Highly-Soluble Fluorocarbon Surfactant in Supercritical Carbon Dioxide: Effect of Counter Cation on Solubility

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(Received January 5, 2000; CL-000004)

We have developed a new series of branch-structured anionic surfactants dissolved significantly well in sc-CO_2. We found that, the variation of counter ion species has a significant effect on the solubility of the surfactants in sc-CO_2. Among these, the solubility of surfactant with ammonium ion exceeded 16 wt% at 40 °C and 15 MPa, while that of surfactant with K^+ was neglectable. This effect can be used for complete recovery of the surfactant.

Supercritical fluids are often considered attractive as alternatives to conventional solvents for a variety of applications.[1, 2] Supercritical carbon dioxide, in particular, is generally viewed as an environmentally acceptable, benign alternative solvent because it is inexpensive, essentially nontoxic, exhibits moderate critical point (Tc = 31 °C, Pc = 7.5 MPa), nonflammable, and can easily be recaptured and recycled after use. However, as most of highly polar molecules are insoluble in supercritical carbon dioxide (sc-CO_2), the application of sc-CO_2 has been limited.

In the past decade, several approaches have been made to enhance the solubility of polar substances in sc-CO_2.[1, 2] Addition of polar solvent such as alcohol or acetone, so called cosolvents, may increases the polarity of sc-CO_2.[3] In this case, a large amount of additional polar solvent is needed, and this may void the benefits of sc-CO_2 as an environmental fluid. Complexation method[4] was used as an effective way to extract metal ions, but it can be used only for a specific metal ion, and the solubility is very low in batch system.

Reversed phase micelle solubilization is considered to be more suitable to widen the use of sc-CO_2 because of its non-selectivity to solutes.[5] More recently, several surfactants have been developed for the aim for use in sc-CO_2.[6] Unfortunately, these surfactants very poorly dissolve in sc-CO_2,[7] or the vapor pressure is too high (> 35 MPa) for sufficient solubility.[8] Development of surfactant with efficient solubility is desired for the practical use of sc-CO_2. On the other hand, one must not neglect the environmental aspect of these surfactants to be use together with sc-CO_2. The surfactants itself must be environmentally acceptable or it must be completely recoverable.

We have developed and studied a new series of surfactant for sc-CO_2 at relatively low pressure (< 15 MPa). We found that a series of branch-structured anionic fluorocarbon surfactant dissolve well in sc-CO_2, and the effect of counter cations are very significant on the solubility. We suggest the counter cations effect can be used for complete recovery of the surfactant.

Surfactants were synthesized by oligomerization method.[9,10] HFP-trimer was synthesized by oligomerization of hexafluoropropene (HFP). Tryethylamine (0.3 mol), *p*-hydroxybenzonic acid (0.6 mol), and HFP-trimer (0.3 mol) were added to 150 ml of acetonitrile. Reaction solution was stirred for 30 min under cooling condition (< 10 ºC). After the reaction, the solution was poured into 0.3 mol/L of HCl aqueous solution with stirring. Then the solution was filtered by glass filter, and the filtrate was washed with water and dried. White powder products were recrystallized with acetone, and these free acid type derivatives were neutralized by alkaline solution containing the equivalent counter cation. Finally, these surfactants were completely dried until the water contents were under 0.1 mol%, confirmed by Karl Fischer titration method.

Carbon dioxide was purchased from Sumitomo Fine Chemical (PURE Grade). All other chemicals were commercial reagent and were used as received. Ion exchange water was use for all preparations.

For observation of dissolution of surfactants in sc-CO_2, a high pressure view cell consisted of a stainless-steel block with two sapphire windows were used. It has a volume of 10.0 cm^3 and withstands maximum pressure of 45 MPa. The surfactants in the cell were stirred by a magnetic stir bar. The temperature was controlled using a temperature controller jacket with circulator.

Dissolution condition of surfactants was determined by visual observations using the high pressure view cell. A weighed amount of surfactant powder was introduced to the cell, and the cell was sealed. Carbon dioxide was poured, and heated to the experimental temperature. The fluid was stirred at a fixed pressure to obtain almost equilibrium state. Stirring was stopped for observation. The pressure was increased gradually until the white powder disappeared and the sc-CO_2 turned completely transparent ; this pressure was defined as dissolution pressure. This measurement was carried out at least three times for each condition.

For the screening of counter cations, dissolution pressure of variety amount of surfactants was observed at a fixed temperature, and the solubility at fixed condition (40 °C, 15 MPa) was estimated.

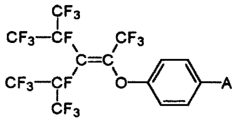
Table 1 shows the solubility of surfactants in sc-CO_2. The two skeletons, PFNA (4-(perfluoro-2-isopropyl-1,3-dimethyl-1-butenyloxy)benzoic acid) and PFNS (4-(perfluoro-2-isopropyl-1,3-dimethyl-1-butenyloxy)benzene sulfonic acid) were studied in terms of the

Table 1. Effect of counter cation on solubility of surfactants to supercritical carbon dioxide (40°C, 15 MPa)

	H^+	Li^+	Na^+	K^+
PFNA	0.35 mol/l	0.10 mol/l	0.034 mol/l	-
PFNS	0.10 mol/l	0.032 mol/l	-	-

	NH_4^+	$N^+(CH_3)_4$	$N^+(C_4H_9)_4$
PFNA	0.21 mol/l	0.031 mol/l	-
PFNS	0.064 mol/l	-	-

-: negligible



A = -COOH : free acid type PFNA
A = $-SO_3H$: free acid type PFNS

effect of polar functional group. For each skeletons, two series of counter cation (alkaline metal ion or ammonium ion) were exchanged and studied to compare the difference in counter ion.

The species of counter cation make large difference in solubilities. NH_4^+ gives the highest solubility among all surfactants (0.21 mol/L = 16 wt% at 40 °C, 15 MPa). Concerning the ammonium salts, the more hydrophilic cation seems to indicate the higher solubility. This is an unexpected result because it was generally thought that the more hydrophilic chemicals have lower solubility in sc-CO_2. In addition, alkaline metal cation series shows that ion with smaller diameter gives higher solubility in sc-CO_2. These tendencies of counter cation, which is against the generally thought, were observed in both PFNA and PFNS.

On the other hand, comparing the two polar functional groups, PFNS series have lower solubility than PFNA series. This result could be explained by general thought on the tendency of hydrophilic chemical in sc-CO_2 which contradicts with the foregoing data.

At the moment, we can not explain the above solubility mechanism on evidence. These effects of counter ion or functional groups have never been systematically studied by any previous studies about surfactants in sc-CO_2. The solubility tendency may be caused by a kind of salting out effect which may be induced by a slight amount of water from CO_2 cylinder.

For practical use, however, these results about counter ions (ex. NH_4^+ gives high solubility, while the solubility of both surfactants with K^+ was neglectable) suggested that recoverability of surfactant after use can be easily done by adding appropriate counter ion into the system. This means the surfactant can be completely recovered by adding potassium ion. For use as a reaction media, a reaction in the reversed phase micelle can be terminated using the same technique.

Though the free acid compound well dissolved to sc-CO_2, the free acid compounds were unstable as surfactants, and they have been barred in this study. After the above screenings, 4-(perfluoro-2-isopropyl-1,3-dimethyl-1-butenyloxy)benzoic acid ammonium salt (PFNA ammonium salt) was chosen for detailed measurement.

Figure 1 shows temperature versus pressure plot which gives complete dissolution and transparent phase containing constant amount of surfactant. Unlike most liquid solvents, the solubility of the surfactants in sc-CO_2 decreases with temperature. This phenomenon is mainly due to the decrease of sc-CO_2 density itself. The observation demonstrated that this surfactant is well dissolved in sc-CO_2 even under low pressure conditions.

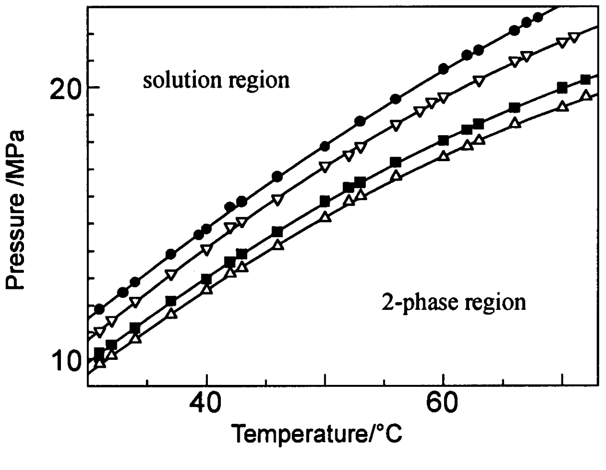


Figure 1. Dissolution condition of PFNA-NH_4 in sc-CO_2.
●: 0.15 mol/l, ▽: 0.10 mol/l, ■: 0.050 mol/l, △: 0.025 mol/l

Figure 2 shows that the solubility increases linearly with pressure under constant temperatures. Significant solubility, over 10 wt%, was observed at the desirable condition – low temperatures (< 40 °C) and relatively low pressure (< 15 MPa) (cf. the solubility of PFPE was reported as 1.4 wt% at 45 °C, 14 MPa)[7]. We confirmed over 30 wt% of solubility at over 40 MPa on trial. This properties would give the good stabilization of polar molecule in sc-CO_2.

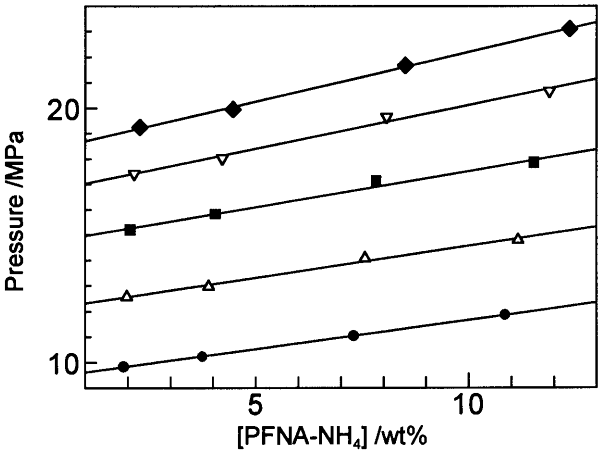


Figure 2. Solubility of PFNA-NH_4 in sc-CO_2.
◆: 70°C, ▽: 60°C, ■: 50°C, △: 40°C, ●: 32°C

This work gives a new concept to the development of surfactant for sc-CO_2 concerning the effect of counter ions, and hints the retrievability of surfactants. This may extend the application of sc-CO_2 for fine washing and reaction medium. Further study on the solubility mechanism of surfactants in sc-CO_2 is in progress.

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