfactant micelles assumed that neutron scattering occurred from FC-cores and HC-shells in the micelles due to the large differences between the scattering length densities $\rho_{\text{FC}}$, $\rho_{\text{HC}}$ and $\rho_{\text{D2O}}$ ($\rho_{\text{FC}} = 3.58 \times 10^{10}$ cm$^{-2}$, $\rho_{\text{HC}} = -0.30 \times 10^{10}$ cm$^{-2}$, and $\rho_{\text{D2O}} = 6.32 \times 10^{10}$ cm$^{-2}$ as shown in supporting information S4). Then SANS data for micelles in D$_2$O were analysed with theoretical curves for a core/shell cylinder/disk particle form factor\textsuperscript{46} with square well structure factor.
3. Results and Discussion

3.1 Effects of catanionic surfactant structure on interfacial properties and micelle formation in water

To investigate effects of catanionic surfactant structures on dilute aqueous phase properties, namely critical micelle concentration (CMC) and the surface tension at CMC (\(\gamma_{\text{CMC}}\)), surface tensions of aqueous surfactant solutions were measured at 23 °C as a function of surfactant concentration. Tensiometric data are displayed in Figure 1 and interfacial properties (CMC and \(\gamma_{\text{CMC}}\)) estimated from these data are listed in Table 2. The surface tension data and interfacial properties of [C\(_6\)F\(_{13}\)mim][C\(_6\)F\(_{13}\)S] and [C\(_3\)F\(_{11}\)mim][C\(_5\)F\(_{11}\)S] shown in the figure and the table were previously reported\(^{35}\). All the catanionic surfactants effectively and efficiently lowered aqueous surface tension, and finally achieved the very low limiting value at the cmc of \(\gamma_{\text{CMC}}\) of 13.5-16.8 mN/m at concentrations < 1 mM. From the table, the CMC was found to decrease with increasing total fluorine content, as expected.\(^9\)\(^{-}\)15 The lowest surface tension and CMC are respectively lower by ~9 mN/m and ~100 times than the parent anionic single FC-tail surfactants with a sodium counterion. These results clearly demonstrate synergistic effects of surfactant anion-cation pairing on surface activity and surface tension lowering in water. It suggests that a higher hydrophobicity and more densely-packed surfactant monolayers at air/water surface are generated by surfactant anion-cation pairing as compared to the parent surfactants.

Nanostructures of catanionic surfactant micelles in D\(_2\)O were examined at a surfactant concentration of 20 x CMC by SANS measurements (Figure 2). All the SANS profiles have extensive regions of \(Q^2\) scattering. In the low \(Q\) region, scattering may scale follow \(I(Q) \sim Q^D\), where \(D\) is a characteristic distinctive “mass fractal” for the micellar particles; hence, the gradient slope 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 cylinders and 2 for disks.\(^{45}\) In the cases of catanionic surfactant micelles, the slope of \(Q^2\) suggests the formation of 2-dimensional disk-like micelles or vesicles.

One method approach to obtain approximate average radii from SANS data for the globular and disk-like micelles is via Guinier plot\(^{35}\) (\(\ln[I(Q)]\) vs \(Q^2\)) as shown displayed in supporting information.
(Figure S2). In the all plots of Ln $[I(Q)]$ vs $Q^2$, linearity was noted over an extended $Q$-range, and the gradients slopes allowed enabling the calculation of radii of gyration, $R_g$ (the slope = $-R_g^2/3$). This $R_g$ may also be related to a principal disk radius $R_{g-disk}$ as $R_g = 4^{-0.5} R_{g-disk}$. The $R_{g-disk}$ values are listed in Table S1 along with $R_g$ values. Porod analyses of SANS data was also carried out as shown in Figure S3, and the sphere radius ($R_{p-sph}$) obtained from the $Q$ value at 1st maximum was also listed in Table S1 as a reference.

The values of disk radii $R_{g-disk}$ obtained provided by Guinier analysis were employed used as the starting points for model fitting using with the core/shell disk/cylinder form factor models with an additional square well structure factor. [Note the “cylinder” form factor model is quite general, and by inverting the aspect ratio can be used to simulate scattering from disk-like particles]. A square well structure factor was used for obtaining better fits to the SANS data at low $Q$ values $< 0.02$ Å$^{-1}$ as discussed in supporting information S6. The fitted parameters for disk-like FC-core radius ($R_{f-Cdisk}$) and thickness ($t_{f-Cdisk}$), HC-shell thickness ($t_{f-Sdisk}$), aspect ratio, well depth and width are listed in Table 3. Cloud point temperatures at the concentrations of 20 × CMC were determined by visual observation as shown in supporting information S7, and are also listed in the table.

At these concentrations, the cloud temperature of FC-branched catanionic surfactant [C$_6$F$_{13}$mim][(CF$_3$)$_3$S] was ~30 ºC, hence stabilizing a clear single solution at room temperature. However, that of the non-FC-branched surfactant [C$_5$F$_{11}$mim][C$_5$F$_{11}$S] was below 0 ºC, giving a translucent solution implying presence of larger aggregates (e.g. vesicles) 23-26. Actually, the SANS profiles for [C$_5$F$_{11}$mim][C$_5$F$_{11}$S] and [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] can be fitted with the theoretical curves for spherical vesicles having radius larger than 100 nm and micro-segregated FC and HC layers, although that for [C$_6$F$_{13}$mim][(CF$_3$)$_3$S] cannot, as shown in supporting information (Fig. S6 for log-log plots, Fig. S7 for lin-lin plots, and Table S3 for the structure parameter estimated for the vesicles). However, better fits were obtained using the disk model as compared to the vesicle model. The discussion below addresses the structure parameters applied to the disk model.
In the Table 3, the structure factor \( S(Q) \) parameters for well depth and width, were almost same for \([\text{C}_5\text{F}_{11}\text{mim}][\text{C}_5\text{F}_{11}\text{S}]\) and \([\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]\). However, the depth and the width for \([\text{C}_6\text{F}_{13}\text{mim}][\text{CF}_3_3\text{S}]\) was smaller and larger than those of straight chain surfactants, respectively. This suggests the attractive interactions between \([\text{C}_6\text{F}_{13}\text{mim}][\text{CF}_3_3\text{S}]\) micelles are not so strong. This results are consistent with the difference in cloud temperature between \([\text{C}_6\text{F}_{13}\text{mim}][\text{CF}_3_3\text{S}]\) and \([\text{C}_5\text{F}_{11}\text{mim}][\text{C}_5\text{F}_{11}\text{S}]\), namely the higher cloud temperature of \([\text{C}_6\text{F}_{13}\text{mim}][\text{CF}_3_3\text{S}]\) indicates a weaker hydrophobicity and weaker attractive inter-micellar interactions.

Focusing on thicknesses of the disk-like FC-core \( t_{\text{C-disk}} \) and HC-shell \( t_{\text{Shell}} \), the total disk-thickness \( (t_{\text{C-disk}} + 2t_{\text{Shell}}) \) values are similar to twice the hydrophobic tail length of the catanionic surfactants (13.6 Å for \([\text{C}_6\text{F}_{13}\text{S}]\), 12.3 Å for \([\text{C}_6\text{F}_{13}\text{mim}][\text{C}_5\text{F}_{11}\text{S}]\), 11.0 Å for \([\text{C}_5\text{F}_{11}\text{mim}]\) and 7.1 Å for \([\text{CF}_3_3\text{S}]\)) as obtained by the MM2 calculation (Figure S7 in supporting information), suggesting a bilayer cross-section structure of the disk-like micelles. On the other hand, the disk core radius \( R_{\text{C-disk}} \) increased in the order of \([\text{C}_6\text{F}_{13}\text{mim}][\text{CF}_3_3\text{S}] < [\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}] < [\text{C}_5\text{F}_{11}\text{mim}][\text{C}_5\text{F}_{11}\text{S}]\). The radial dimensions of disk-like micelles are known to increase with increasing difference in Gibbs energy between the edge (hemi-rod-like micelle) and the main body (bilayer) \(^{47,48}\), i.e. a larger disk radius generated with energy of the edge >> main body. For catanionic surfactants, a combination of straight FC-chains is likely to promote growth of disk-like micelles with an increasing energy difference.\(^{23-26}\)

Taken together, these results showing formation of disk-like micelles in water implies the catanionic surfactants have sufficiently high CPP values suitable for forming reverse micelles. In addition, the low CMC values < 1 mM and very low \( \gamma_{\text{CMC}} \) of 13.5-16.8 mN/m suggests a low HLB and high surface activity of these catanionic surfactants. All of these features suggest a low hydrophilic-CO\(_2\)-philic balance (HCB) \(^{49,50}\) and good affinity to scCO\(_2\), which are promising characteristics for stabilizing W/CO\(_2\) μEs.
3.2 Effect of catanionic surfactant structure on stabilization of reverse micelles and microemulsions in scCO₂

To examine phase behaviour of catanionic surfactants/water/CO₂ mixtures in detail, the pressures at which a transparent clear single phase cloud start to appear cloudy, \( P_{\text{trans}} \), were measured for water/surfactant/CO₂ mixtures at various temperatures of (35 – 75 °C) and \( W₀ \) values of 6 – 84. Figure 3 shows phase diagrams in terms of \( P_{\text{trans}} \) and CO₂ density for [C₆F₁₃mim][C₆F₁₃S]/water/CO₂ mixtures with different each \( W₀ \) values value at [surfactant]/[CO₂] = 8 \times 10^{-4} as a function of temperature. At values higher than \( P_{\text{trans}} \), [C₆F₁₃mim][C₆F₁₃S] with [surfactant]/[CO₂] = 8 \times 10^{-4} with added water gave stable transparent systems in scCO₂. However, the other catanionic surfactants [C₅F₁₁mim][C₅F₁₁S] and [C₆F₁₃mim][(CF₃)₃S] always remained turbid phases or two-phase, even at the highest pressure and temperature 400 bar and 75 °C. A simple mixture of the individual surfactants Na[C₆F₁₃S] and MeS[C₆F₁₃mim] was also tested for formation of W/CO₂ μE. Interestingly, the surfactant mixture was almost insoluble in scCO₂. This is probably due to the low solubility of both the single-tail surfactants compared with the catanionic surfactant. This result suggests that formation of the catanionic surfactant beforehand, namely ion-pairing the parent surfactants and removing the counterion salt (NaMeS), is important to generate the good solubility and W/CO₂ microemulsion formation.

With increasing temperature from 35 °C to 75 °C, \( P_{\text{trans}} \) increased by 80-110 bar but the CO₂ density decreased by 0.9-1.3 g cm⁻³. Solubility of a compound in scCO₂ is known to mainly depend on CO₂ density (rather than pressure per say), resulting in an increase in solvating CO₂ molecules.\(^1\) Higher temperatures (higher thermal motion and weaker interactions between surfactant molecules) are expected to enable generation of W/CO₂ microemulsion at lower CO₂ densities.\(^1\) Increasing \( W₀ \) feeds through to an increase in \( P_{\text{trans}} \) (\( W₀ = 36 \) from to 48). Significant increase in \( P_{\text{trans}} \) with increasing \( W₀ \) was also reported in the use of high HCB surfactants like CO₂-soluble HC-surfactants or short FC-surfactants (e.g. CF₃(CF₂)ₙ⁻ with \( n = 0 \) - 3)\(^{41}\), and it could be caused by greater CO₂ solvation of the surfactant tails.\(^1\) Based on the phase behaviour observations, transparent phases identified as W/CO₂ μEs were observed at pressures > 260 bar (CO₂ density > 0.84 g cm⁻³), even with the very high \( W₀ \) value of 84. However, this
is not really clear evidence for formation of Winsor IV-type W/CO₂ μEs at these large W₀ values (up to 84), and it is possible that transparent phases with high W₀ values may be Winsor II-type (albeit with the excess water phase out of view, and below the pressure cell windows).

Comparing the P⁺ values at W₀ = 10 for the double-FC-tail surfactants nFS(EO)₂ and nFG(EO)₂ (n = 4, 6, 8) as shown in Figure S9 (supporting information)\(^1\)+, to those at W₀ = 12 for [C₆F₁₃mim][C₆F₁₃S] shows they are quite similar, especially to 6FG(EO)₂. It suggests the same FC-length surfactants [C₆F₁₃mim][C₆F₁₃S] and 6FG(EO)₂ have similar CO₂-philicity (or HCB) and ability to stabilize W/CO₂ μEs, even with different types of headgroups (anionic sulfonate for 6FG(EO)₂ and anionic sulfonate + cationic methylimidazolium for the catanionic).

The appearance of transparent single-phases with high W₀ values > 10 is consistent with the formation of W/CO₂ μEs. To explore formation of hydrogen bonded μE water cores, FT-IR spectra were recorded of 16.7 mM surfactant/H₂O/CO₂ mixtures with different W₀ values at 350 bar and 45 °C (Figures 4 and S10). Typically, the O-H stretching vibration in a non-polar solvent appears ~ 3630 cm⁻¹, but can shift to lower wavenumbers depending on the hydrogen bond environment.\(^5\)\(^2\),\(^5\)\(^3\) A seen in Figures 4 and S10 absorbance over 3100-3500 cm⁻¹ in the FT-IR spectra increased with increasing added water W₀. These spectra and the changes with increasing W₀ are very similar to those for W/CO₂ μEs formed by anionic fluorinated surfactants FC₆-HC₄ and 8FS(EO)₂.\(^5\)\(^3\) The absorbance for the [C₆F₁₃mim][C₆F₁₃S]/W/CO₂ μEs grew with W₀ up until W₀ = 50, suggesting a maximum water-solubilizing power W₀⁰ₐₓ ~50. In contrast with the behavior for [C₆F₁₃mim][C₆F₁₃S], there were no changes in FT-IR spectra for [C₆F₁₃mim][(CF₃)₃S] and [C₅F₁₁mim][C₅F₁₃S] even on increasing W₀ from 10.2 up to 30.6 (Fig. S10). The parent surfactant with a sodium counterion Na[C₆F₁₃S] did not show any clear absorbance in the water OH stretching region (Fig. S10).

It is intriguing why [C₆F₁₃mim][C₆F₁₃S] can stabilize μEs whereas the other surfactants do not, especially since the differences in chemical structures are so small: just two more -CF₂- units for [C₆F₁₃mim][C₆F₁₃S] compared to the other catanionics. The longer fluorocarbon tails of [C₆F₁₃mim][C₆F₁₃S] are expected to produce a higher CO₂-philicity and a higher solubility in scCO₂.\(^1\)-\(^1\)\(^6\)
Hence, the total number of fluorinated carbons C_{12} per surfactant may represent a lower limit for the catanionic surfactant to achieve good compatibility with scCO_2, whereas a smaller number of fluorinated carbons is insufficient. With an impressive water-solubilizing power $W_0^\text{max} = \sim 50$ of [C_6F_{13}mim][C_6F_{13}S] can be identified as a superefficient CO_2-philic surfactant for W/CO_2 µEs, at least comparable to the best performance reported to date with 8FG(EO)_2.\textsuperscript{1-16} This appears to be the first case of a highly effective CO_2-philic surfactant based on ion-pairing of anionic and catanionic single FC-tail surfactants, and especially interesting for its environmental acceptability.

To demonstrate the [C_6F_{13}mim][C_6F_{13}S]/D_2O/CO_2 µEs, SANS $I(Q)$ profiles were measured obtained at $W_0 = 20, 45$ °C and 350 bar. SANS data along with the fitted $I(Q)$ functions are shown plotted in Figure 5 (or Figure S11). This $W_0$ value was chosen for comparison with the SANS data of a related double FC-tail surfactant (i.e. nFG(EO)_2 and nFS(EO)_2)/W/CO_2 microemulsions with $W_0 = 20$ reported earlier.\textsuperscript{14} The transparent single-phase displayed a SANS profile consistent with nano-scale D_2O droplets, and in the low $Q$ region < 0.01 Å⁻¹ the SANS profiles showed $D = \sim 0$, suggesting the presence of globular nanodomains. To obtain approximate µE core dimensions Guinier\textsuperscript{45} and Porod plots\textsuperscript{34} were prepared to estimate $R_g$ and $R_p$-sph values (see supporting information Figure S12). Principal sphere radii $R_g$-sph were also obtained using $R_g = (3/5)^{0.5} R_g$-sph\textsuperscript{45}, and values of $R_g$, $R_g$-sph and $R_p$-sph are displayed in Fig. S12. The polydisperse Schultz spherical model was employed at first for the analysis, but did not fit well the SANS data at low $Q < 0.03$ Å⁻¹ (Fig. S11). Hence, to test for other possible globular shapes, these $R_g$-sph values were employed as starting points for model fit analyses using a polydisperse Schultz ellipsoid form factor (oblate and prolate shapes). Theoretical curves of both ellipsoid models fitted well and gave similar fit qualities: the parameter outputs $R_{c-ell,a}$ and $R_{c-ell,b}$ shown in Fig. 5 are the average values of radii for oblate D_2O cores. Aspect ratios for the D_2O cores ($X_{core} = R_{ell-b}/R_{ell-a}$) and reverse micelles ($X_{RM} = [R_{ell-b} + l_c]/[R_{ell-a} + l_c]$, where $l_c$ is the average hydrophobic tail length 13 Å) were calculated as $X_{core} = 0.545$ and $X_{RM} = 0.683$ for oblate and $X_{core} = 2.19$ and $X_{RM} = 1.71$ for prolate types. Some earlier papers\textsuperscript{15,22} found anisotropic reverse micelles to form in scCO_2, and increase CO_2 viscosity. In the most effective case, CO_2
viscosity was expected to increase by three times with rod-like reverse micelles having a rod-length of ~880 Å.\textsuperscript{15}

There is known to be a clear relationship between viscosity and vs aspect ratio for nano-aggregates reverse micelles. To normalise for concentration, it is helpful to evaluate an intrinsic viscosity $[\eta]$ at infinite dilution. The values of $[\eta]$ and viscosity of reverse micelle/CO$_2$ solutions were estimated as follows\textsuperscript{15}. The $[\eta]$ value is sensitive linked to particle aggregate shape, for hard spheres $[\eta] = 2.5$, whereas for one-dimensional, anisotropic particles $[\eta]$ is greater than this and can be calculated using equation (1)\textsuperscript{55,56}:

$$[\eta] = 2.5 + 0.4075 \left(X_{\text{micelle}} - 1\right)^{1.508} \quad (1)$$

where $X_{\text{micelle}}$ is the aggregate aspect ratio of the aggregate, namely reverse micelle (which can be obtained by analyses of SANS data). Next $[\eta]$ can be used allows estimation of $\eta_{sp}$ based on structural parameters from SANS analyses, and the known sample volume fraction $\phi_p$. As such, equation (2) offers an approximate formula which is valid for the dilute regime system of $\phi_p < 0.2$: viscosities calculated by this way approach have been confirmed to coincide with experimental values:

$$\eta_{sp} = [\eta] \phi_p + K_H [\eta]^2 \phi_p^2 \quad (2)$$

where the $K_H$ is the Huggins coefficient for rods (in this case ~0.4)\textsuperscript{56}, calculated from the shear rate and rotational diffusion coefficient $D_{rot}$; shear rate being obtained by analytical solution of the Navier–Stokes equation and $D_{rot}$ being estimated from the SANS structural parameters and neat solution viscosity.

As the [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] molecular volume was estimated to be 750 Å$^3$ from $\nu_{FC} = 332$ Å$^3$, $\nu_{HC} = 167$ Å$^3$, $\nu_{sulf} = 117$ Å$^3$ and $\nu_{mim} = 134$ Å$^3$ in the experimental section (Sec. 2.4), the required volume fraction $\phi_p$ of reverse micelles with aqueous cores was calculated as 1.36 x 10$^{-2}$ based on the known concentrations of surfactant and D$_2$O. On the assumption that prolate reverse micelles form, equation (1) and (2) gave $[\eta] = 2.74$ and $\eta_{sp} = 0.038$ for the prolate W/CO$_2$ μE, suggesting viscosity enhancement of CO$_2$ by ~4%. Unfortunately, it is not a significant CO$_2$-thickening ability due to the low surfactant concentration and the $W_0$ value. As found with different fluorinated surfactants\textsuperscript{15}, the viscosity enhancement may improve
at higher surfactant concentration and optimal $W_0$ values by formation of long rod-like reverse micelles, which might be employed to enhance sweep efficiency in CO$_2$-enhanced oil recovery (EOR).\textsuperscript{15}

Previous SANS studies\textsuperscript{15,43}, with W/CO$_2$ μEs stabilized by double FC-tail surfactants ($n$FG(EO)$_2$ and $n$FS(EO)$_2$) and different FC lengths ($n = 4$ and 8) found spherical D$_2$O cores of radius $R = 17.9$-18.9 at $W_0 = 20$-22, 45 °C, and 350 bar. When comparing double FC-tail surfactants and [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] \((R_{\text{ell-a}}^2 R_{\text{ell-b}})^{1/3} = 24.4$-24.8 Å), the core radius for the catanionic surfactant is 1.3-1.4 times larger. The larger aqueous cores (i.e. the smaller negative curvature of W/CO$_2$ interface) suggests the catanionic has a smaller effective CPP value and/or a larger aggregation number.\textsuperscript{15,31,32,43} Considering both $n$FG(EO)$_2$ and [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] to be di-FC-chain surfactant molecules, differences in CPP and/or aggregation number are likely to come from the headgroup structure and interactions, i.e. electrostatic interactions between the anionic and catanionic headgroups, respectively.\textsuperscript{23-30}
4. Conclusions

W/CO₂ microemulsions (W/CO₂ μEs) are promising potential universal green-solvents having both polar and nonpolar solvent properties, which can be used for various applications such as extraction, dyeing, dry cleaning, metal-plating, and organic or nanomaterial synthesis. Eventually, these μEs should ideally be prepared will hopefully be available with low levels of surfactant, be inexpensive cost-effective and environmentally benign environmentally-friendly. Therefore, finding low F-content surfactants which attain with high solubilizing power is key to designing developing useful CO₂-philic surfactants.

Chemical industries using surfactants usually employ mixtures, surfactant/co-surfactant, surfactant/co-solvent or surfactant/other additives to obtain surfactant properties unavailable in only single surfactant systems. Such surfactant mixtures have also been tried in supercritical CO₂, but with only limited success: for example, in the case of a anionic hybrid surfactant FC6-HC4 mixed with an anionic double FC-tail surfactant 8FS(EO)₂ the synergism was rather weak. Therefore, the usefulness of employing surfactant mixtures was unclear.

This study explored a new set of catanionic surfactants, which can be generally considered as “mixed surfactants”. Most importantly, one of these compounds [C₆F₁₃mim][C₆F₁₃S] represents the first successful case of a catanionic surfactant for stabilization of W/CO₂ μEs, furthermore, it has a high water-solubilizing power (W₀max = ~50). It seems that a catanionic surfactant structure is a good way to generate a large CPP and a low HCB (hydrophilic-CO₂-philic balance) required for stabilizing W/CO₂ μEs. This finding of the strong synergistic effects from surfactant anion-cation pairing could be a key advance in the design of mixed surfactant systems for W/CO₂ μEs.

Formation of high water content water cut W/CO₂ μEs comprising shape-anisotropic reverse micelles could help access a new generation the next class of universal solvents with attractive characteristics unique properties. This is especially true if anisotropic reverse micelles with a high aspect ratios can be formed, since they increase CO₂ viscosity, which would help significantly improve the
efficiency of realize efficient EOR CO$_2$-flooding$^{15}$. Such anisotropic reverse micelles would also act as nanoreactors to produce anisotropic nanomaterials having interesting quantum effects.

Future efforts will be focused on effects of temperature pressure, and $W_0$ on solubilization of water and/or ionic substances, and aggregate nanostructures. This will help clarify how to generate synergistic effects with mixed catanionic systems by surfactant molecular design.
5. ASSOCIATED CONTENT

Supporting Information. Synthetic route to catanionic surfactants. Chemical structures of surfactants tested in earlier W/CO₂ microemulsion studies. Surface tension measurements of aqueous surfactant solutions. Calculation of scattering length densities for reversed micelle shells (ρ_shell), aqueous cores (ρ_core), and CO₂ (ρ_CO₂) in the D₂O/CO₂ µEs. Estimation of radius of micelles in catanionic surfactant/D₂O solutions by Guinier and Porod analyses of SANS data. Use of square well structure form factor for SANS data from catanionic surfactant micelles in water. Cloud temperatures of catanionic surfactants in water. Comparison between theoretical curves with a core-shell cylinder/disk particle model (for disk-like micelles) and core-multi-shell spherical particle model (for vesicles) with SANS data from catanionic surfactant/water mixtures. Structures of steric models and tail lengths of surfactant ions employed in catanionic surfactants. $P_{\text{trans}}$ for nFS(EO)₂ and nFG(EO)₂/W/CO₂ mixtures. FT-IR spectra of 16.7 mM surfactant/water/CO₂ mixtures with different $W₀$ values. Theoretical curves for spherical and ellipsoidal particles models fitted to the SANS profile of 16.7 mM [C₆F₁₃mim][C₆F₁₃S]/D₂O/CO₂ µE with $W₀ = 20$. Estimation of D₂O core radius in 16.7 mM [C₆F₁₃mim][C₆F₁₃S]/D₂O/CO₂ reversed micelles by Guinier and Porod analyses of SANS data.

This material is available free of charge via the Internet at “http://pubs.acs.org.”

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Notes. The authors declare no competing financial interest.

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Figure captions

Figure 1. Change in surface tension of aqueous surfactant solutions as a function of surfactant concentration at $23 \pm 0.5 \, ^\circ\text{C}$ and 1 bar. Surface tension data for $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]$ and $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]$ are taken from an earlier paper.\(^{29}\)

Figure 2. SANS profiles for surfactant/D$_2$O solutions at [surfactant]$=20 \times \text{CMC}, \, 25 \, ^\circ\text{C}$ and 1 bar. Solid lines are theoretical curves for core/shell disk form factor model with square well structure factor fitted to the experimental data (symbols).

Figure 3. Changes in $P_{\text{trans}}$ (top) and corresponding CO$_2$ density (bottom) for $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]$/water/CO$_2$ mixtures with different $W_0$ values at [surfactant]/[CO$_2$] = $8 \times 10^{-4}$ as a function of temperature.

Figure 4. FT-IR spectra of 16.7 mM $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]$/water/CO$_2$ mixtures with different $W_0$ values at 350 bar and 45 $^\circ\text{C}$.

Figure 5. SANS profile of 16.7 mM $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]/\text{D}_2\text{O}/\text{CO}_2$ $\mu\text{E}$ with $W_0 = 20$ at 45 $^\circ\text{C}$ and 350 bar. Solid line is the fitted curve for an oblate ellipsoid form factor.


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