Water in Supercritical CO_2 Microemulsion Formation by Fluorinated Surfactants

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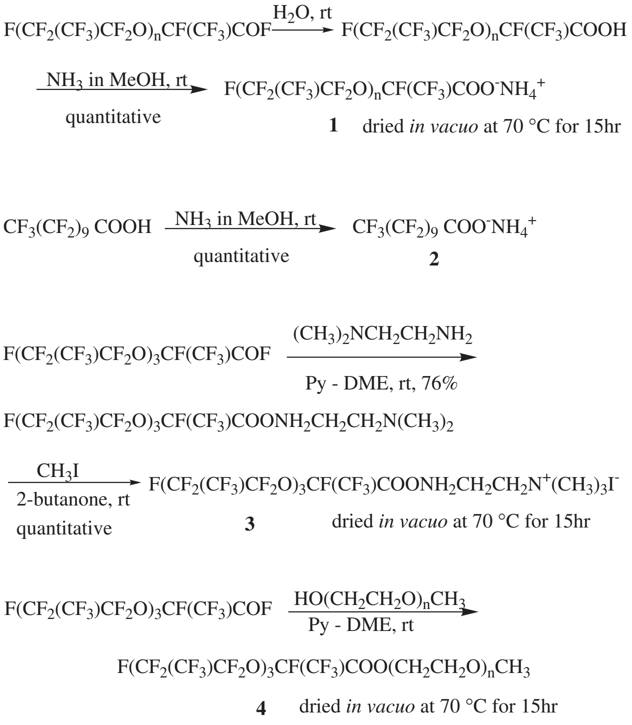
We examined the ability for microemulsion formation of fluorinated surfactants containing perfluoropolyether moieties for the CO_2-philic tail group and carboxylic acid ammonium or poly(ethylene glycol) methyl ether for the hydrophilic groups and found that the hydrophilic CO_2-philic balance of surfactants plays an important role in the formation of microemulsions.

Supercritical carbon dioxide ($scCO_2$) is an attractive substitute for toxic organic solvents used in many industrial processes.[1–7] Because CO_2 is nonpolar and has weak van der Waals forces, it is not suitable for dissolving polar substances. To overcome this limitation, there are two different methods. One is the addition of a polar solvent, such as alcohol or acetone, to increase the polarity of $scCO_2$.[8] However, this approach may void the benefits of $scCO_2$, since a relatively large amount of additional solvent is needed. The other is to employ specialized $scCO_2$ soluble surfactants that induce the formation of reverse micelles in a continuous $scCO_2$ phase, in other words, water-in $scCO_2$ (W/$scCO_2$) microemulsion.[9] However, Smith et al. have shown that commercial surfactants generally display poor solubility in $scCO_2$.[10] Therefore, to this end, many amphiphilic compounds have been synthesized.[11–16] However, only two fluorinated surfactants, namely, a hybrid-type surfactant[15] and a fluorinated AOT-analog,[16] have been reported so far to make microemulsions having large amounts of water in their core. Furthermore, there are few systematical studies concerning the relationship between the structure and the ability for microemulsion formation of the surfactant.[17–20] Therefore, in this study, we examined the ability for microemulsion formation of fluorinated surfactants containing perfluoropolyether (PFPE) moieties for the CO_2-philic tail group and ammonium carboxylate or poly (ethylene glycol) methyl ether (PEGM) for the hydrophilic head groups to evaluate the important factor for the molecular design of useful surfactants for the W/$scCO_2$ microemulsion.

These fluorinated compounds were synthesized according to the reaction sequences shown in Scheme 1. Ammonium carboxylate **1** and **2** were obtained in almost quantitative yield from the corresponding carboxylic acid with ammonia in methanol at room temperature.[21] The cationic surfactant **3**[21] was obtained from the reaction of PFPE carbonyl fluoride with *N*,*N*-dimethylethylenediamine followed by methylation using methyl iodide.

The PEGM ester of PFPE carboxylic acid **4**[21] was obtained by the reaction of PFPE carbonyl fluoride with the PEGM in dimethoxyethane (DME) in the presence of pyridine.

To evaluate the ability for microemulsion formation, W_0 (water/surfactant molar ratio) was measured by a variable volume high-pressure view cell as shown in Figure 1. A 6-port valve with a sample loop and a circulation pump were attached to the view cell in order to titrate the selected amounts of water into the system. A weighed amount of surfactants (2 wt% for CO_2) was introduced to the cell, and the cell was sealed. Carbon dioxide was poured into the cell, and the cell was heated to experimental temperature. In this study, the formation of a clear mixture that contains water rather than the solubility to the pure CO_2 was regarded as the formation of microemulsion.



$$F(CF_2(CF_3)CF_2O)_nCF(CF_3)COF \xrightarrow{H_2O,\ rt} F(CF_2(CF_3)CF_2O)_nCF(CF_3)COOH$$

$$\xrightarrow[\text{quantitative}]{NH_3\text{ in MeOH, rt}} F(CF_2(CF_3)CF_2O)_nCF(CF_3)COO^-NH_4^+$$

1 dried *in vacuo* at 70 °C for 15hr

$$CF_3(CF_2)_9\,COOH \xrightarrow[\text{quantitative}]{NH_3\text{ in MeOH, rt}} CF_3(CF_2)_9\,COO^-NH_4^+$$

2

$$F(CF_2(CF_3)CF_2O)_3CF(CF_3)COF \xrightarrow[\text{Py - DME, rt, 76\%}]{(CH_3)_2NCH_2CH_2NH_2} F(CF_2(CF_3)CF_2O)_3CF(CF_3)COONH_2CH_2CH_2N(CH_3)_2$$

$$\xrightarrow[\text{2-butanone, rt, quantitative}]{CH_3I} F(CF_2(CF_3)CF_2O)_3CF(CF_3)COONH_2CH_2CH_2N^+(CH_3)_3I^-$$

3 dried *in vacuo* at 70 °C for 15hr

$$F(CF_2(CF_3)CF_2O)_3CF(CF_3)COF \xrightarrow[\text{Py - DME, rt}]{HO(CH_2CH_2O)_nCH_3} F(CF_2(CF_3)CF_2O)_3CF(CF_3)COO(CH_2CH_2O)_nCH_3$$

4 dried *in vacuo* at 70 °C for 15hr

Scheme 1. Synthesis of fluorinated surfactants.

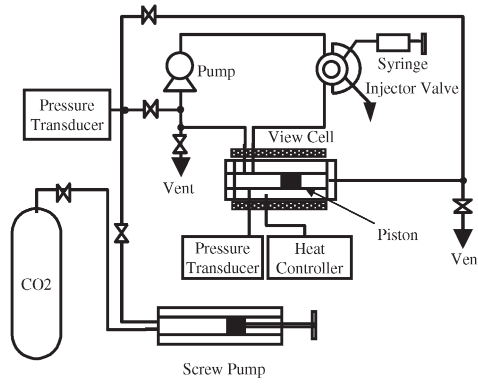


Figure 1. Schematic figure of the experimental apparatus for W_0 measurements.

Table 1. Microemulsion formation ability of **1** $F(CF_2(CF_3)CF_2O)_nCF(CF_3)COO^-NH_4^{+a}$

	Compd.				
	1-1	**1-2**	**1-3**	**1-4**	**1-5**
n^{22}(MW)	3 (679)	4 (845)	5 (1011)	7 (1343)	14^{22} (2500^{c})
W_0^{b}	5	6	12	8	11

^{a}The examination was performed at 50 °C and at 13 MPa.
^{b}Corrected for the solubility of water
^{c}MW average

Table 2. Microemulsion formation ability of **4** $F(CF_2(CF_3)CF_2O)_3CF(CF_3)COO(CH_2CH_2O)_nCH_3{}^{a}$

	Compd.				
	4-1	**4-2**	**4-3**	**4-4**	**4-5**
n^{22}(MW)	3 (808)	5 (896)	7.2^{22} (984^{c})	11.8^{22} (1183^{c})	16.3^{22} (1381^{c})
W_0^{b}	0	6	3	2	5

^{a}The examination was performed at 50 °C and at 13 MPa.
^{b}Corrected for the solubility of water
^{c}MW average

As shown in Table 1, ability for the microemulsion formation of **1** was as follows: **1-1**<**1-2**<**1-4**<**1-5**<**1-3**. **1-3** (n^{22} for PFPE = 5) has the largest W_0. These results suggested that the chain length of the PFPE group affected the ability of **1** and the chain length of **1-3** ($n^{22} = 5$) was suitable for the ability.

Furthermore, we examined the ability for microemulsion formation of ammonium perfluoroalkylcarboxylate **2** to estimate the effect of the perfluoroalkyl group for the CO_2-philic group. However, we could not estimate the W_0 of **2**, since the solubility of **2** for the CO_2 was much lower than that of the surfactants containing perfluoropolyether groups.

On the other hand, ability for the microemulsion formation of **4** was as follows: **4-1**<**4-4**<**4-3**<**4-5**<**4-2**, as shown in Table 2. **4-2** (n^{22} for PEG = 5) has the largest W_0. These results suggested that the chain length of the PEG group affected the ability of **4** and the chain length of **4-2** ($n^{22} = 5$) was suitable for the ability.

Furthermore, W_0 of cationic surfactant, **3**, was 8. These results suggested that anionic and cationic surfactants have higher ability for the microemulsion formation than nonionic surfactants, since hydrophilicity of these ionic groups is higher than that of nonionic ones.

From all these results, the following conclusions can be drawn. (1) The ability for microemulsion formation was affected by the structure of the CO_2-philic and hydrophilic groups, especially the chain length of these groups. More work to pick out the best-matched pair of CO_2-pilic and hydrophilic groups is necessary. (2) The ionic hydrophilic group is more useful than a nonionic one. (3) The perfluoropolyether group is more suitable than a perfluoroalkyl group for the CO_2-philic group, since the solubility of a compound containing a perfluoropolyether group for CO_2 is higher than that of a compound containing a perfluoroalkyl group. (4) In this study, the largest W_0 value obtained was about 10 and is lower than that of surfactants in earlier reports. More work on examination of the molecular shape of the CO_2-philic group is necessary for the molecular design of useful surfactants for the W/scCO_2 microemulsion.

References and Notes

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21 IR, NMR, MS spectra confirmed the structure of these compounds.
22 Number average degree of polymerization. **1-1**, **1-2**, **1-3**, **1-4**, **4-1**, and **4-2** are monodisperse oligomers (purity>95%), respectively. **1-5**, **4-3**, **4-4** and **4-5** are disperse oligomers and *n* and MW are mean average value, respectively.