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, F$_7$H$_7$ has been found to have a limited applicability, as it degrades easily at room temperature. Systematic research will then be necessary on W/scCO$_2$ microemulsion formation to develop more effective surfactants.

We have synthesized some branched-tail fluorinated anionic surfactants that have different CO$_2$-philic tail structure such as a hybrid type or a fluorinated AOT analogue type [14-25], and examined the effects of temperature, pressure (CO$_2$ density), water composition and CO$_2$-philic tail structure on W/scCO$_2$ 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 (PFPECOONH$_4$; CF$_3$CF$_2$(CF$_2$OCF(CF$_3$)$_4$COONH$_4$) 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 D$_2$O (Wako Pure Chemical Industries Ltd.; purity 99.9%) were used. CO$_2$ of 99.99% in purity (Tomoe Shokai Co. Ltd.) was used in all experiments without further treatment.

<table>
<thead>
<tr>
<th>surfactant</th>
<th>chemical structure</th>
<th>Krafft point, K$_P$ (°C)</th>
<th>CMC × 10$^8$ (mol/L)</th>
<th>interfacial tension, γ$_{int}$ (mN/m)</th>
<th>occupied area per molecule (Å$^2$/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol-OT (AOT)</td>
<td>CH$_2$CH$_2$H(CH$_2$)$_2$CH$_2$OOCOCH$_2$H(CH$_2$)$_4$CH$_2$OOCOCH$_2$SO$_3$Na</td>
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<td>2.6×10$^2$</td>
<td>30.8</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>CH$<em>3$CH$<em>2$C$</em>{6}$F$</em>{13}$</td>
<td>48</td>
<td>5.5</td>
<td>16.2</td>
<td>107.3</td>
</tr>
<tr>
<td></td>
<td>C$<em>{6}$H$</em>{13}$CH$_2$SO$_3$Na</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>di-HCF$_n$</td>
<td>H(CF$_2$)$_n$CH$_2$OOCOCH$_2$</td>
<td>n=4</td>
<td>&lt; 0</td>
<td>1.1×10$^3$</td>
<td>23.4</td>
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<td>28</td>
<td>9.0</td>
<td>21.6</td>
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<td>52</td>
<td>1.0</td>
<td>21.4</td>
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<td>F(CF$_2$)$_m$H(CH$<em>2$CO)$</em>{m+2}$OCH$_2$</td>
<td>m=2</td>
<td>73</td>
<td>1.0</td>
<td>12.8</td>
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<td>F(CF$_2$)$_m$H(CH$<em>2$CO)$</em>{m+2}$OCH$_2$SO$_3$Na</td>
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<td>&lt; 0</td>
<td>2.4</td>
<td>13.8</td>
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<tr>
<td></td>
<td>F(CF$_2$)$_m$H(CH$<em>2$CO)$</em>{m+2}$OCH$_2$SO$_3$Na</td>
<td>m=4</td>
<td>&lt; 0</td>
<td>2.4</td>
<td>13.8</td>
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<tr>
<td></td>
<td>CF$_3$CF$_2$-c(CF$_2$OCF)$_d$COONH$_4$</td>
<td></td>
<td>0.6</td>
<td>15.3</td>
<td>33.5</td>
</tr>
</tbody>
</table>

| Table 1 Aqueous solution properties of the surfactants at 30 ºC$^a$ |
|-------------------------|----------------------------------------------------|---------------------|

$^a$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 PRESSURE AND FT–IR SPECTRA MEASUREMENTS
Formation of a microemulsion was examined through visual observation and FT-IR measurement of W/scCO$_2$ mixtures containing surfactants (0.08 mol % in CO$_2$). Figure 1 is a
FT-IR
HPLC
pump
6-port valve with sample loop
Pressure transducer
Vent
Screw pump
CO₂ cylinder
Observation
Stirrer bar
Moving piston
Variable volume view cell

Figure 1 Schematic representation of 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].

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-HCFₙ 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 W₀c-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, µE: microemulsion phase, P: two phases (including surfactant precipitate phase like a liquid crystal [24,25]), R₉: number of fluorine atoms in one surfactant molecule, Kₚ: 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 W₀c=32, while PFPECOONH₄ yielded W/scCO₂ microemulsion with W₀c up to 11. The value of 32 is the highest W₀c 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 N₉ means a stronger CO₂-philicity of tails, in addition to a stronger hydrophobicity (or a lower solubility in water). Kₚ is an indicator of the solubility of surfactant in water, because the solubility drastically increases above Kₚ due to the formation of micelles with a hydrophobic core. Namely, surfactants that have a high Kₚ 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 N₉ or Kₚ 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 \( W_0^\circ \)-temperature phase diagrams for W/scCO₂ mixtures with 0.08 mol % surfactants at various CO₂ densities. E: macroemulsion phase, µE: microemulsion phase, P: two phases, \( N_F \): number of fluorine atoms in one surfactant molecule, \( K_P \): Krafft Point in water.
REFERENCES