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Sagisaka, M., Saito, T., Yoshizawa, A., Rogers, S. E., Guittard, F., Hill, C., Eastoe, J., & Blesic, M. (2019). Water-in-CO₂ microemulsions stabilized by fluorinated cation-anion surfactant pairs. *Langmuir*, 35(9), 3445. <https://doi.org/10.1021/acs.langmuir.8b03942>

Published in:
Langmuir

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
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Langmuir, **Just Accepted Manuscript** • DOI: 10.1021/acs.langmuir.8b03942 • Publication Date (Web): 11 Feb 2019

Downloaded from <http://pubs.acs.org> on February 11, 2019

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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 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

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 μ Es) or IL-in-scCO₂ μ Es.^{2,3} 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 production^{2,3}, amongst other applications.

In order to be considered a green and economical technology, the level of surfactants present for stabilizing μ Es 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 μ Es for individual applications. One approach to satisfy these requirements is to develop super-efficient surfactant stabilizers and solubilizers for the μ Es. 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 μ E (W_0^{max}) can be called the water-solubilizing power of the surfactant. (As such W_0^{max} represents the

maximum number of water molecules which can be solubilized by one surfactant molecule). The studies aiming to find efficient CO₂-philic solubilizers started in the 1990s⁴ and continue nowadays⁵⁻¹⁵.

Therefore, exploring CO₂-philic hydrocarbon (HC) surfactants for scCO₂ remains an important task.⁴⁻⁷ However, most commercial and popular HC surfactants are insoluble and unusable in the scCO₂ 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 $W_0^{\max}$ values in water-in-oil μ Es (e.g. $W_0^{\max} = \sim 80$ in *n*-heptane at 25 °C)⁸, $W_0^{\max}$ was found to be zero in dense scCO₂.⁹ It has been realized that conventional surfactant-design theory is inapplicable to W/CO₂ systems, and that CO₂-philicity is not directly comparable to oleo-philicity. Therefore, molecular-design theory for CO₂-philic surfactants has to be advanced with new directions and paradigms in the field of surfactant chemistry. In looking for CO₂-soluble compounds, highly branched HCs⁴⁻⁷, especially with methyl-branches and ester groups have been found to exhibit high solubility in scCO₂. However, an efficient and cost-effective HC solubilizer for W/CO₂ μ Es, like the AOT utilized widely for W/O μ Es⁴⁻⁹ 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 CO₂ and surface-active at the W/CO₂ interface, promising formation of W/CO₂ μ Es.⁹⁻¹⁵ In the cases of the PFPE surfactant (PFPECOONH₄), the hybrid surfactant FC6-HC4 and the double perfluorooctyl tail surfactant 8FG(EO)₂ (**Figure S1** in supporting information), the $W_0^{\max}$ values were found to be ~ 20 , ~ 80 and ~ 60 , respectively.^{9,14,15}

Along with the efforts to explore and develop CO₂-philic surfactants, applied research into using W/CO₂ μ Es has also been conducted for nanoparticle (NP) synthesis¹⁶, enzymatic reactions¹⁷, dry cleaning¹⁸, and extraction¹⁹. However, in these applications, employing ionic surfactants often leads to disadvantages. For example, in NP synthesis¹⁶ of ZnS, CdS, and TiO₂ using W/CO₂ μ Es, 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 CO₂ usually

1 include surfactant residues, requiring further purification and removal processes. Since these extra
2 processes require the use of additional solvents, overall the processes cannot be identified as truly
3 environmentally friendly. For extraction and dry cleaning using μ Es, washings and extracts are also
4 suspected to have surfactant residue in the same manner as for NP production. For enzymatic reactions in
5 W/ CO_2 μ Es, enzymes are known to be deactivated/denatured by ionic surfactants²⁰. These problems will
6 always crop up in applications using ionic surfactant-stabilized μ Es. Keeping these limitations in mind,
7 an efficient and cost-effective CO_2 -philic surfactant for practical applications could be tailored to contain
8 nonionic and small headgroups (i.e. not a conventional poly(ethylene oxide) (PEO) group with a high
9 MW) that are CO_2 -philic, whilst being less polar and therefore less likely to bind unfavorably to other
10 materials.
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23 On the other hand, there are some reports of low-polarity compounds for solubilizing ionic
24 substances in liquid or supercritical CO_2 phase^{3,21}. For example, DeSimone *et al.*²¹ demonstrated that
25 dendrimers having FC shells dissolved in liquid CO_2 and solubilized an ionic dye methyl orange in the
26 dendrimer cores. Liu *et al.*³ reported that the fluorinated compound N-ethylperfluorooctylsulfonamide
27 generated IL/ CO_2 μ Es with three ILs of 1,1,3,3-tetramethylguanidinium acetate, lactate and
28 trifluoroacetate, and that these μ Es solubilized ionic compounds like methyl orange, CoCl_2 and HAuCl_4 .
29 These findings show that additives with non-traditional surfactant architectures can potentially play the
30 roles of polar solubilizers and microemulsifiers in scCO_2 . Recently, a FC-HC compound without a
31 headgroup (Nohead FC6-HC n , **Figure S1** in supporting information) as an analogue of the superefficient
32 surfactant FC6-HC n was found to stabilize W/ CO_2 μ Es.²² Even that Nohead FC6-HC4 is not formally
33 recognized as a traditional surfactant (no identifiable head group), W/ CO_2 μ Es were formed even under a
34 mild pressure and temperature conditions (approaching the critical point of CO_2), whereas similar
35 analogues with different HC-tail lengths did not form μ Es. Those nonionic solubilizers introduced above
36 are likely to adhere to target materials in the applications of W/ CO_2 μ Es. Unfortunately, these solubilizers
37 were inefficient ($W_0^{\text{max}} < 10$), expensive, and therefore not really much use for applications with high
38 water-content W/ CO_2 μ Es.
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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 μ Es.

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 μ E 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 μ 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/CO₂ μ Es. 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 scCO₂ and properties of the μ E droplets. The results help identify important design criteria for inexpensive and environmental-friendly catanionic surfactants to stabilize W/CO₂ μ Es as green and universal solvents for potential applications.

Experimental Section

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 M Ω cm was produced by a Millipore Milli-Q Plus system. CO₂ 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/scCO₂ 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/scCO₂ 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/CO₂ μ Es was investigated by FT-IR spectroscopy with a pressure cell (volume: 1.5 cm³), 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/scCO₂ systems was carried out at temperatures of 35 – 75 °C and pressures < 400 bar. The densities of CO₂ were estimated using the Span-Wagner equation of state (EOS)⁴¹. Pre-determined amounts of surfactant and CO₂ (20.0g), where the molar ratio of surfactant to CO₂ was fixed at 8×10^{-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/CO₂ µE (i.e. single-phase W/CO₂ 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 scCO₂ 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 scCO₂ were assumed to be equivalent to those of pure CO₂.

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 CO₂. The HP-SANS measurements of the D₂O/surfactant/scCO₂ 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 ($\text{\AA}^{-1}$), which is defined as $Q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The accessible Q range was $0.002\text{--}1 \text{ \AA}^{-1}$ on SANS2D arising from an incident neutron wavelength, λ , of $2.2\text{--}10 \text{ \AA}$. 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_2O and surfactant, where the molar ratio of surfactant to CO_2 was fixed at 8.0×10^{-4} ($= 16.7 \text{ mM}$ 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_2O / 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 ($\text{W}/\text{CO}_2 \text{ }\mu\text{E}$) or a turbid phase. Finally, the HP-SANS experiments were performed for not only single-phase $\text{W}/\text{CO}_2 \mu\text{Es}$, but also the turbid phases formed below the cloud point phase transition pressure P_{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 (ρ_{shell}), aqueous cores (ρ_{core}), and CO_2 (ρ_{CO_2}) in the $\text{D}_2\text{O}/\text{CO}_2 \mu\text{E}$ were calculated as $\rho_{\text{shell}} = 2.28 \times 10^{10} \text{ cm}^{-2}$, $\rho_{\text{core}} = 4.92 \times 10^{10} \text{ cm}^{-2}$, and $\rho_{\text{CO}_2} = 2.29 \times 10^{10} \text{ cm}^{-2}$ as shown in supporting information (see **S4**). As ρ_{shell} was close to ρ_{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 $\text{D}_2\text{O}/\text{CO}_2 \mu\text{Es}$ was assumed to only be from the so-called aqueous core contrast. For model fitting data analysis, the $\text{W}/\text{CO}_2 \mu\text{E}$ droplets were treated as spherical or ellipsoidal particles with a Schultz distribution in core radii⁴². The polydispersities in spherical and ellipsoid radii were fixed at 0.3 as found in spherical $\text{D}_2\text{O}/\text{CO}_2 \mu\text{Es}$ with the double FC-tail surfactants (polydispersity = 0.17-0.40)⁴³. Full accounts of the scattering laws are given elsewhere^{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/>)⁴⁴. 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})⁴⁵.

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 $\lambda = 6 \text{ \AA}$ and two sample detector positions (2 and 7.5 m) providing an accessible Q range of $0.005\text{--}0.2 \text{ \AA}^{-1}$. All samples were made in D_2O using 2 mm path length rectangular quartz cells at $25 \text{ }^\circ\text{C}$. Raw SANS data were reduced by subtracting the scattering of the empty cell and D_2O 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 ρ_{FC} , ρ_{HC} and ρ_{D_2O} ($\rho_{FC} = 3.58 \times 10^{10} \text{ cm}^{-2}$, $\rho_{HC} = -0.30 \times 10^{10} \text{ cm}^{-2}$, and $\rho_{D_2O} = 6.32 \times 10^{10} \text{ cm}^{-2}$ as shown in supporting information S4). Then SANS data for micelles in D_2O were analysed with theoretical curves for a core/shell cylinder/disk particle form factor⁴⁶ 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 (γ_{CMC}), surface tensions of aqueous surfactant solutions were measured at $23 \text{ }^\circ\text{C}$ as a function of surfactant concentration. Tensiometric data are displayed in **Figure 1** and interfacial properties (CMC and γ_{CMC}) estimated from these data are listed in **Table 2**. The surface tension data and interfacial properties of $[C_6F_{13}mim][C_6F_{13}S]$ and $[C_5F_{11}mim][C_5F_{11}S]$ shown in the figure and the table were previously reported³⁵. All the catanionic surfactants effectively and efficiently lowered aqueous surface tension, and finally achieved the very low limiting value at the cmc of γ_{CMC} of $13.5\text{--}16.8 \text{ mN/m}$ at concentrations $< 1 \text{ mM}$. 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_2O were examined at a surfactant concentration of $20 \times \text{CMC}$ 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.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 plot³⁵ ($\ln [I(Q)]$ 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 $R_g = 4^{-0.5} R_{g\text{-disk}}$.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 $< 0.02 \text{ \AA}^{-1}$ 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 $20 \times \text{CMC}$ 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 $[\text{C}_6\text{F}_{13}\text{mim}][(\text{CF}_3)_3\text{S}]$ was $\sim 30^\circ\text{C}$, hence stabilizing a clear single solution at room temperature. However, that of the non-FC-branched surfactant $[\text{C}_5\text{F}_{11}\text{mim}][\text{C}_5\text{F}_{11}\text{S}]$ was below 0°C , giving a translucent solution implying presence of larger aggregates (*e.g.* vesicles)²³⁻²⁶. Actually, the SANS profiles for $[\text{C}_5\text{F}_{11}\text{mim}][\text{C}_5\text{F}_{11}\text{S}]$ and $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]$ 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 $[\text{C}_6\text{F}_{13}\text{mim}][(\text{CF}_3)_3\text{S}]$ 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 of 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. These 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 $t_{\text{F-Cdisk}}$ and HC-shell $t_{\text{F-Shell}}$, the total disk-thickness ($t_{\text{F-Cdisk}} + 2 t_{\text{F-Shell}}$) 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 $[\text{C}_6\text{F}_{13}\text{mim}]$ and $[\text{C}_5\text{F}_{11}\text{S}]$, 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 $R_{\text{F-Cdisk}}$ 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 $\gg$ 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 γ_{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-CO₂-philic balance (HCB)^{49,50} and good affinity to scCO₂, which are promising characteristics for stabilizing W/CO₂ μ Es.

Effect of catanionic surfactant structure on stabilization of reverse micelles and microemulsions in scCO₂

To examine phase behaviour of catanionic surfactant/water/CO₂ mixtures in detail, the pressures at which clear single phases start to appear cloudy, P_{trans} , were measured for water/surfactant/CO₂ mixtures at temperatures of 35 – 75 °C and W_0 values of 6 – 84. **Figure 3** shows phase diagrams in terms of P_{trans} and CO₂ density for [C₆F₁₃mim][C₆F₁₃S]/water/CO₂ mixtures with each W_0 value at [surfactant]/[CO₂] = 8×10^{-4} as a function of temperature. At values higher than P_{trans} , [C₆F₁₃mim][C₆F₁₃S] with [surfactant]/[CO₂] = 8×10^{-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 μ E. 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_{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.¹⁻¹⁶ Higher temperatures (higher thermal motion and weaker interactions between surfactant molecules) are expected to enable generation of W/CO₂ microemulsion at lower CO₂ densities.¹⁻¹⁶ Increasing W_0 feeds through to an increase in P_{trans} ($W_0 = 36$ from to 48). Significant increase in P_{trans} with increasing W_0 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.¹⁻¹⁶ 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 W_0 value of 84. However, this is not really clear evidence for formation of Winsor IV-type W/CO₂ 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_{trans} values at $W_0 = 10$ for the double-FC-tail surfactants $n\text{FS}(\text{EO})_2$ and $n\text{FG}(\text{EO})_2$ (*n* = 4, 6, 8) as shown in **Figure S9** (supporting information)¹⁴, to those at $W_0 = 12$ 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 W_0 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 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} As 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/CO₂ μEs formed by

anionic fluorinated surfactants FC6-HC4 and 8FS(EO)₂.⁵³ The absorbance for the [C₆F₁₃mim][C₆F₁₃S]/W/CO₂ μEs grew with W_0 up until $W_0 = 50$, suggesting a maximum water-solubilizing power $W_0^{\max} \sim 50$. In contrast with the behavior for [C₆F₁₃mim][C₆F₁₃S], there were no changes in FT-IR spectra for [C₆F₁₃mim][(CF₃)₃S] and [C₅F₁₁mim][C₅F₁₁S] even on increasing W_0 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 scCO₂.¹⁻¹⁶ Hence, the total number of fluorinated carbons C₁₂ per surfactant may represent a lower limit for the catanionic surfactant to achieve good compatibility with scCO₂, whereas a smaller number of fluorinated carbons is insufficient. With an impressive water-solubilizing power $W_0^{\max} = \sim 50$ of [C₆F₁₃mim][C₆F₁₃S] can be identified as a superefficient CO₂-philic surfactant for W/CO₂ 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 CO₂-philic surfactant based on ion-pairing of anionic and cationic single FC-tail surfactants, and especially interesting for its environmental acceptability.

To demonstrate the [C₆F₁₃mim][C₆F₁₃S]/D₂O/CO₂ 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/CO₂ microemulsions with $W_0 = 20$ reported earlier.¹⁴ The transparent single-phase displayed a SANS profile consistent with nano-scale D₂O droplets, and in the low Q region $< 0.01 \text{ \AA}^{-1}$ the SANS profiles showed $D = \sim 0$, suggesting the presence of globular nanodomains. To obtain approximate μE core dimensions Guinier⁴⁵ and Porod plots⁵⁴ 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 $Q < 0.03 \text{ \AA}^{-1}$ (**Fig. S11**). Hence, to test for other possible globular shapes, these $R_{g\text{-sph}}$ 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 $R_{f\text{-ell,a}}$ and $R_{f\text{-ell,b}}$ shown in **Fig. 5** are the average radii for oblate D₂O cores. Aspect ratios for the D₂O cores ($X_{\text{core}} = R_{\text{ell-b}} / R_{\text{ell-a}}$) and reverse micelles ($X_{\text{RM}} = \{R_{\text{ell-b}} + l_c\} / \{R_{\text{ell-a}} + l_c\}$, where l_c is the average hydrophobic tail length 13 Å) were calculated as $X_{\text{core}} = 0.545$ and $X_{\text{RM}} = 0.683$ for oblate and $X_{\text{core}} = 2.19$ and $X_{\text{RM}} = 1.71$ for prolate types. Some earlier papers^{15,22} found anisotropic reverse micelles to form in scCO₂, and increase CO₂ viscosity. In the most effective case, CO₂ 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/CO₂ solutions were estimated as follows¹⁵. 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}:

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

where X_{micelle} is the aggregate aspect ratio (which can be obtained by analyses of SANS data). Next $[\eta]$ allows estimation of η_{sp} using structural parameters from SANS analyses, and the known sample volume fraction ϕ_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 values⁵⁷.

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

where the K_H is the Huggins coefficient for rods (in this case ~0.4)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 [C₆F₁₃mim][C₆F₁₃S] molecular volume was estimated to be 750 Å³ from $v_{\text{FC}} = 332 \text{ \AA}^3$, $v_{\text{HC}} = 167 \text{ \AA}^3$

$v_{\text{sulf}} = 117 \text{ \AA}^3$ and $v_{\text{mim}} = 134 \text{ \AA}^3$ in the experimental section (Sec. 2.4), the required volume fraction ϕ_p of reverse micelles with aqueous cores was calculated as 1.36×10^{-2} based on the known concentrations of surfactant and D_2O . 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 μE , 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 surfactants¹⁵, 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 μEs stabilized by double FC-tail surfactants ($n\text{FG}(\text{EO})_2$ and $n\text{FS}(\text{EO})_2$) and different FC lengths ($n = 4$ and 8) found spherical D_2O cores of radius $R = 17.9\text{--}18.9$ at $W_0 = 20\text{--}22$, 45°C , and 350 bar. When comparing double FC-tail surfactants and $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]$ ($(R_{\text{ell-a}}^2 R_{\text{ell-b}})^{1/3} = 24.4\text{--}24.8 \text{ \AA}$), 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 μEs) 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 μEs 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^{53,58}: 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.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 [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 ($W_0^{\max} = \sim 50$). 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 W/CO₂ μEs 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 CO₂ viscosity, which would help realize efficient EOR CO₂-flooding¹⁵. 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.

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_{CO_2}) 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_{trans} for $n\text{FS}(\text{EO})_2$ and $n\text{FG}(\text{EO})_2/\text{W}/\text{CO}_2$ 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 $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]/\text{D}_2\text{O}/\text{CO}_2$ μE with $W_0 = 20$. Estimation of D_2O core radius in 16.7 mM $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]/\text{D}_2\text{O}/\text{CO}_2$ 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.

ACKNOWLEDGEMENT

This project was supported by JSPS [KAKENHI, Grant-in-Aid for Scientific Research (B), No. 26289345, Grant-in-Aid for Challenging Exploratory Research, No. 26630383, Grant-in-Aid for Challenging Research (Exploratory), No.17K19002], and Leading Research Organizations (RCUK [through EPSRC EP/I018301/1], ANR [13-G8ME-0003]) under the G8 Research Councils Initiative for Multilateral Research Funding–G8-2012. We also acknowledge STFC for the allocation of beam time, travel, and consumables grants at ISIS. The authors thank Pia McAleenan for synthesis of some compounds used in the study.

Figure Captions

Figure 1. Change in surface tension of aqueous surfactant solutions as a function of surfactant concentration at 23 ± 0.5 °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/D₂O solutions at $[\text{surfactant}] = 20 \times \text{CMC}$, 25 °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_{trans} (top) and corresponding CO₂ density (bottom) for $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]$ /water/CO₂ mixtures with different W_0 values at $[\text{surfactant}]/[\text{CO}_2] = 8 \times 10^{-4}$ as a function of temperature.

Figure 4. FT-IR spectra of 16.7mM $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]$ /water/CO₂ mixtures with different W_0 values at 350 bar and 45 °C.

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

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Figure 1

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 [C₆F₁₃mim][C₆F₁₃S] and [C₆F₁₃mim][C₆F₁₃S] are taken from an earlier paper.²⁹

Figure 2

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Figure 2 SANS profiles for surfactant/ D_2O solutions at $[\text{surfactant}] = 20 \times \text{CMC}$, 25°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_{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 $[\text{surfactant}]/[\text{CO}_2] = 8 \times 10^{-4}$ as a function of temperature.

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

Figure 5

Figure 5 SANS profile of 16.7 mM $[\text{C}_6\text{F}_{13}\text{mim}][\text{C}_6\text{F}_{13}\text{S}]/\text{D}_2\text{O}/\text{CO}_2$ 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.

[C ₆ F ₁₃ S]	
[C ₅ F ₁₁ S]	
[(CF ₃) ₃ S]	
[C ₆ F ₁₃ mim]	
[C ₅ F ₁₁ mim]	

Table 2

Table 2 Properties of aqueous surfactant solutions at 25 °C and 1 bar

Surfactant	CMC / mM	γ_{CMC} / (mN m ⁻¹)
[C ₆ F ₁₃ mim][C ₆ F ₁₃ S]	$0.8\text{-}1.1 \times 10^{-1}$	13.5
[C ₅ F ₁₁ mim][C ₅ F ₁₁ S]	7.0×10^{-1}	15.3
[C ₆ F ₁₃ mim][(CF ₃) ₃ S]	1.0	16.8
Na[C ₆ F ₁₃ S]	1.3×10^1	22.6
Na[(CF ₃) ₃ S]	1.3×10^2	25.7

CMC and γ_{CMC} data for [C₆F₁₃mim][C₆F₁₃S] and [C₆F₁₃mim][C₆F₁₃S] are taken from the earlier paper²⁹

Table 3 FC-core radius ($R_{f-Cdisk}$) and thickness ($t_{f-Cdisk}$), HC-shell thickness ($t_{f-Sdisk}$), aspect ratio, well depth and width for catanionic surfactant disk-like micelles in D₂O at [Surfactant] = 20 x CMC, 25 °C 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.

Surfactant	$R_{f-Cdisk}$ / Å	$t_{f-Cdisk}$ / Å	$t_{f-Shell}$ / Å	Aspect ratio	Well depth / kT	Well width	Cloud temp / °C
[C ₅ F ₁₁ mim][C ₅ F ₁₁ S]	2180	12.0	5.0	0.003	1.5	1.0	< 0
[C ₆ F ₁₃ mim][C ₆ F ₁₃ S]	636	13.3	4.7	0.010	1.5	1.0	–
[C ₆ F ₁₃ mim][(CF ₃) ₃ S]	130	11.5	5.0	0.045	0.3	2.8	29.8