# Novel Fluorinated Double-tail Surfactant Having a High Microemulsifying Power in Water/Supercritical CO$_2$ System

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To develop an efficient surfactant for a water-in-scCO$_2$ microemulsion (W/scCO$_2$ μE), we synthesized a novel double-tail anionic surfactant, sodium bis(1$H$,1$H$,2$H$,2$H$-heptadecafluorodecyl)-2-sulfoglutaconate (8FG(EO)$_2$), and examined phase behavior of the 8FG(EO)$_2$/water/CO$_2$ mixture at several CO$_2$ densities from 0.70 to 0.85 g/cm$^3$ and water-to-surfactant molar ratios ($W_0^c$). 8FG(EO)$_2$ yielded a transparent single-phase with water contents larger than the solubility of water in pure CO$_2$, i.e. a W/scCO$_2$ μE phase. With increasing $W_0^c$, a phase transition occurred from the μE phase to a macroemulsion or a two-phase. Interestingly, this surfactant was found to microemulsify with $W_0^c$ up to 60 through visual observation and UV-visible absorption spectrum measurements.

## 1. INTRODUCTION

Supercritical CO$_2$ (scCO$_2$) is nonpolar and has weak van der Waals forces [1]. It is not suitable for dissolving polar substances. This disadvantage has limited the application of scCO$_2$ to chemical processes such as separation, reaction, and material formation [1]. One of the most promising approaches for enhancing the solubility is to use reversed micelles with high-density aqueous cores in the continuous scCO$_2$ phase, in other words, water-in-scCO$_2$ microemulsion (W/scCO$_2$ μE). Since such an organized fluid has the attractive characteristics of scCO$_2$ as well as the solvating properties of bulk water, it is expected to behave as a universal solvent [2-11].

A number of studies have been directed toward the development of a surfactant system that stabilizes W/scCO$_2$ μE formation. We have recently shown that a fluorinated analogue of Aerosol-OT surfactant, sodium bis(1$H$,1$H$,2$H$,2$H$-heptadecafluorodecyl)-2-sulfosuccinate (8FS(EO)$_2$), is the most effective formulation for stabilizing a transparent single-phase W/scCO$_2$ μE (Winsor-IV W/scCO$_2$ μE), where the molar water-to-surfactant-ratio $W_0^c$ reaches a maximum value of 32 [2–11]. It was also found, however, that 8FS(EO)$_2$ forms a liquid crystal (LC)-like precipitate at values of $W_0^c$ larger than 32. A promising strategies to prevent LC formation are to decrease length-to-breadth (L/B) ratio and to increase the critical packing parameter (CPP) of 8FS(EO)$_2$. As pointed out in our earlier paper [6], the smaller the L/B ratio is, the lower the stability of the LC structure is.

In the present work, with the aim of examining a suitable structure for W/scCO$_2$ μE formation, we synthesized a 8FS(EO)$_2$-analogue surfactant, sodium bis(1$H$,1$H$,2$H$,2$H$-heptadecafluorodecyl)-2-sulfoglutaconate (8FG(EO)$_2$), which has an extra –CH$_2$- spacer in the head group region compared with 8FS(EO)$_2$, and studied the phase behavior of the 8FG(EO)$_2$W/scCO$_2$ mixture through visual/microscopic observations and UV-visible absorption spectrum measurements. The microemulsifying power of 8FG(EO)$_2$ in scCO$_2$ was

evaluated with the maximum $W_0^c$ of W/scCO$_2$ μE.


## 2. MATERIALS AND METHODS
### 2.1 MATERIALS

1$H$,1$H$,2$H$,2$H$-heptadecafluoro-1-decanol (Kanto Chemical) and Glutaconic acid (Fluka) were used without further purification. The regent grade acetone, ethyl acetate, 1,4-dioxane, toluene, $p$-toluene sulfonic acid monohydrate, sodium hydrogensulfite were commercially obtained from wako pure chemical industries, and employed as received.

The surfactants used in this work was sodium bis(1$H$,1$H$,2$H$,2$H$-heptadecafluorodecyl)-2-sulfoglutaconate, (8FG(EO)$_2$). This surfactant was synthesized in our laboratory and purified to > 99%, as described in **2.2 Synthesis**. Compared with 8FS(EO)$_2$, 8FG(EO)$_2$ has an extra –CH$_2$– spacer between the fluorocarbon chain and sulfonate group, and it would bring in a lower L/B ratio and a larger CPP. The surfactant molecular structures and their properties in water are summarized in Table 1[12-13].

Ultrapure water of 18.2 MΩcm resistivity was taken from a Milipore Milli-Q Plus system and used for the experiments. CO$_2$ of 99.99% purity (Ekika Carbon Dioxide Co. Ltd.) and methyl orange (Acros Organics) were used without further treatment. Methyl orange (MO) was purchased from Acros organics and was used directly without further treatment.


Table 1 Surfactant structures and their properties in water.

| Surfactant structure | Surfactant | $n$ | Krafft point (ºC) | CMC [a] (mol/$l$) | $\gamma_{CMC}$ [b] (mN/m) |
|---|---|---|---|---|---|
| F(CF$_2$)$_8$CH$_2$CH$_2$O–C(=O)–(CH$_2$)$_n$ | 8FS(EO)$_2$ | 1 | 73 | 2.7 x 10$^{-4}$ | 20 |
| F(CF$_2$)$_8$CH$_2$CH$_2$O–C(=O)–CHSO$_3$Na | 8FG(EO)$_2$ | 2 | – | 4.8 x 10$^{-4}$ | 14 |

[a] Critical micelle concentration in water at 75ºC. [b] Surface tension at CMC at 75ºC.


### 2.2 SYNTHESIS

Synthesis of Bis(1$H$,1$H$,2$H$,2$H$-heptadecafluorodecyl) Glutaconate: A mixture of 1$H$,1$H$,2$H$,2$H$-heptadecafluoro-1-decanol 30.0g (64.6 mmol), glutaconic acid 4.3 g (33.1 mmol), $p$-toluene sulfonic acid monohydrate 1.2 g (6.3 mmol) as a catalyst in 120 cm$^3$ toluene was refluxed under stirring at 110 ºC for 24h. During the reaction, the water liberated was removed azeotropically from the reaction system to shift the equilibrium of the esterification reaction. After the reaction, to the residue was added 60 cm$^3$ ethyl acetate, and the mixture was washed sufficiently with brine to remove $p$-toluene sulfonic acid and excess glutaconic acid, and dried over Na$_2$SO$_4$. After the removal of the drying agent, toluene, ethyl acetate and 1$H$,1$H$,2$H$,2$H$-heptadecafluoro-1-decanol (bp. 113 ºC at 10 mmHg) in the mixture were evaporated under vacuum. Recrystallization from ethanol gave a white solid, bis(1$H$,1$H$,2$H$,2$H$-heptadecafluorodecyl) glutaconate (yield 16.3 g, 49%); mp 72.2-73.0 ºC; $^1$H-NMR (400MHz, solvent CDCl$_3$, standard TMS) $\delta_H$ /ppm: 2.4-2.6 (a, m(multiplet), 4H), 3.2-3.4 (c, t(triplet), 4H), 4.4-4.5 (b, t, 4H), 5.9-6.0 (e, d(doublet), 1H), 7.0-7.1 (d, m, 1H) for C$_8$F$_{17}$CH$_2$$^a$CH$_2$$^b$OCOCH$_2$$^c$CH$^d$=CH$^e$COOCH$_2$$^b$CH$_2$$^a$C$_8$F$_{17}$; IR (KBr) $\nu_{max}$ /cm$^{-1}$; 1739, 1723, 1661, 1398, 1344, 1275, 1248, 1204, 1148, 1135, 1117, 1062, 1004, 957, 938, 658, 514; Elemental analysis for C$_{25}$H$_{12}$O$_4$F$_{34}$: Found C, 29.4; H, 1.2. Calcd C, 29.4, H, 1.2.

Synthesis of sodium bis(1$H$,1$H$,2$H$,2$H$-heptadecafluorodecyl)-2-sulfoglutaconate, 8FG(EO)$_2$: The diester (16.3g, 15.9 mmol) was dissolved in 1,4-dioxane (265 cm$^3$); then the

mixture was heated to 50 ºC. To the mixture was added a solution of sodium hydrogensulfite (6.5 g, 6.25 mmol) in water (110 cm$^3$). The reaction mixture was stirred under reflux at 120 h. The white solid product precipitated was separated from the reaction mixture by filtration, and washed with 1,4-dioxane to remove the unreacted diester. The product was extracted by Soxhlet with acetone to remove excess NaHSO$_3$, and recrystallized from acetone. A white powder, 8FG(EO)$_2$, was obtained after vacuum drying (yield 0.63 g, 10%); ; $^1$H-NMR (400MHz, solvent CF3COOD, standard TMS) $\delta_H$ /ppm: 2.6-2.7 (a, m, 4H), 2.9-3.1 (d, m, 2H), 3.2-3.4 (c, m, 2H), 3.2-3.4 (d, m, 2H), 4.2-4.4 (e, m, 1H), 4.6-4.7 (b, t, 4H) for C$_8$F$_{17}$CH$_2$$^a$CH$_2$$^b$OCOCH$_2$$^c$CH$_2$$^d$CH$^e$(SO$_3$Na)COOCH$_2$$^b$CH$_2$$^a$C$_8$F$_{17}$; IR (KBr) $v_{max}$ /cm$^{-1}$; 3610, 3115, 1739, 1237, 1204, 1136, 1118, 1062,705, 659; Elemental analysis for C$_{25}$H$_{13}$O$_7$F$_{34}$Na: Found C, 26.7; H, 1.2. S, 2.9  Calcd C, 26.6, H, 1.2., S, 2.8.

## 2.3 APPARATUS AND MEASUREMENTS

**Figure 1** is a schematic representation of the experimental apparatus. A high-pressure vessel with an optical window and a moving piston inside the vessel was used to observe the changes in the phase with varying pressure and temperature but constant composition. A detailed description of the experimental apparatus and procedures of the measurements can be found in the literatures [2–11].

In order to examine the solution properties of the aqueous core in an 8FS(EO)$_2$/W/scCO$_2$ µE, UV-visible absorption spectrum measurements were carried out using MO, a double-beam



**Fig. 1** Schematic representation of experimental apparatus.

spectrometer (Hitachi High-Technologies, Co., U-2810), and a quartz window cell (volume: 1.5 cm$^3$), which was connected to the experimental apparatus. The quartz window cell was made of stainless steel (SUS316) and had three 8-mm-thick quartz windows. Each window had an i.d. of 10 mm; the windows were positioned so as to provide a perpendicular 10-mm optical path. Each window was attached to the stainless steel body of the cell using PTFE kel-F packing. The windows were tightly screwed to the steel body thereby compressing the packing between the stainless steel parts and the sapphire window and providing excellent sealing. The sealing was tested for up to 400 bar. The temperature of the quartz window cell was controlled by circulating water in a thermostat. Using spectroscopic measurements, the absorption spectra of the quartz window cell were compared with those of a standard quartz cell for an aqueous MO solution at ambient pressure; it was observed that both the spectra were in good agreement with each other.

The measurements of the water/surfactant/scCO$_2$ system were carried out at temperatures ranging from 35 to 75°C, with CO$_2$ densities of 0.70 to 0.85 g/cm$^3$. The $W_0^c$ parameter is generally used to express a water-to-surfactant molar ratio in a reversed micelle in scCO$_2$.The solubility of water in scCO$_2$ is taken into account as [2-11]:

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

(1)

where [water]$_0$ is the number of moles of water in the system, [water]$_S$ is the number of moles of water that are soluble in a given amount of pure CO$_2$, and [surfactant]$_0$ is the number of moles of surfactant in the system. Predetermined amounts of 8FS(EO)$_2$ and CO$_2$, where the molar ratio of 8FG(EO)$_2$ to CO$_2$, $R_{S/C}$, was fixed at 8 × 10$^{-4}$, were loaded in a variable-volume high-pressure optical cell. Then, water or an aqueous MO solution (0.1 wt%) was added into
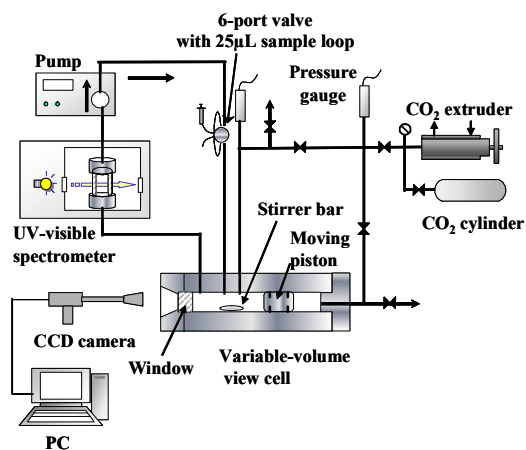
the optical cell through a six-port valve until the clear Winsor-IV W/scCO$_2$ μE (IVμE) solution became a turbid macroemulsion (E) solution or a precipitated hydrated surfactant. The value of $W_0^c$ was determined for each temperature and CO$_2$ density. The value of [water]$_S$ was obtained from literature data [11]. The densities of CO$_2$ were calculated using Span-Wagner EOS [14].

During the spectroscopic measurement, the scCO$_2$ mixture was stirred and circulated between the optical vessel and the quartz window cell until the absorbance became constant. The circulation was then stopped, and the valves between the vessel and quartz window cell were closed and the measurement was performed. The physical properties of the continuous phase of scCO$_2$ were assumed to be equivalent to those of pure CO$_2$.
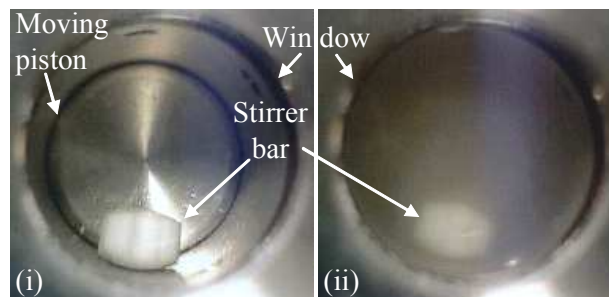
## 3. RESULTS

**Figure 2** shows the appearances of various 8FG(EO)$_2$/W/scCO$_2$ mixtures. **Fig. 2 (i)** displays the transparent single-phase having added amount of water larger than the solubility in scCO$_2$, and suggests the formation of the Winsor-IV W/scCO$_2$ μE. **Fig. 2 (ii)** is a photograph of the turbid macroemulsion when the phase transition from IVμE to E occurred due to the decrease in pressure and CO$_2$ density. The phase transition was the result of promoted aggregation and fusion due to decreased CO$_2$ density. It was observed that when the stirring of the mixture stopped, creaming of the turbid macroemulsion occurred, resulting in the formation of a 2Ø.
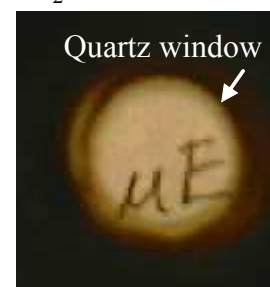


**Fig. 2** Photographs of the 8FG(EO)$_2$/W/scCO$_2$ mixture at different pressures. (i) Winsor IV W/scCO$_2$ μE, (ii) W/scCO$_2$ macroemulsion



**Fig. 3** Photographs of Winsor-IV W/scCO$_2$ μE with 8FG(EO)$_2$ and MO in the quartz window cell at $W_0^c$ of 17, 300 bar, and 45 °C.

Swelling of aqueous cores in Winsor-IV W/scCO$_2$ μE was examined by the absorbance of MO. It was found that as the local environment of the spectroscopic probe became more polar, the absorbance maximum $\lambda_{max}$ shifted to longer wavelengths [9,10]. **Figure 3** shows the photograph of the 8FG(EO)$_2$/scCO$_2$ solution with aqueous MO in the quartz window cell. Transparent appearance of the dyed scCO$_2$ phase visualized the letters "μE" written on a paper, which confirms the formation of the IVμE.

**Figure 4** shows the UV-visible absorption spectra of several MO/scCO$_2$ mixtures and also the benchmarks for the $\lambda_{max}$ values of surfactant-free solvents, including methanol (421 nm) and water (464 nm) [9,10]. It can be observed that the absorption spectrum of MO in pure scCO$_2$ showed a discernible shoulder at 329 nm (**Fig. 4, (a)**). This shoulder was identified as the absorbance of MO that is slightly soluble in pure scCO$_2$. Similar to spectrum (a), the spectrum of MO soluble in scCO$_2$ saturated by water (**Fig. 4, (b)**) showed no significant peak between 350 and 600 nm. On the other hand, when MO was dissolved in a W/scCO$_2$ μE, a broad peak appeared at 360–520 nm, and $\lambda_{max}$ was at 425 nm (**Fig. 4, (c)**). This result suggests that MO in a W/scCO$_2$ μE dissolved in a methanol-like environment and not in a water-like environment, which indicates that most MO molecules located at μE surface not in bulk-like free water in aqueous μE core.

The Winsor-IV μE became reddish with the increase in the $W_0^c$ value of the aqueous MO solution. In order to examine the effect of $W_0^c$ on μE in detail, the UV-visible absorption spectra of MO in water/8FG(EO)$_2$/CO$_2$ mixtures were measured for different values of $W_0^c$ at 45 °C and 300 bar. The changes in $\lambda_{max}$ and the absorbance as a function of $W_0^c$ were shown in **Fig. 5**. It can be observed the absorbance of $\lambda_{max}$ linearly increased with an increase in $W_0^c$
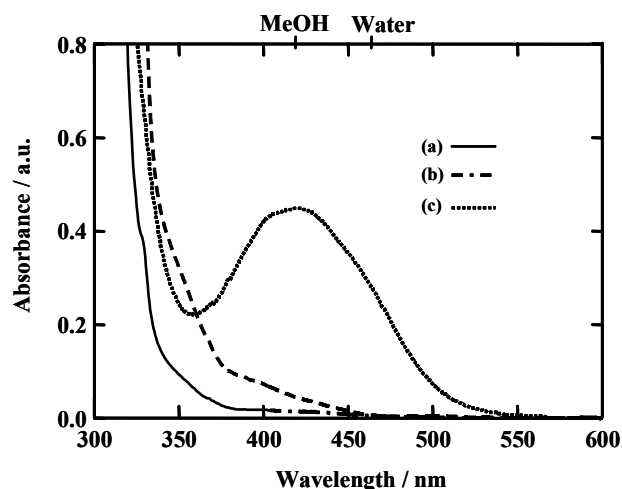
until $W_0^c$ reached to 60. These results suggest that 8FG(EO)$_2$ could microemulsify with $W_0^c$ up to 60, and the μE swelled with an increase in $W_0^c$. Since the maximum $W_0^c$ value of 60 was larger than that of the 8FS(EO)$_2$ microemulsion, the addition of methylene spacer into the 8FS(EO)$_2$ sulfosuccinate group presumably decreased L/B ratio and/or increased CPP. At $W_0^c < 20$, the $\lambda_{max}$ shifted to longer wavelength with a larger $W_0^c$. It means that, with increasing $W_0^c$, MO most likely dissolved in a water-like environment, namely, bulk-like free water in aqueous cores. In a typical W/O μE system with $W_0^c > 15$ [15], the increase in the amount of bulk-like free water is greater than that in the amount of water at W/O μE surface. For this reason, when Winsor-IV W/scCO$_2$ μE was used, the amount of bulk-like free water became greater than that of surface water with an increase in $W_0^c$. Further, some MO molecules were presumably transferred from surface water to free water, resulting in greater $\lambda_{max}$.

At $W_0^c$ from 60 to 80, $\lambda_{max}$ and the absorbance were almost constant in spite of different $W_0^c$ values, which imply the formation of Winsor-II W/scCO$_2$ μE (W/scCO$_2$ microemulsion having separated excess water). This suggests that although $W_0^c$ increased in this system, (i) the Winsor-II W/scCO$_2$ μE continued to exist without the formation of



**Fig. 4** UV-visible absorption spectra of MO in (a) pure scCO$_2$, (b) scCO$_2$ phases saturated by water, and (c) the Winsor-IV 8FG(EO)$_2$/W/scCO$_2$ μE with $W_0^c = 42$. The mixtures of spectra (a) and (b) were without 8FS(EO)$_2$. The experimental pressure, temperature, and CO$_2$ density were 300 bar, 45 °C, and 0.890 g/cm$^3$, respectively.



**Fig. 5** Change in $\lambda_{max}$ and the absorbance of MO in the 8FG(EO)$_2$/W/scCO$_2$ mixture as a function of $W_0^c$ at 300 bar and 45 °C.

the LC, (ii) the water-to-surfactant molar ratio of reversed micelles encapsulating an aqueous core was constant at 60, and (iii) separated excess water increased by an amount equal to ($W_0^c$ − 60).
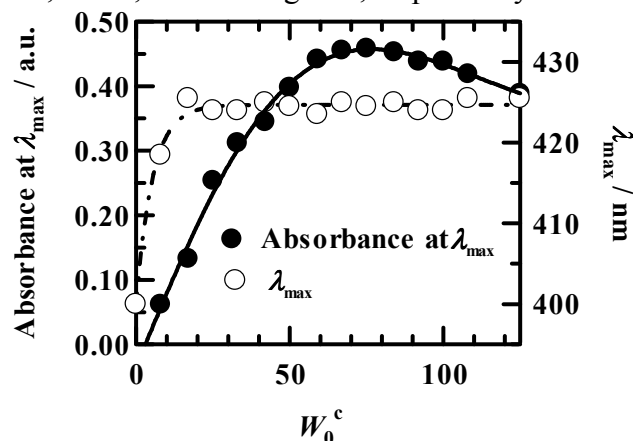
When $W_0^c$ became > 80, the absorbance slightly decreased with increasing $W_0^c$, though $\lambda_{max}$ was constant at 425 nm. From the stand point of a white precipitate appearing at $W_0^c >$ 100, W/scCO$_2$ μE would gradually transferred to the precipitate phase with increasing $W_0^c$.


**CONCLUSION**

To develop an efficient surfactant for W/scCO$_2$ μE, we synthesized a fluorinated double-tail anionic surfactant 8FG(EO)$_2$, which is an analogue of the good W/scCO$_2$ type microemulsifer 8FS(EO)$_2$ but has one more methylene spacer in hydrophilic group than 8FG(EO)$_2$. The phase behavior measurement found 8FG(EO)$_2$/water/scCO$_2$ mixtures to form a transparent single-phase Winsor-IV W/scCO$_2$ μE, a two-phase Winsor-II W/scCO$_2$ μE, a turbid W/scCO$_2$ macroemulsion, and liquid crystal like precipitate. To reveal the

microemulsifying power, i.e., the maximum number of water molecules that can be microemulsified by one surfactant molecule, $W_0^c$, UV-visible absorption spectra of MO in 8FG(EO)$_2$/W/scCO$_2$ mixture were measured at several $W_0^c$ values. Interestingly, as loading aqueous MO solution in 8FG(EO)$_2$/scCO$_2$ solution at 45 ºC and 300 bar, the appearance of the mixture kept a transparent single-phase and the absorbance of MO increased until $W_0^c$ become 60. These results suggest that 8FG(EO)$_2$ could microemulsify water in scCO$_2$ at least $W_0^c$ up to 60, which was larger than that of 8FS(EO)$_2$. Then, the added methylene spacer of 8FG(EO)$_2$ was expected to stabilize W/scCO$_2$ µE formation with a larger CPP and/or a lower L/B ratio than those of 8FS(EO)$_2$.

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