

Development of Fluorinated Surfactant for Water-in-Supercritical CO₂ Microemulsion

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The phase behavior of water-in-supercritical CO₂ (W/scCO₂) microemulsions formed with aid of several fluorinated surfactants was examined as aiming at knowing structure suitable to form the microemulsion. The fluorinated surfactants used are a perfluoropolyether (PFPE) type, a fluorocarbon – hydrocarbon hybrid type and a fluorinated Aerosol-OT (AOT)-analogue type. In the surfactants examined, one of the fluorinated AOT-analogue surfactants gave a transparent single phase, identified as W/scCO₂ microemulsion, with a water-to-surfactant molar ratio, W_0^c up to 32 – the highest ever reported.

Introduction

Supercritical CO₂ (scCO₂) fluid having reversed micelles with encapsulated aqueous cores, in other words, water-in-scCO₂ (W/scCO₂) microemulsion, is expected to behave as a “universal solvent”, since such an organized fluid has an attractive characteristics of scCO₂ as well as a solvating properties of bulk water.

Several recent reports have aimed at identifying and/or designing CO₂-soluble surfactants capable of yielding W/scCO₂ microemulsions [1-13]. While in the early 1990s, more than 130 surfactants were systematically examined, none was able to solubilize more than a few molecules of water (~3) per surfactant molecule, i.e. a water-to-surfactant molar ratio (W_0^c) > 3 [1]. Recently, several fluorinated surfactants have been shown to dissolve in CO₂ and have a high activity at the water/CO₂ interface, suggesting the feasibility of yielding W/scCO₂ microemulsions [1-13]. In 1996, a perfluoropolyether (PFPE) surfactant was found to stabilize W/scCO₂ microemulsion with $W_0^c = 14$ [2]. After that, many reports dealing with W/scCO₂ microemulsion were related to PFPE surfactant [3-7]. Among others, two surfactants described in this work are noteworthy for generating microemulsions having large amounts of water in their cores. One is a hybrid type surfactant, sodium 1-pentadecafluoroheptyl-1-octanesulfate (F₇H₇), that has both a hydrocarbon and a fluorocarbon chain in one molecule [12,13]. F₇H₇ was found to microemulsify up to its own weight of water to form a stable W/scCO₂ microemulsion. The other is a fluorinated Aerosol-OT (AOT) analogue surfactant, sodium bis(1H,1H,5H-octafluoropentyl)-2-sulfosuccinate (di-HCF₄), that has two fluorocarbon chains [8-11]. Di-HCF₄ yielded a W/CO₂ microemulsion with a W_0^c value close to 20. The W_0^c values for F₇H₇ and di-HCF₄ are extremely large compared with the values for perfluoropolyether (PFPE) surfactants and other surfactants reported previously

[1-13]. However, the water content in these systems is still low for industrial scale applications. At the same time, F₇H₇ has been found to have a limited applicability, as it degrades easily at room temperature. Systematic research will then be necessary on W/scCO₂ microemulsion formation to develop more effective surfactants.

We have synthesized some branched-tail fluorinated anionic surfactants that have different CO₂-philic tail structure such as a hybrid type or a fluorinated AOT analogue type [14-25], and examined the effects of temperature, pressure (CO₂ density), water composition and CO₂-philic tail structure on W/scCO₂ microemulsion formation.

EXPERIMENTAL

(a) MATERIALS

The surfactants used are a hybrid type surfactant, sodium 1-oxo-1-[4-(tridecafluorohexyl)phenyl]-2-octanesulfonates (FC6-HC6), and five fluorinated AOT analogue surfactants, sodium bis(1H,1H,5H-octafluoropentyl)-2-sulfosuccinate (di-HCF4), sodium bis(1H,1H,7H-dodecafluoroheptyl)-2-sulfosuccinate (di-HCF6), sodium bis(1H,1H,9H-hexadecafluorononyl)-2-sulfosuccinate (di-HCF8), sodium bis(1H,1H,2H,2H-heptadecafluorodecyl)-2-sulfosuccinate (8FS(EO)₂) and sodium bis((1H,1H,2H,2H-heptadecafluorodecyl)-oxyethylene)-2-sulfosuccinate (8FS(EO)₄). The surfactants were synthesized in our laboratory as reported previously [14-25], and were purified repeatedly to >99 %. A hydrocarbon surfactant AOT (Aldrich, purity 98 %) and Perfluoropolyether ammonium carboxylate (PFPECOONH₄: CF₃CF₂(CF₂OCF(CF₃))₄COONH₄) were used as a control sample. Table 1 summarizes aqueous solution properties of the surfactants [14-25]. Injection grade distilled water (Ohtsuka Pharmaceutical Co., Ltd., pH = 6.5) and D₂O (Wako Pure Chemical Industries Ltd.; purity 99.9 %) were used. CO₂ of 99.99 % in purity (Tomoe Shokai Co. Ltd.) was used in all experiments without further treatment.

Table 1 Aqueous solution properties of the surfactants at 30 °C^a

surfactant	chemical structure	Krafft point, K _p (°C)	CMC × 10 ⁵ (mol/L)	interfacial tension, γ _{CMC} ^b (mN/m)	occupied area per molecule ^b (Å ² /molecule)
Aerosol-OT (AOT)	$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \\ \text{H}(\text{CH}_2)_4\text{CHCH}_2\text{OCOCH}_2 \\ \\ \text{H}(\text{CH}_2)_4\text{CHCH}_2\text{OCOCHSO}_3\text{Na} \end{array}$	< 0	2.6 × 10 ² ^c	30.8 ^c	75 ^c
FC6-HC6	$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \\ \text{C}_6\text{F}_{13} - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) \\ \\ \text{C}_6\text{H}_{13}\text{CHSO}_3\text{Na} \end{array}$	48	5.5 ^d	16.2 ^d	107.3 ^d
di-HCF _n	$\begin{array}{c} \text{H}(\text{CF}_2)_n\text{CH}_2\text{OCOCH}_2 \\ \\ \text{H}(\text{CF}_2)_n\text{CH}_2\text{OCOCHSO}_3\text{Na} \end{array}$	$n=4$ < 0 $n=6$ 28 $n=8$ 52	1.1×10^3 9.0 1.0 ^e	23.4 21.6 21.4 ^e	143.3 107.5 60.0 ^e
8FS(EO) _m	$\begin{array}{c} \text{F}(\text{CF}_2)_8(\text{CH}_2\text{CH}_2\text{O})_{m/2}\text{COCH}_2 \\ \\ \text{F}(\text{CF}_2)_8(\text{CH}_2\text{CH}_2\text{O})_{m/2}\text{COCHSO}_3\text{Na} \end{array}$	$m=2$ 73 $m=4$ < 0	1.0 ^f 2.4	12.8 ^f 13.8	38.1 ^f 94.5
PFPECOONH ₄	$\begin{array}{c} \text{CF}_3\text{CF}_2-(\text{CF}_2\text{OCF}(\text{CF}_3))_4\text{COONH}_4 \\ \\ \text{CF}_3 \end{array}$	< 0	0.6	15.3	33.5

^a Data taken from refs. [14-25]. ^b At air/aqueous solution at cmc. ^c At 25 °C. ^d At 50 °C. ^e At 53 °C. ^f At 73 °C.

(b) CLOUD PRESURE AND FT-IR SPECTRA MEASUREMENTS

Formation of a microemulsion was examined through visual observation and FT-IR measurement of W/scCO₂ mixtures containing surfactants (0.08 mol % in CO₂). Figure 1 is a

schematic representation of the experimental apparatus. A high-pressure vessel with an optical window and a moving piston inside was used to observe phase changes in the mixture at varying pressures and temperatures without changing composition. Known amounts of surfactant and CO₂ were mixed in the optical cell, and the mixture was equilibrated at 75 °C and 400 bar overnight, thereby allowing the surfactant to dissolve and making the mixture clear and transparent. A 6-port valve (Valco Instruments Co. Ltd.) with a sample loop (25 μL, Valco Instruments Co. Ltd.) and a circulation pump (Nihon Seimitsu Kagaku, NP-S-321) were attached to the optical cell to introduce a certain amount of water into the system. A clear mixture with water content larger than the solubility in pure scCO₂ is presumed to characterize microemulsion formation. The mixture became turbid when the pressure was decreased, suggesting a transition of microemulsion to macroemulsion. The cloud pressure was determined by changing the pressure at various temperatures. The observation was conducted at temperatures from 35 to 75 °C, and pressures up to 470 bar. The water uptake or the number of water molecules solubilized by one surfactant molecule, W_0^c , was calculated subtracting the solubility of water in pure scCO₂ [26] from the feed composition as follows:

$$W_0^c = \frac{[\text{water}]_0 - [\text{water}]_s}{[\text{surfactant}]_0}$$

where $[\text{water}]_0$ is the number of water molecules added to the system, $[\text{water}]_s$ is the solubility of water to pure scCO₂ [26], and $[\text{surfactant}]_0$ is the number of surfactant molecules. The existence of a core of bulk water in scCO₂ was confirmed with a high-pressure FT-IR photometer (JASCO Co. Ltd., FT/IR 620) connected to the experimental apparatus with D₂O [24].

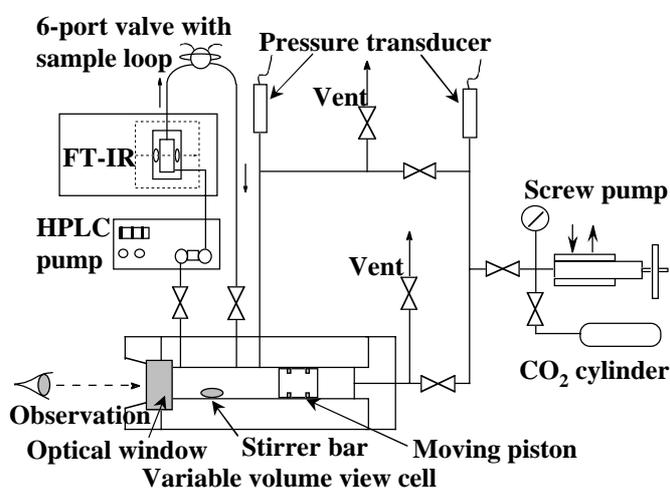


Figure 1 Schematic representation of apparatus.

RESULTS AND DISCUSSION

As the initial step in this study, the solubility of the surfactants in dry scCO₂ was examined by visual observation. Dry CO₂ means CO₂ in the absence of water. Figure 2 shows dissolution pressures for 0.08 mol % surfactants except AOT, 8FS(EO)₂, and a series of di-HCF_n at various temperatures. Compared with the other surfactants reported previously [2-7], PFPE surfactants, particularly PFPE carboxylates, were much soluble in dry scCO₂. On the other hand, 0.08 mol % the fluorinated AOT analogue surfactants except 8FS(EO)₄ were almost insoluble and remained solid in dry scCO₂ under our experimental conditions. However, they dissolved suddenly in scCO₂ after being added a few loops (0.24–0.73 mol %) of water by way of

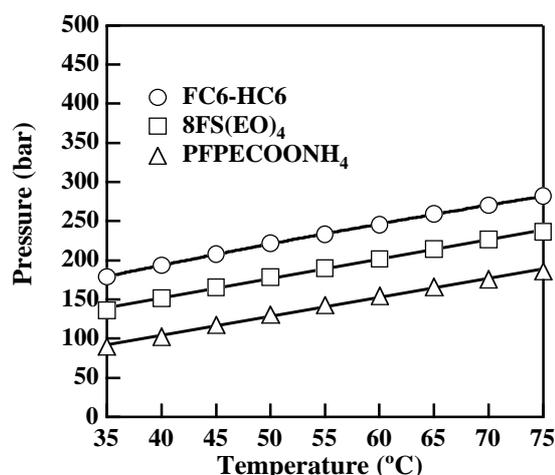


Figure 2 Dissolution Pressures for 0.08 mol % surfactants in dry CO₂ at various temperatures.

formation of reversed micelles [27-29].

As reported earlier [12], A hydrocarbon surfactant AOT was insoluble throughout the whole experimental condition. We postulate that AOT is unable to form a stable microemulsion in scCO₂, because its branched alkyl groups cannot play the role of a CO₂-philic component. Further, the alkyl groups also cause induced dipole-induced dipole interaction among AOT molecules.

The effects of the structural factors of surfactants on the formation of W/scCO₂ type microemulsions were examined at various temperatures, pressures, and water compositions for each anionic surfactant. With most of the fluorinated surfactants used, transparent single-phase of water, a surfactant and scCO₂ mixture, or a W/scCO₂ microemulsion phase, was formed at certain conditions. With an increase in the water composition, the microemulsion phase became a turbid W/scCO₂ macroemulsion phase or completely separated into two phases. On the other hand, when pressure (CO₂ density) or temperature was increased, the macroemulsion phase turned into a microemulsion phase.

Figure 3 shows W_0^c -temperature phase diagrams for W/scCO₂ mixtures with 0.08 mol % each anionic surfactant at various CO₂ densities. Here, the symbols mean E: macroemulsion phase, μ E: microemulsion phase, P: two phases (including surfactant precipitate phase like a liquid crystal [24,25]), N_F : number of fluorine atoms in one surfactant molecule, K_p : Krafft point in water, respectively. Some surfactants were found to have a higher water-microemulsifying power than those of di-HCF₄ and PFPECOONH₄ as reported in earlier papers [2-11]. In particular, 8FS(EO)₂ had great water-microemulsifying power able to yield W/scCO₂ microemulsion with $W_0^c=32$, while PFPECOONH₄ yielded W/scCO₂ microemulsion with W_0^c up to 11. The value of 32 is the highest W_0^c in W/scCO₂ microemulsion system ever reported [1-13], and equal to that of F₇H₇ [12,13].

Since highly-fluorinated carbons show weak van der Waals forces and have no dipole moment like CO₂, they are CO₂-philic and exhibit little mutual or other interactions between them [1-12]. The specific solute-solvent interactions between CO₂ and fluorinated compounds were also reported [30]. Thus, a larger N_F means a stronger CO₂-philicity of tails, in addition to a stronger hydrophobicity (or a lower solubility in water). K_p is an indicator of the solubility of surfactant in water, because the solubility drastically increases above K_p due to the formation of micelles with a hydrophobic core. Namely, surfactants that have a high K_p are hard to dissolve in water, and able to yield a stable W/scCO₂ microemulsion with a large amount of water. Considering that highly-fluorinated surfactant has a low hydrophilic/CO₂-philic balance (HCB), a high water/CO₂ interfacial activity and a little mutual interactions to stabilize W/scCO₂ microemulsion droplets [5,6,24,25], their microemulsifying power should strongly depends on N_F or K_p such as shown in Figure 3. On the other hand, the existence of the optimum fluorinated-tail length has also been reported on formation of a W/scCO₂ microemulsion using PFPE surfactants [7].

CONCLUSION

A PFPE surfactant, a hybrid surfactant, five fluorinated AOT analogue surfactants, and commercially available AOT were examined for their water-microemulsifying power in scCO₂. As a result, 8FS(EO)₂ was found to microemulsify an amount of water as large as the largest previously reported amount in similar systems, while to have a poor solubility in scCO₂ and in water. 8FS(EO)₂ is a useful surfactant for novel technologies employing W/scCO₂ microemulsions.

Fluorinated AOT analogue surfactants are expected to possess a suitable structure for forming W/scCO₂ microemulsion. Their molecular shape, strong CO₂-philic/hydrophobic

fluorocarbon chains showing a weak attraction and strong steric repulsion among each other, and strong CO₂-phobic/hydrophilic sulfonate groups will all enhance their adsorption ability.

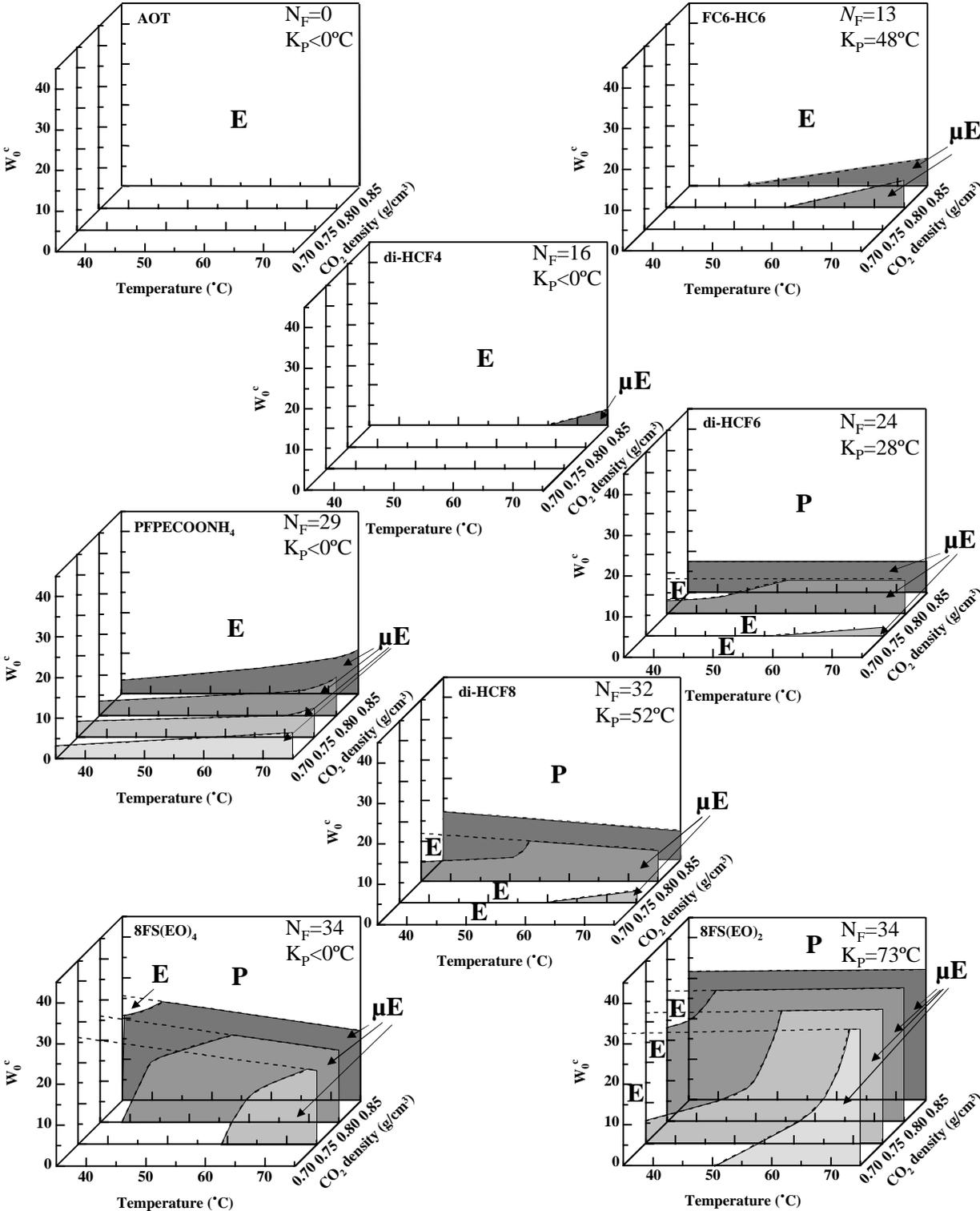


Figure 3 W_0^c -temperature phase diagrams for $W/scCO_2$ mixtures with 0.08 mol % surfactants at various CO_2 densities. E: macroemulsion phase, μE : microemulsion phase, P: two phases, R_F : number of fluorine atoms in one surfactant molecule, K_p : Krafft Point in water.

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