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Water-in-CO₂ microemulsions stabilized by fluorinated cation-anion surfactant pairs

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Abstract

High water-content water-in-supercritical CO$_2$ (W/CO$_2$) 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 C$_4$-C$_6$-tails have been studied in terms of interfacial properties, aggregation behavior and solubilizing power in water and/or CO$_2$. 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/CO$_2$ microemulsions with a water-to-surfactant molar ratio up to ~50. This is the first successful demonstration of the formation of W/CO$_2$ 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/CO$_2$ microemulsions.

Keywords: Supercritical CO$_2$, Microemulsion, catanionic surfactant, Solubilizing power, Small-Angle Neutron Scattering
Introduction

Above its critical point (31.1 °C and 73.8 bar) supercritical fluid CO₂ (scCO₂) has multifarious practical applications for replacing volatile organic compounds (VOCs) and freons¹. Furthermore, scCO₂ has other attractive properties for industrial applications like inexpensiveness, inflammability, natural abundance, high mass transfer, and CO₂ density-tunable solvency¹. On the other hand, recovery of CO₂ 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 scCO₂ is currently employed for organic reactions, dry cleaning, polymerization, extraction, nanomaterial processing amongst others¹. Unfortunately, scCO₂ can realistically dissolve only nonpolar and low molecular weight (MW) compounds, and more often than not polar and/or high MW solutes are incompatible with scCO₂². Hence, enhancing the poor solubility of polar and/or high-MW compounds is a key target for developing potential applications of scCO₂. One of the most useful approaches to increase the solubility is to form molecular assemblies having hydrocarbon cores or polar cores able to solubilize those CO₂-insoluble materials. In the latter case, it would be reverse micelles with aqueous or ionic liquid (IL) nanodroplets in the scCO₂ phase, these are water-in-scCO₂ microemulsions (W/CO₂ µEs) or IL-in-scCO₂ µEs.²³ Since such thermodynamically-stable nano-dispersions exhibit the advantageous characteristics of scCO₂, 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, inorganic/organic nanocomposites production²³, amongst other applications.

In order to be considered a green and economical technology, the level of surfactants present for stabilizing µEs should be decreased as far as possible, and this needs to be balanced against that required for appropriate levels of dispersed water and/or interfacial areas in µEs for individual applications. One approach to satisfy these requirements is to develop 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 highest $W_0$ attainable in a single-phase W/CO₂ µE ($W_0^{\text{max}}$) can be 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, exploring CO\(_2\)-philic hydrocarbon (HC) surfactants for scCO\(_2\) remains an important task.\(^4\)-\(^7\) However, most commercial and popular HC surfactants are insoluble and unusable in the scCO\(_2\) solvent medium.\(^4\) 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\(_2\).\(^9\) It has been realized that conventional surfactant-design theory is inapplicable to W/CO\(_2\) systems, and that CO\(_2\)-philicity is not directly comparable to oleo-philicity. Therefore, molecular-design theory for CO\(_2\)-philic surfactants has to be advanced with new directions and paradigms in the field of surfactant chemistry. In looking for CO\(_2\)-soluble compounds, highly branched HCs \(^4\)-\(^7\), especially with methyl-branches and ester groups have been found to exhibit high solubility in scCO\(_2\). However, an efficient and cost-effective HC solubilizer for W/CO\(_2\) µEs, like the AOT utilized widely for W/O µEs\(^4\)-\(^9\) has not yet been 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 be highly soluble in CO\(_2\) and surface-active at the W/CO\(_2\) interface, promising 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 \(W_0^{\text{max}}\) values were found to be \(\sim 20\), \(\sim 80\) and \(\sim 60\), respectively.\(^9\),\(^{14,15}\)

Along with the efforts to explore and develop CO\(_2\)-philic surfactants, applied research into using W/CO\(_2\) µEs has also been conducted for nanoparticle (NP) synthesis\(^{16}\), enzymatic reactions\(^{17}\), dry cleaning\(^{18}\), and extraction\(^{19}\). However, in these applications, employing ionic surfactants often 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 via (electrostatic) attractive interactions between the headgroups and charged NP surfaces. Therefore, the NP products collected after removing CO\(_2\) usually
include surfactant residues, requiring further purification and removal processes. Since these extra processes require the use of additional solvents, overall the processes cannot be identified as truly environmentally friendly. For extraction and dry cleaning using µEs, washings and extracts are also suspected to have surfactant residue in the same manner as for NP production. For enzymatic reactions in W/CO$_2$ µEs, enzymes 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, an efficient and cost-effective CO$_2$-philic surfactant for practical applications could be tailored to contain nonionic and small 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 bind unfavorably to other materials.

On the other hand, there are some reports of low-polarity compounds for solubilizing ionic substances in liquid or supercritical CO$_2$ phase$^{3,21}$. For example, DeSimone et al.$^{21}$ demonstrated that dendrimers having FC shells dissolved in liquid CO$_2$ and solubilized an ionic dye methyl orange in the dendrimer cores. Liu et al.$^3$ reported that the fluorinated compound N-ethylperfluorooctylsulfonamide generated IL/CO$_2$ µEs with three ILs of 1,1,3,3-tetramethylguanidinium acetate, lactate and trifluoroacetate, and that these µEs solubilized ionic compounds like methyl orange, CoCl$_2$ and HAuCl$_4$. These findings show that additives with non-traditional surfactant architectures can potentially play the roles of polar solubilizers and microemulsifiers in scCO$_2$. Recently, a FC-HC compound without a headgroup (Nohead FC6-HC$n$, Figure S1 in supporting information) as an analogue of the superefficient surfactant FC6-HC$n$ was found to stabilize W/CO$_2$ µEs.$^{22}$ Even that Nohead FC6-HC4 is not formally recognized as a traditional surfactant (no identifiable head group), W/CO$_2$ µEs were formed even under a mild pressure and temperature conditions (approaching the critical point of CO$_2$), 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/CO$_2$ µEs. Unfortunately, these solubilizers were inefficient ($W_0^{\text{max}} < 10$), expensive, and therefore not really much use for applications with high water-content W/CO$_2$ 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).23-30 These unique, or improved, surfactant properties mainly come from an increased critical packing parameter (CPP)31,32 and a decreased hydrophilic-lipophilic balance (HLB)33-35 based on the strong electrostatic interactions between anionic and cationic headgroups23-30. With increasing CPP and decreasing HLB reverse micelles become more stable31-35, 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.24 For example, the reverse micelles in ternary system of the catanionic surfactant octylammoniumoctanoate, octane and water were reported to grow uniaxially as \( W_0 \) and surfactant concentration increased or the temperature decreased.30 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.30 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 studies36-40 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/CO₂ µEs.

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/CO₂ µEs. These catanionic surfactants (Table 1) have environmentally-acceptable C₄-C₆ 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$_2$ µEs as green and
universal solvents for potential applications.

Experimental Section

Materials

The catanionic surfactants used in this study were surfactant cation-anion pairs of
[C$_6$F$_{13}$mim][CF$_3$S], [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] and [C$_5$F$_{11}$mim][C$_5$F$_{11}$S] (Table 1), respectively. The
synthesis and purification of surfactants [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] and [C$_5$F$_{11}$mim][C$_5$F$_{11}$S] were reported in a
previous study.$^{35}$ [C$_6$F$_{13}$mim][CF$_3$S] was newly synthesized as described in supporting information
(Scheme S1). The individual single FC-tail surfactants with Na$^+$ or CH$_3$SO$_3^-$ (MeS: methyl sulfonate)
counterions, namely Na[C$_6$F$_{13}$S], Na[(CF$_3$)$_3$S] and MeS[C$_6$F$_{13}$mim] were also employed as a control.

Ultrapure water with a resistivity of 18.2 MΩ cm was produced by a Millipore Milli-Q Plus system. CO$_2$ of 99.99% purity was purchased from Ekika Carbon Dioxide Co., Ltd. The structures of the
steric models and the lengths of surfactants were estimated by MM2 (Molecular Mechanics program 2)
calculations (Chem 3D; CambridgeSoft Corp., Cambridge, MA).

Phase behavior observation and FT-IR spectral measurements for surfactant/scCO$_2$ mixtures

A high-pressure (HP) cell with a metal-to-glass sealed glass window (KP-308-3, Nihon Klingage
co., ltd) and a moveable piston inside the cell was employed to examine phase behaviour of
surfactant/water/scCO$_2$ mixtures by operating pressure and temperature. A detailed description of the
experimental apparatus and procedures was introduced in earlier papers.$^{9,14-16}$

Formation of W/CO$_2$ µEs was investigated by FT-IR spectroscopy with a pressure cell (volume:
1.5 cm$^3$), connected to the HP-apparatus mentioned above. The FT-IR spectra were 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 was controlled by circulating water with a thermostat bath.

Visual observation of the water/surfactant/scCO$_2$ systems was carried out at temperatures of 35 – 75 °C and pressures < 400 bar. The densities of CO$_2$ were 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 HP-cell. Then, water was loaded into the 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 ºC 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 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$_2$.

**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 ºC 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 $\times$ 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)$^{43}$. Full accounts of the scattering laws are given elsewhere$^{15,22}$.
Data have been fitted to the models described above using the SasView small-angle scattering analysis software package (http://www.sasview.org/). The fitted parameters are the core radii perpendicular to the rotation axis \( R_{f-ell,a} \) and along the rotation axis \( R_{f-ell,b} \) for ellipsoidal particles, or the core radius \( R_{sph} \) for spherical particles; these values were initially obtained by preliminary Guinier analysis \( (R_{g-sph}) \).

Catanionic 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 ºC. 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 catanionic 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 \( \rho_{FC} \), \( \rho_{HC} \) and \( \rho_{D2O} \) (\( \rho_{FC} = 3.58 \times 10^{10} \) cm\(^{-2}\), \( \rho_{HC} = -0.30 \times 10^{10} \) cm\(^{-2}\), and \( \rho_{D2O} = 6.32 \times 10^{10} \) 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 with square well structure factor.

Results and Discussion

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 \( (\gamma_{CMC}) \), surface tensions of aqueous surfactant solutions were measured at 23 ºC as a function of surfactant concentration. Tensiometric data are displayed in Figure 1 and interfacial properties (CMC and \( \gamma_{CMC} \)) 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\(_5\)F\(_{11}\)mim][C\(_5\)F\(_{11}\)S] shown in the figure and the table were previously reported. All the catanionic surfactants effectively and efficiently lowered aqueous surface tension, and finally achieved the very low limiting value at the cmc of \( \gamma_{CMC} \) 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.\textsuperscript{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\textsubscript{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 follow \( I(Q) \sim Q^{D} \), where \( D \) is a distinctive “mass fractal” for the micellar particles; hence, the 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.\textsuperscript{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 approach to obtain average radii from SANS data for the globular and disk-like micelles is via Guinier plot\textsuperscript{35} (\( \ln \{I(Q)\} \) vs \( Q^2 \)) as 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 slopes enabled 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 \( R_g^{-\text{disk}} \) as \( R_g = 4^{-0.5} R_g^{-\text{disk}} \).\textsuperscript{45} The \( R_g^{-\text{disk}} \) 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 (\( R_{p\text{-sph}} \)) obtained from the \( Q \) value at 1st maximum was also listed in Table S1 as a reference.

The values of disk radii \( R_{g\text{-disk}} \) provided by Guinier analysis were used as the starting points for model fitting with the core/shell disk/cylinder form factor models and 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\textsuperscript{-1} as discussed in supporting information S6. The fitted parameters for disk-like FC-core radius (\( R_{F\text{-Cdisk}} \)) and thickness (\( t_{F\text{-Cdisk}} \)), HC-shell thickness (\( t_{F\text{-Sdisk}} \),
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 [C₆F₁₃mim][(CF₃)₃S] was ~30 ºC, hence stabilizing a clear single solution at room temperature. However, that of the non-FC-branched surfactant [C₅F₁₁mim][C₅F₁₁S] was below 0 ºC, giving a translucent solution implying presence of larger aggregates (e.g. vesicles)⁹⁻¹². Actually, the SANS profiles for [C₃F₁₁mim][C₅F₁₁S] and [C₆F₁₃mim][C₆F₁₃S] 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 [C₆F₁₃mim][(CF₃)₃S] 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 [C₅F₁₁mim][C₅F₁₁S] and [C₆F₁₃mim][C₆F₁₃S]. However, the depth and the width for [C₆F₁₃mim][(CF₃)₃S] was smaller and larger than those of straight chain surfactants, respectively. This suggests the attractive interactions between [C₆F₁₃mim][(CF₃)₃S] micelles are not so strong. These results are consistent with the difference in cloud temperature between [C₆F₁₃mim][(CF₃)₃S] and [C₅F₁₁mim][C₅F₁₁S], namely the higher cloud temperature of [C₆F₁₃mim][(CF₃)₃S] indicates a weaker hydrophobicity and weaker attractive inter-micellar interactions.

Focusing on thicknesses of the disk-like FC-core tₐ-Cdisk and HC-shell tₐ-Shell, the total disk-thickness (tₐ-Cdisk + 2 tₐ-Shell) values are similar to twice the hydrophobic tail length of the catanionic surfactants (13.6 Å for [C₆F₁₃S], 12.3 Å for [C₆F₁₃mim] and [C₅F₁₁S], 11.0 Å for [C₅F₁₁mim], and 7.1 Å for [(CF₃)₃S]) 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 \(R_{t-Cdisk}\) increased in the order of [C₆F₁₃mim][(CF₃)₃S] < [C₆F₁₃mim][C₆F₁₃S] < [C₅F₁₁mim][C₅F₁₁S].
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)\textsuperscript{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.\textsuperscript{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)\textsuperscript{49,50} and good affinity to scCO$_2$, which are promising characteristics for stabilizing W/CO$_2$ μEs.

**Effect of catanionic surfactant structure on stabilization of reverse micelles and microemulsions in scCO$_2$**

To examine phase behaviour of catanionic surfactant/water/CO$_2$ mixtures in detail, the pressures at which clear single phases start to appear cloudy, $P_{\text{trans}}$, were measured for water/surfactant/CO$_2$ mixtures at temperatures of 35 – 75 ºC and $W_0$ values of 6 – 84. Figure 3 shows phase diagrams in terms of $P_{\text{trans}}$ and CO$_2$ density for [C$_6$F$_{13}$mim][C$_6$F$_{13}$S]/water/CO$_2$ mixtures with each $W_0$ value at [surfactant]/[CO$_2$] = 8 × 10$^{-4}$ as a function of temperature. At values higher than $P_{\text{trans}}$, [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] with [surfactant]/[CO$_2$] = 8 × 10$^{-4}$ with added water gave stable transparent systems in scCO$_2$. However, the other catanionic surfactants [C$_5$F$_{11}$mim][C$_5$F$_{11}$S] and [C$_6$F$_{13}$mim][(CF$_3$)$_3$S] always remained turbid phases or two-phase, even at the highest pressure and temperature 400 bar and 75 ºC. A simple mixture of the individual surfactants Na[C$_6$F$_{13}$S] and MeS[C$_6$F$_{13}$mim] was also tested for formation of W/CO$_2$ μE. Interestingly, the surfactant mixture was almost insoluble in scCO$_2$. 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/CO$_2$ microemulsion formation.
With increasing temperature from 35 °C to 75 °C, $P_{\text{trans}}$ increased by 80-110 bar but the CO$_2$ density decreased by 0.9-1.3 g cm$^{-3}$. Solubility of a compound in scCO$_2$ is known to mainly depend on CO$_2$ density (rather than pressure per say), resulting in an increase in solvating CO$_2$ molecules.$^{1-16}$ Higher temperatures (higher thermal motion and weaker interactions between surfactant molecules) are expected to enable generation of W/CO$_2$ microemulsion at lower CO$_2$ densities.$^{1-16}$ Increasing $W_0$ feeds through to an increase in $P_{\text{trans}}$ ($W_0 = 36$ from to 48). Significant increase in $P_{\text{trans}}$ with increasing $W_0$ was also reported in the use of high HCB surfactants like CO$_2$-soluble HC-surfactants or short FC-surfactants (e.g. CF$_3$(CF$_2$)$_n$ with $n = 0$ - 3)$^{41}$, and it could be caused by greater CO$_2$ solvation of the surfactant tails.$^{1-16}$ Based on the phase behaviour observations, transparent phases identified as W/CO$_2$ μEs were observed at pressures > 260 bar (CO$_2$ density > 0.84 g cm$^{-3}$), even with the very high $W_0$ value of 84. However, this is not really clear evidence for formation of Winsor IV-type W/CO$_2$ μEs at these large $W_0$ values (up to 84), and it is possible that transparent phases with high $W_0$ values may be Winsor II-type (albeit with the excess water phase out of view, and below the pressure cell windows).

Comparing the $P_{\text{trans}}$ values at $W_0 = 10$ for the double-FC-tail surfactants $n$FS(EO)$_2$ and $n$FG(EO)$_2$ ($n = 4, 6, 8$) as shown in Figure S9 (supporting information)$^{14}$, to those at $W_0 = 12$ for [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] shows they are quite similar, especially to 6FG(EO)$_2$. It suggests the same FC-length surfactants [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] and 6FG(EO)$_2$ have similar CO$_2$-philicity (or HCB) and ability to stabilize W/CO$_2$ 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 $W_0$ values > 10 is consistent with the formation of W/CO$_2$ μEs. To explore formation of hydrogen bonded μE water cores, FT-IR spectra were recorded of 16.7 mM surfactant/H$_2$O/CO$_2$ mixtures with different $W_0$ 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.$^{52,53}$ A seen in Figures 4 and S10 absorbance over 3100-3500 cm$^{-1}$ in the FT-IR spectra increased with increasing added water $W_0$.

These spectra and the changes with increasing $W_0$ are very similar to those for W/CO$_2$ μEs formed by
anionic fluorinated surfactants FC6-HC4 and 8FS(EO)\(_2\).\(^{53}\) The absorbance for the [C\(_6\)F\(_{13}\)mim][C\(_6\)F\(_{13}\)S]/W/CO\(_2\) μEs grew with \(W_0\) up until \(W_0 = 50\), suggesting a maximum water-solubilizing power \(W_{0\text{ max}} \sim 50\). In contrast with the behavior for [C\(_6\)F\(_{13}\)mim][C\(_6\)F\(_{13}\)S], there were no changes in FT-IR spectra for [C\(_6\)F\(_{13}\)mim][(CF\(_3\))\(_3\)S] and [C\(_5\)F\(_{11}\)mim][C\(_5\)F\(_{11}\)S] even on increasing \(W_0\) from 10.2 up to 30.6 (Fig. S10). The parent surfactant with a sodium counterion Na[C\(_6\)F\(_{13}\)S] did not show any clear absorbance in the water OH stretching region (Fig. S10).

It is intriguing why [C\(_6\)F\(_{13}\)mim][C\(_6\)F\(_{13}\)S] can stabilize μEs whereas the other surfactants do not, especially since the differences in chemical structures are so small: just two more -CF\(_2\)- units for [C\(_6\)F\(_{13}\)mim][C\(_6\)F\(_{13}\)S] compared to the other catanionics. The longer fluorocarbon tails of [C\(_6\)F\(_{13}\)mim][C\(_6\)F\(_{13}\)S] are expected to produce a higher CO\(_2\)-philicity and a higher solubility in scCO\(_2\).\(^{1-16}\) 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\(_6\)F\(_{13}\)mim][C\(_6\)F\(_{13}\)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)\(_2\).\(^{1-16}\) This appears to be the first case of a highly effective CO\(_2\)-philic surfactant based on ion-pairing of anionic and cationic single FC-tail surfactants, and especially interesting for its environmental acceptability.

To demonstrate the [C\(_6\)F\(_{13}\)mim][C\(_6\)F\(_{13}\)S]/D\(_2\)O/CO\(_2\) μEs, SANS \(I(Q)\) profiles were obtained at \(W_0 = 20, 45\) °C and 350 bar. SANS data along with the fitted \(I(Q)\) functions are 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. \(n\)FG(EO)\(_2\) and \(n\)FS(EO)\(_2\))/W/CO\(_2\) microemulsions with \(W_0 = 20\) reported earlier.\(^{14}\) The transparent single-phase displayed a SANS profile consistent with nano-scale D\(_2\)O 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\(^{45}\) and Porod plots\(^{54}\) were prepared to estimate \(R_g\) and \(R_{p\text{-sph}}\) values (see supporting information Figure S12). Principal sphere radii \(R_{g\text{-sph}}\) were also obtained using \(R_g = (3/5)^{0.5} R_{g\text{-sph}}^{45}\), and values of \(R_g\), \(R_{g\text{-sph}}\) and \(R_{p\text{-sph}}\) 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 $R_{f-ell,a}$ and $R_{f-ell,b}$ shown in Fig. 5 are the average radii for oblate D$_2$O cores. Aspect ratios for the D$_2$O 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$^{15,22}$ 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.$^{15}$

There is known to be a clear trend in viscosity vs aspect ratio for nano-aggregates. 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$^{15}$. The [$\eta$] value is linked to aggregate shape, for hard spheres [$\eta$] = 2.5, whereas for one-dimensional, anisotropic particles [$\eta$] is larger than this and can be calculated using equation (1)$^{55,56}$:

$$\eta = 2.5 + 0.4075 \times (X_{micelle} - 1)^{1.508}$$

where $X_{micelle}$ is the aggregate aspect ratio (which can be obtained by analyses of SANS data). Next [$\eta$] allows estimation of $\eta_{sp}$ using structural parameters from SANS analyses, and the known sample volume fraction $\phi_p$. As such, equation (2) offers an approximate formula which is appropriate for the dilute system of $\phi_p < 0.2$: viscosities calculated by this approach have been demonstrated to coincide with experimental values$^{57}$.

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

where the $K_H$ is the Huggins coefficient for rods (in this case ~0.4)$^{56}$, 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 $v_FC = 332$ Å$^3$, $v_HC = 167$ Å$^3$

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\[ v_{\text{sulf}} = 117 \, \text{Å}^3 \text{ and } v_{\text{mim}} = 134 \, \text{Å}^3 \] in the experimental section (Sec. 2.4), the required volume fraction \( \phi \) of reverse micelles with aqueous cores was calculated as \( 1.36 \times 10^{-2} \) 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 \( \eta_{\text{sp}} = 0.038 \) for the prolate W/CO\(_2\) \( \mu \)E, suggesting viscosity enhancement of CO\(_2\) by \( \sim 4\% \). 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\(^{15}\), 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).\(^{15}\)

Previous SANS studies\(^{15,43}\), with W/CO\(_2\) \( \mu \)Es stabilized by double FC-tail surfactants \( (n\text{FG}(\text{EO})_2 \text{ and } n\text{FS}(\text{EO})_2) \) and different FC lengths \( (n = 4 \text{ and } 8) \) found spherical D\(_2\)O cores of radius \( R = 17.9-18.9 \) at \( W_0 = 20-22, \, 45 \, ^\circ \text{C} \), and 350 bar. When comparing double FC-tail surfactants and \( [\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}] \) \( ((R_{\text{ell}}-a^2 \, R_{\text{ell-b}})^{1/3} = 24.4-24.8 \, \text{Å} \), 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.\(^{15,31,32,43}\) Considering both \( n\text{FG}(\text{EO})_2 \) and \( [\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}] \) 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.\(^{23-30}\)

Conclusions

W/CO\(_2\) microemulsions (W/CO\(_2\) \( \mu \)Es) are potential universal green-solvents having both polar and nonpolar solvent properties, which can be used for various chemical applications as mentioned in the Introduction.\(^2,3\) Eventually, these \( \mu \)Es will hopefully be available with low levels of surfactant, be cost-effective and environmentally-friendly. Therefore, finding low F-content surfactants with high solubilizing power is key to developing useful CO\(_2\)-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.\(^{23-30,35-40}\) Such surfactant mixtures have also been tried in supercritical CO\(_2\), but
with only limited success\textsuperscript{53,58}; for example, in the case of a anionic hybrid surfactant FC6-HC4 mixed with an anionic double FC-tail surfactant 8FS(EO)\textsubscript{2} the synergism was rather weak.\textsuperscript{53} 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 [C\textsubscript{6}F\textsubscript{13}mim][C\textsubscript{6}F\textsubscript{13}S] represents the first successful case of a catanionic surfactant for stabilization of W/CO\textsubscript{2} \textmu Es, furthermore, it has a high watersolubilizing power (W\textsubscript{0}\textsubscript{max} = \sim 50). It seems that a catanionic surfactant structure is a good way to generate a large CPP and a low HCB (hydrophilic-CO\textsubscript{2}-philic balance) required for stabilizing W/CO\textsubscript{2} \textmu Es. 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/CO\textsubscript{2} \textmu Es.

Formation of W/CO\textsubscript{2} \textmu Es comprising shape-anisotropic reverse micelles could help access the next class of universal solvents with attractive characteristics. This is especially true if anisotropic reverse micelles with high aspect ratios can be formed, since they increase CO\textsubscript{2} viscosity, which would help realize efficient EOR CO\textsubscript{2}-flooding\textsuperscript{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\textsubscript{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.

ASSOCIATED CONTENT

Supporting Information. Synthetic route to catanionic surfactants. Chemical structures of surfactants tested in earlier W/CO\textsubscript{2} microemulsion studies. Surface tension measurements of aqueous surfactant solutions. Calculation of scattering length densities for reversed micelle shells (\rho_{shell}), aqueous cores (\rho_{core}), and CO\textsubscript{2} (\rho_{CO2}) in the D\textsubscript{2}O/CO\textsubscript{2} \textmu Es. Estimation of radius of micelles in catanionic surfactant/D\textsubscript{2}O 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 $nFG(EO)_2/W/CO_2$ mixtures. FT-IR spectra of 16.7 mM surfactant/water/CO$_2$ mixtures with different $W_0$ values. Theoretical curves for spherical and ellipsoidal particles models fitted to the SANS profile of 16.7 mM $[C_6F_{13}\text{mim}][C_6F_{13}\text{S}]/D_2O/CO_2 \mu E$ with $W_0 = 20$. Estimation of D$_2$O core radius in 16.7 mM $[C_6F_{13}\text{mim}][C_6F_{13}\text{S}]/D_2O/CO_2$ 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 ± 0.5 ºC and 1 bar. Surface tension data for [C₆F₁₃mim][C₆F₁₃S] and [C₆F₁₃mim][C₆F₁₃S] are taken from an earlier paper.²⁹

**Figure 2.** SANS profiles for surfactant/D₂O solutions at [surfactant]=20 × CMC, 25 ºC 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 CO₂ density (bottom) for [C₆F₁₃mim][C₆F₁₃S]/water/CO₂ mixtures with different $W₀$ values at [surfactant]/[CO₂] = 8 × 10⁻⁴ as a function of temperature.

**Figure 4.** FT-IR spectra of 16.7mM [C₆F₁₃mim][C₆F₁₃S]/water/CO₂ mixtures with different $W₀$ values at 350 bar and 45 ºC.

**Figure 5.** SANS profile of 16.7 mM [C₆F₁₃mim][C₆F₁₃S]/D₂O/CO₂ μE with $W₀ = 20$ at 45 ºC and 350 bar. Solid line is the fitted curve for an oblate ellipsoid form factor.
References


SYNOPSIS TOC

Ionic single FC₆-tail surfactants with high HCB & small CPP

In supercritical CO₂
Solubility
Reverse micelle formation
Water solubilization
No or Very poor

In water
Surface activity
Lowering surface energy
Normal

Cationic surfactant with low HLB (HCB) & large CPP

Synergistic effect !!
Excellent

W/CO₂ microemulsions as a Green & Universal Solvent
**Figure 1** Change in surface tension of aqueous surfactant solutions as a function of surfactant concentration at 23 °C and 1 bar. Surface tension data for [C\textsubscript{6}F\textsubscript{13}mim][C\textsubscript{6}F\textsubscript{13}S] and [C\textsubscript{6}F\textsubscript{13}mim][C\textsubscript{6}F\textsubscript{13}S] are taken from an earlier paper.\textsuperscript{29}
Figure 2 SANS profiles for surfactant/D$_2$O solutions at [surfactant]=20 x CMC, 25 ºC 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 [C$_6$F$_{13}$mim][C$_6$F$_{13}$S] /water/CO$_2$ mixtures with different $W_0$ values at [surfactant]/[CO$_2$] = 8 x 10$^{-4}$ as a function of temperature.
Figure 4 FT-IR spectra of 16.7 mM [C$_6$F$_{13}$mim][C$_6$F$_{13}$S]/water/CO$_2$ mixtures with different $W_0$ values at 350 bar and 45 °C.
Figure 5 SANS profile of 16.7 mM [C₆F₁₃mim][C₆F₁₃S]/D₂O/CO₂ μE with $W_0 = 20$ at 45 °C and 350 bar. Solid line is the fitted curve for an oblate ellipsoid form factor.
Table 1 Chemical structures of surfactant ions.

<table>
<thead>
<tr>
<th>Chemical Structure</th>
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<tbody>
<tr>
<td>$[\text{C}<em>6\text{F}</em>{13}\text{S}]$</td>
<td>$[\text{C}<em>6\text{F}</em>{13}\text{mim}]$</td>
</tr>
<tr>
<td>$[\text{C}<em>5\text{F}</em>{11}\text{S}]$</td>
<td>$[\text{C}<em>5\text{F}</em>{11}\text{mim}]$</td>
</tr>
<tr>
<td>$[(\text{CF})_3\text{S}]$</td>
<td>$[(\text{CF})_3\text{C}]$</td>
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Table 1: Chemical structures of surfactant ions.
Table 2 Properties of aqueous surfactant solutions at 25 °C and 1 bar

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>CMC / mM</th>
<th>$\gamma_{\text{CMC}}$ / (mN m$^{-1}$)</th>
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<tbody>
<tr>
<td>$[\text{C}<em>6\text{F}</em>{13}\text{mim}][\text{C}<em>6\text{F}</em>{13}\text{S}]$</td>
<td>0.8-1.1 $\times 10^{-1}$</td>
<td>13.5</td>
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<tr>
<td>$[\text{C}<em>5\text{F}</em>{11}\text{mim}][\text{C}<em>5\text{F}</em>{11}\text{S}]$</td>
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<td>15.3</td>
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<td>$[\text{C}<em>6\text{F}</em>{13}\text{mim}][(\text{CF}_3)_3\text{S}]$</td>
<td>1.0</td>
<td>16.8</td>
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<tr>
<td>$\text{Na}[\text{C}<em>6\text{F}</em>{13}\text{S}]$</td>
<td>$1.3 \times 10^{1}$</td>
<td>22.6</td>
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<tr>
<td>$\text{Na}[(\text{CF}_3)_3\text{S}]$</td>
<td>$1.3 \times 10^{2}$</td>
<td>25.7</td>
</tr>
</tbody>
</table>

CMC and $\gamma_{\text{CMC}}$ 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 the earlier paper$^{29}$
Table 3 FC-core radius ($R_{f-C_{disk}}$) and thickness ($t_{f-C_{disk}}$), HC-shell thickness ($t_{f-S_{disk}}$), aspect ratio, well depth and width for catanionic surfactant disk-like micelles in D$_2$O at [Surfactant] = 20 x CMC, 25 ºC and 1 bar, obtained by SANS data analysis with theoretical curves for core/shell disk form factor model with square well structure factor, and cloud temperatures.

<table>
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<tr>
<th>Surfactant</th>
<th>$R_{f-C_{disk}}$ / Å</th>
<th>$t_{f-C_{disk}}$ / Å</th>
<th>$t_{f-Shell}$ / Å</th>
<th>Aspect ratio</th>
<th>Well depth / kT</th>
<th>Well width</th>
<th>Cloud temp / ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C$<em>5$F$</em>{11}$mim][C$<em>5$F$</em>{11}$S]</td>
<td>2180</td>
<td>12.0</td>
<td>5.0</td>
<td>0.003</td>
<td>1.5</td>
<td>1.0</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>[C$<em>6$F$</em>{13}$mim][C$<em>6$F$</em>{13}$S]</td>
<td>636</td>
<td>13.3</td>
<td>4.7</td>
<td>0.010</td>
<td>1.5</td>
<td>1.0</td>
<td>–</td>
</tr>
<tr>
<td>[C$<em>6$F$</em>{13}$mim][(CF$_3$)$_3$S]</td>
<td>130</td>
<td>11.5</td>
<td>5.0</td>
<td>0.045</td>
<td>0.3</td>
<td>2.8</td>
<td>29.8</td>
</tr>
</tbody>
</table>