Ability of Fluorinated AOT Analogues for Microemulsion Formation in Carbon Dioxide

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To clarify the relationship between the structure and the ability of fluorinated AOT analogues for W/scCO_2 microemulsion formation, we examined the AOT analogues having fluoroalkyl groups of different lengths, and CF_2H, CF_3, or $CF(CF_3)_2$ moieties at the terminal of the fluorinated CO_2-philic tails. It was found that both the length and the structure of the fluoroalkyl groups contained in AOT molecules affect the ability.

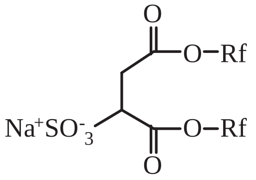
Supercritical carbon dioxide (scCO_2) is an attractive substitute for toxic organic solvents used in many industrial processes.[1] Because CO_2 is nonpolar and has weak van der Waals forces, it is not suitable for dissolving polar substances. One of the most promising approaches for enhancing the solubility is to employ specialized scCO_2 soluble surfactants that induce the formation of water-in-scCO_2 (W/scCO_2) microemulsion.[2] However, Consani and Smith have shown that commercial surfactants generally display poor ability for the formation of W/scCO_2 microemulsion.[3] Therefore, to this end, many amphiphilic compounds have been synthesized.[4]

Recently, Sagisaka et al.[5] and Eastoe et al.[6] demonstrated that 1) fluorinated AOT analogues could give W/scCO_2 microemulsions with significantly large amount of water compared to other surfactants, 2) an AOT analogue containing C_8F_{17} moieties for the CO_2-philic tails was the most effective, and 3) the replacement of the terminal CF_3- of the CO_2-philic tails by CF_2H- lowered the ability of that analogue.

Further systematic research to clarify the relationship between the structure and the ability of a surfactant is necessary in order to develop more effective surfactants. We examined several fluorinated AOT analogues having fluoroalkyl groups of different length and CF_3, CF_2H, or $CF(CF_3)_2$ moieties at the terminal of the fluoroalkyl groups. The structure of surfactants used in this study is shown in Scheme 1. These were synthesized by reported procedures.[7] To evaluate the ability for microemulsion formation, $W_0{}^c$ (corrected water/surfactant molar ratio)[8] was measured by a variable volume high-pressure view cell using 2 wt % for CO_2 of the surfactant. The technical procedures of the measurements have been described in a previous report.[9]

The results obtained from these examinations are summarized in Table 1 and Figure 1.

As shown in Figure 1, AOTs, **1**, **2**, and **3** having a relatively shorter fluoroalkyl group need higher pressure to dissolve in CO_2. Furthermore, pressure to stabilize microemulusion composed of these AOTs is higher than that of other AOTs. These results suggest that shorter fluoroalkyl chains produce unstable microemulsion, since they have lower affinity to CO_2.



Sample No.	Structures of Rf group
1	$-CH_2CF_2CHFCF_3$
2	$-CH_2CF_2CF_2CF_3$
3	$-CH_2CF_2CF_2CF_2CF_2H$
4	$-CH_2CH_2CF_2CF_2CF_2CF_3$
5	$-CH_2CF_2CF_2CF_2CF_2CF_2CF_2H$
6	$-CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$
7	$-CH_2CH_2CF_2CF_2CF(CF_3)_2$
8	$-CH_2CH_2CF_2CF_2CF_2CF_2CF(CF_3)_2$
9	$-CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3$
10	$-CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3$

Scheme 1. Structures of AOT analogues.

Table 1. Microemulsion formation ability

Sample No.	Cloud pressure[a] for CO_2 at 50 °C	Maximum water uptake[b] at 50 °C	W_0^{cc}	Cloud pressure[a] for W_0^c at 50 °C
1	17[d]	0.1	4	31
2	16[d]	0.3	9	34
3	20[d]	0.2	7	31
4	13[d]	0.4	14	19
5	15[d]	0.3	13	19
6	13[d]	0.4	21	18
7	13[e] (13[d])	0.3	12	18
8	17[e] (14[d])	0.3	16	20
9	15[d]	0.4	23	23
10	—[d,f]	—[f]	—[f]	—[f]

[a]MPa. [b]Weight (g) of water in microemulsion containing 1 g of surfactant at W_0^c. [c]Corrected for the solubility of water. [d]CO_2 containing 0.14 wt % of water. [e]Dry CO_2. [f]**10** was slightly soluble in CO_2.

As shown in Table 1, $W_0{}^c$ increases with increasing length of the fluoroalkyl chain as follows: **2** < **4** < **6** < **9**, **3** < **5**, and **7** < **8**, respectively. However, we could not measure the $W_0{}^c$ of **10**, since the solubility of **10** for CO_2 was much lower than that of other AOTs.

It was reported that wettability of the monolayer consisted

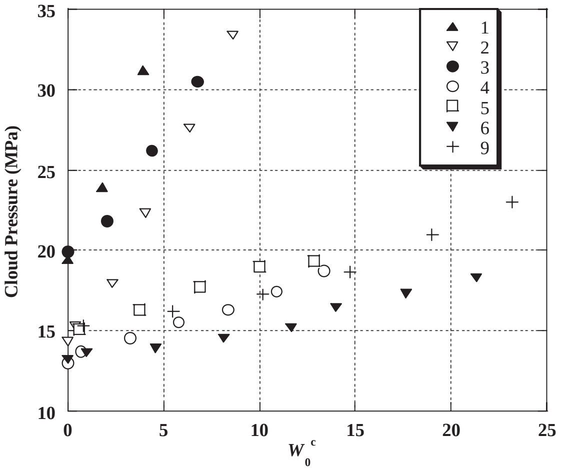


Figure 1. Effects of water content on the cloud point of W/$scCO_2$ microemulsion (surfactant content: 2 wt % to CO_2, temperature: 50 °C).

of fluorinated fatty acid, $CF_3(CF_2)_n(CH_2)_mCOOH$, was affected by the presence of the dipole in the $–CF_2–CH_2–$ linkage. Furthermore, it was well known that fluoroalkyl acrylate having a fluoroalkyl pendant group with at least seven carbon atoms have useful water- and oil-repellent property.[10] Therefore, it was suggested that AOTs having a fluoroalkyl group with 8 carbon atoms make the interaction between each micelle in $scCO_2$ weaker than other AOTs, since the effect of the dipole resulting from the $–CF_2–CH_2–$ linkage on the outermost CF_3 moiety of the fluoroalkyl group in the AOTs was reduced as the chain length of the perfluoroalkyl group was longer. On the other hand, maximum water uptake of **4**, **6**, and **9** was almost the same at 50 °C, since AOTs having higher molecular weight tend to have higher W_0^c.

The ability of AOTs with the $–(CF_2)_nCF_3$ group at the CO_2-philic tail was higher than that of AOTs with the CFH moiety in the fluoroalkyl groups as follows: **1** < **2**, **3** < **4**, and **5** < **6**. It is known that, different from perfluoroalkyl compounds, hydrofluoroalkyl compounds have attractive interactions with each other, such as $^{\delta+}C–F^{\delta-}$, $^{\delta-}C–H^{\delta+}$ or $–CF_2H\cdots FCHF–$.[11] Therefore, it seems that these polar interactions turn the microemulsion composed of AOTs with the CFH moiety in the fluoroalkyl group unstable to form macroemulsion.

Recently, Ryoo et al. considered that a surfactant with a bulky alkyl chain had higher solubility for CO_2 and could stabilize the W/$scCO_2$ microemulsion composed of it, since sterical repulsion between each microemulsion prevented aggregation of each other to form macroemulsion.[12]

AOTs **7** and **8** having the $–CF(CF_3)_2$ moiety at the terminal of the fluoroalkyl group can dissolve in dry CO_2, although the AOTs with a linear fluoroalkyl group are insoluble in dry CO_2. However, microemulsion formation ability of these AOTs is not higher than that of AOTs having a linear fluoroalkyl group. It was reported that a linear fluoroalkyl group was packed more closely in the fluoroalkyl acid monolayers on the metal surface than a branched one.[13] Therefore, it seems that microemulsions composed of the AOTs having branching fluoroalkyl groups have stronger interaction with each other than that composed of a linear fluoroalkylated one, since fluoroalkyl groups contained in micelle cannot distribute uniformly on the interface of CO_2-water due to their bulkiness.

From all our results, the following conclusions can be drawn. 1) W/$scCO_2$ microemulsion formation ability of fluoroalkyl AOTs increases with an increase in the fluoroalkyl chain length. 2) The ability of AOTs having a polar moiety in the perfluoroalkyl chain was lower than that of other AOTs. 3) The bulky fluoroalkyl group allows the AOTs to have higher solubility in CO_2 than other fluorinated AOTs, but do not contribute to increase ability of microemulsion formation.

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8 W_0^c was calculated by subtracting the solubility of water in pure $scCO_2$ 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 molar concentration of water added to the system, $[\text{water}]_s$ is the solubility of water in pure $scCO_2$, and $[\text{surfactant}]_0$ is the molar concentration of the surfactant in the system.

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