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Phase behavior of the perfluoropolyether microemulsion in supercritical CO_2 and their use for the solubilization of ionic dyes

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Abstract

Phase behavior of the perfluoropolyether surfactant microemulsion in supercritical CO_2 and the solubilization of conventional ionic dyes in the same system have been investigated using Perfluoro 2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoic acid ammonium salt. We found that the surfactant prepared in this study was satisfactorily dissolved in supercritical CO_2 without the presence of entrainer. Moreover dissolved surfactant had an ability to form micellar aggregates and to incorporate a small amount of water in the interior of aggregates. We also found that conventional ionic dyes such as acid dye, reactive dye and basic dye were solubilized in the microemulsion system in supercritical CO_2.

Keywords: Ionic dye; Microemulsion; Supercritical CO_2; Surfactant

1. Introduction

The possibility for the utilization of supercritical (SC) fluid as an alternative medium of conventional solvent has been widely investigated in both academic and industrial fields. In the field of textile industry, supercritical fluid is also noticed as a dyeing media [1,2] because the viscosity (10^{-5}–10^{-4} Pas) and diffusion coefficient (10^{-8}–10^{-7} $m^2 \cdot s$) values of this supercritical fluid are similar to those of water, making it suitable for use as a dyeing medium. In addition, SC-CO_2 is an attractive alternative to water because it is inexpensive, essentially nontoxic, nonflammable, requires relatively gentle critical conditions ($T_C = 305$ K, $P_C = 7.38$ MPa), and can easily be recaptured and recycled after use. Unfortunately, SC-CO_2 is a poor solvent for a wide range of hydrophiles because of its low permittivity [3]. Dyeing of textile fibers in SC-CO_2, therefore, has been limited to synthetic fibers using SC-CO_2-soluble disperse dyes but the dyeing of natural fibers from this medium is still under development [4,5]. In order to dye natural fibers in SC-CO_2, satisfactory solubilization of water-soluble dyes such as acid dye and reactive is necessary.

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In our previous study, we have investigated the solubilization of the water-soluble dye in SC-CO_2 and the application to dyeing process using reverse micellar systems [6,7]. Reverse micelles (or W/O microemulsion) have the remarkable property of solubilizing a small amount of water at the interior of a micelle and to provide a stable aqueous microenvironment, so-called water-pool, in non-aqueous media [8]. Therefore the reverse micellar system has the potential to solubilize water-soluble dyes in SC-CO_2 if a stable water-pool is formed. In fact, our previous investigation indicated that acid dye and the reactive dye could be solubilized in the reverse micellar system up to satisfactory level for dyeing. However, solubility of those dyes was greatly dependent on the characteristics of the co-surfactant. Moreover, the presence of a co-surfactant in the system made it difficult to understand the characteristics of the system. In order to raise the potential of dyeing fibers from the reverse micellar system in SC-CO_2, simplification of the system is necessary. The purpose of this study is the preparation of simple dyeing media using reverse micellar systems in SC-CO_2. In order to achieve this purpose, we have investigated the formation of micellar aggregates and the solubilization of water-soluble dyes in the same system without using any co-surfactant. The surfactant selected in this study was perfluoropolyether (PFPE) derivatives. As is generally known, the PFPE surfactant has a potential to dissolve in SC-CO_2 [9–13]. Since a surfactant that contained in the fluorocarbon tail within a molecule has low intermolecular interaction and surface tension compared to that contained hydrocarbon tail, surface free energy of fluorocarbon surfactant is remarkably low. As a result, some PFPE surfactants exhibit high solubility and ability to form thermodynamically stable micellar aggregate in CO_2. Unfortunately, PFPE surfactants so far proposed are not commercially available at present, making it difficult for the practical applications. In this study, we have examined the preparation of the PFPE surfactant by the simple modification of commercially available PFPE surfactant precursor. In this paper, we report the phase behavior of PFPE surfactant/water/CO_2 system and the solubilization of ionic dyes in the same system.

2. Experimental

2.1. Materials

The PFPE surfactant precursor used in this study was Perfluoro (2,5,8,11- tetramethyl-3,6,9,12-tetraoxapentadecanoyl) fluoride and was obtained from Daikin Chemicals Sales Co., Ltd. The desired PFPE surfactant, ammonium carboxylate perfluoropolyether, was prepared by stirring perfluoropolyether fluoride in ten times molar excess of ammonium hydroxide for 24 h. Most of water and ammonia were liberated within 24 h under constant stirring in a vacuum until the sample became viscous. The sample was then dried in a vacuum desiccator at 298 K for 72 h. Full conversion of fluoride form to carboxylate was confirmed by F-NMR. Initial water content of PFPE surfactant was found to be 1.8%(w/w) through Karl Fisher titration. Carbon dioxide used was pure grade ($>99.9\%$) and was purchased from Sumitomo Seika Chemicals Co., Ltd. Dyes used in this study were acid dye, reactive dye, direct dye and basic dye. These dyes were all graciously gifted from DyStar Japan Co., Ltd., and were used as received. All other chemicals were purchased from Kanto Chemical Co., Inc. and were used after drying with molecular sieve 3A.

2.2. Procedure

High-pressure reaction apparatus was constructed in our laboratory. Schematic diagram of the apparatus is drawn in Fig. 1. The main component of the apparatus is a stainless steel viewing cell (4.6 cm^3 total volume) 3 cm in diameter by a 1.5 cm thick optical window. Liquid CO_2 from a cylinder was compressed via pressurize pump and flowed to reaction cell until pressure reached desirable value. In all experiments, a prescribed amount of solutes such as the PFPE surfactant, water and dyes were previously loaded in the bottom of the cell. The contents of the cell can be stirred by a Teflon-coated bar driven by an outside magnet. Phase boundaries of mixtures were confirmed by both visual inspection and optical observation through optical windows. Optical observations were performed with the Multichannel Spectrophotometer MCPD-100

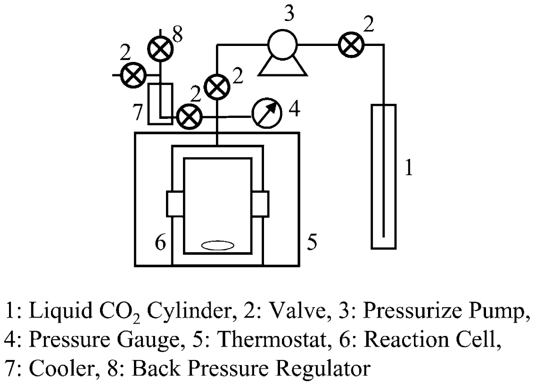

Fig. 1. Schematic diagram of experimental apparatus.

(Otsuka Electronics Co., Ltd.) to determine the disappearance of the visible absorption of the system around the cloud point. In each experiment, pressures at the cloud point were accumulated by several measurements. Average pressures observed at each cloud point were converted to density through the Ely-Haynes-Bain method [14]. Measurements of dye absorption were also carried out using the same equipment and the spectrophotometer. Before recording the spectrum, the contents were equilibrated for 15 min each.

3. Results and discussion

Fig. 2 shows phase boundaries of the PFPE surfactant/CO_2 system at several temperatures. Clear one phase region is given at the upper side of each plot. In this experimental condition, we have found that pressures at the cloud point observed by visual inspection completely agree with those by optical observation. As shown in Fig. 2, the PFPE surfactant obviously dissolves in SC-CO_2. The density of CO_2 that is necessary to obtain clear one phase increases linearly with the increasing concentration of the surfactant. In order to dissolve further amounts of surfactants, further solvent power seems to be necessary for the complete solvation of surfactant molecules. Fig. 2 also shows that a higher temperature is favorable for the dissolution of the surfactant in lower density of CO_2. In other words, the system that has a higher temperature has an ability to dissolve further amounts of surfactants at the constant density of CO_2. These results well agree with the general behaviors in the dissolution of solutes in water. Fig. 3 shows an example of the results of similar investigation when a small amount of water is injected. For comparison, the solubility of water in pure CO_2 is presented as dotted line [15]. In this study, we confirmed that similar behaviors in the phase boundary in this system could be observed when the temperature was varied. As shown in Fig. 3, the solubility of water in this system is significantly higher than that in pure CO_2. Since the amount of water that can dissolve in bulk CO_2 is limited, the majority of injected water seems to be solubilized in another portion of the system. These results indirectly suggest the formation of a water-pool. In each experimental condition, density of CO_2 that requires

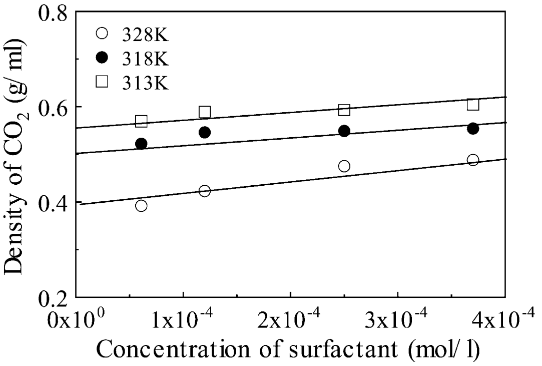

Fig. 2. Phase boundaries of the PFPE surfactant/CO_2 system.

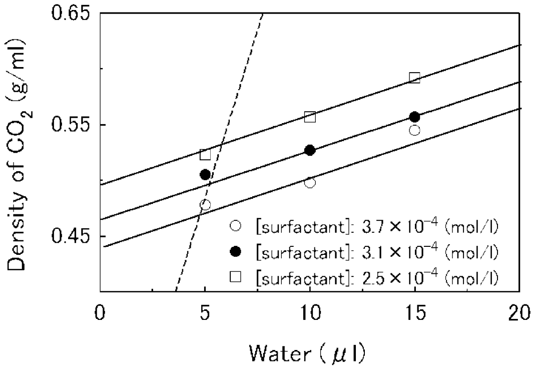

Fig. 3. Phase boundaries of the PFPE surfactant/CO_2/water system at 328 K.

attaining a one phase system is linearly increased with an increasing the amount of water. If the stable micellar aggregate is formed in this system, this result may be explained in terms of the swelling of the micelle. As is generally known, an addition of a further amount of water produces an enlargement of micellar size and an increase in aggregation number [16]. As a result, higher solvent power is necessary to dissolve the grown micelle. Fig. 3 also shows that a PFPE surfactant/water/CO_2 system that has a lower concentration of surfactant requires a higher density of CO_2 to obtain clear one phase when water content is constant. These results are quite different from those in the similar system without water as shown in Fig. 2. The presence of water in the system causes the contrary result. These contradictions may also be explained in terms of the aggregation behavior of surfactant if micellar aggregates are formed. In general, micellar size and aggregation number of the reverse micelle is mainly determined by the molar ratio of water to surfactant. As described above, an increase of the molar ratio of water to surfactant at constant concentration of the surfactant would result in the swelling of micelles and an increase of aggregation number of individual micelles. On the other hand, an increase of the concentration of the surfactant at constant water content would result in an increase of the total number of micelle that has a smaller micellar size and aggregation number. In this case, the latter aggregation behaviors can be applied. Since free energy of the micellar aggregate is greatly dependent on the micellar size [17–19], characteristics of the solubilization of micellar aggregates in this system would be governed by the micellar size. As a result, lower solvent power of CO_2 is required to solvate the smaller aggregate even if the total number of micelle is higher than the similar system that contains large micellar aggregates.

In this way, phase behaviors of this system can be explained in terms of the aggregation behavior of the surfactant. In order to investigate the formation of micellar aggregate more reliably, however, another evaluation method is necessary. In this study, we have examined the determination of cmc in this system using the ionic dye (C.I. Acid red 52) as an optical probe. In the preliminary experiment, we have confirmed that the ionic dye used in this study has no solubility in pure CO_2 even if a small amount of water is present in the system. If stable micellar aggregates that contains water-pool are formed in the SC-CO_2, therefore, the ionic dye may be dissolved in the interior of the water-pool. As a result, the ionic dye can apparently be solubilized in CO_2. Since solubility of the surfactant in SC-CO_2 is greatly dependent on the pressure (or density of CO_2) of the system, determination of intrinsic cmc in SC-CO_2 would be difficult. Nevertheless, estimation of cmc at the certain pressure would become useful knowledge for the determination of experimental conditions in this system. Fig. 4 shows the variation of the absorbance of C.I. Acid Red 52 in a PFPE surfactant/water/CO_2 system when concentration of the surfactant is varied. In this case, all experimental conditions except for the concentration of the surfactant were adjusted to become constant. As shown in Fig. 4, absorption of the dye is scarcely observed when concentration of the surfactant is low, indicating that C.I. Acid Red 52 cannot be solubilized in the system. On the other hand, absorption of the dye is abruptly increased with an increasing the concentration of the surfactant and levels off at a higher range of the surfactant concentration. This phenomenon agrees well with the variations of various chemical parameters in surfactant solutions at the vicinity of cmc [20]. Since the concentration of the dye in the system is constant, abrupt increase in absorption implies the

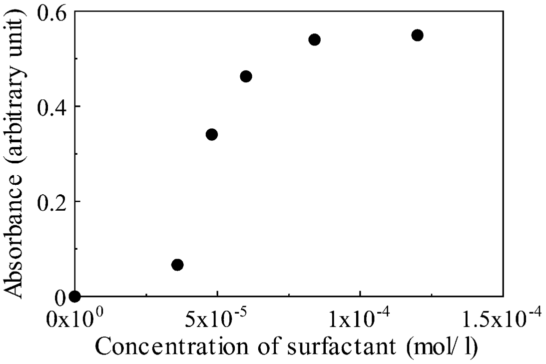

Fig. 4. Variation of absorbance of C.I. Acid Red 52 in the PFPE surfactant/CO_2/water system. Temperature: 328 K, density of CO_2: 0.707 g/ml, water content: 30 µl, [Dye]: 2.5×10^{-6} mol/l, λ_{max}: 553 nm.

formation of micellar aggregates. In the range of low concentration of the surfactant, the surfactant molecule dissolved in SC-CO_2 would be dispersed as monomolecular state. Therefore, most of C.I. Acid Red 52 dissolved in a small amount of water cannot be solubilized in CO_2 and is precipitated at the bottom of the vessel with water. When concentration of the surfactant reaches the cmc, C.I. Acid Red 52 can dissolve in the water-pool rapidly and be stably micro-dispersed in the system. As a result, abrupt increase of the absorption of the dye is observed. After its introduction C.I. Acid Red 52 is completely solubilized in the interior of micellar aggregate and absorption of the dye is not varied even if a further amount of surfactant is present in the system. A slight absorption of the dye just before cmc would be attributed to the dye molecule that has been adsorbed on monomolecular surfactant. From these results, cmc at this experimental condition (CO_2 density:0.707 g/ml) can estimate to be 4×10^{-5} mol/l. This value is lower than those of representative hydrocarbon surfactants in water [21]. Since the surfactant molecule that contains a fluorocarbon tail provides a remarkable reduction of intermolecular interaction and surface tension, the PFPE surfactant prepared in this study would be able to form aggregates in non-polar media even in low concentrations.

Fig. 5 shows the variation of the absorbance of C.I. Acid red 52 observed from the PFPE surfactatnt/water/CO_2 system. In this case, all experimental conditions except for the concentration of the dye were adjusted to become constant. In order to compare the effect of micellar aggregate on the solubility of the dye, the similar system without surfactant was also used. As shown in Fig. 5, absorption of the dye is not observed when the surfactant was not present in the system. On the other hand, absorption of the dye linearly increases by increasing the concentration of the dye, indicating that the dye satisfactorily introduced solubilizes in the interior of micellar aggregate with a small amount of water. From these results, this system seems to have the potential to apply as a dyeing medium. In Fig. 5, it can be estimated that the highest concentration of dye corresponds to 4.3%owf if dye liquor is assumed to 50:1. This fact obviously indicates that the PFPE surfactant/water/CO_2 system has great ability to maintain sufficient dyes for the dyeing of fabrics. In order to obtain fundamental knowledge for the application to the dyeing process, we have examined the solubility test of ionic dyes in this system using several conventional dyes. Table 1 summarizes the results of solubility test. As shown in Table 1, basic dyes used in this study are all solubilized in the system, although direct dyes are not solubilized at all. In contrast, solubility of the acid dyes and the reactive dye seems to be dependent on the characteristics of the individual dye. These differences in the solubility of the dye may be related to certain factors. The first factor to be considered is the stereospecific difference of dyes. Since micellar aggregates prepared in non-aqueous media are generally small compared to those in aqueous system, the PFPE surfactant prepared in this study may not provide suitable solubilizing space to dyes in the size and the structure. As a result, a comparatively large molecular dyes like the direct dye cannot solubilize in the system. Alternatively, electrostatic interaction between the dye and the surfactant may also play an important role in the solubilization of the dye. Barbara et al. have reported [22,23] that dye molecules in the surfactant solution is strongly interacted with surfactant molecules by electrostatic interaction and hydrophobic interaction when the dye and the surfactant has the opposite charge. On the other hand, interaction between the dye and the surfactant never takes place when these molecules have

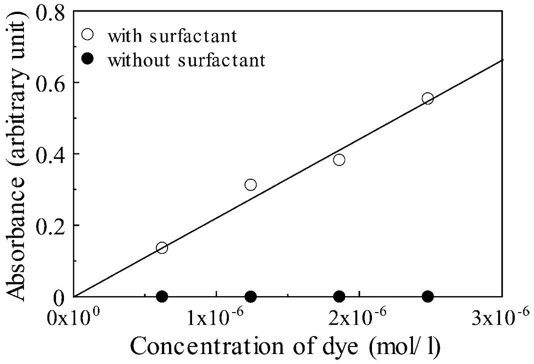

Fig. 5. Solubility of C.I. Acid Red 52 in the PFPE surfactant/CO_2/water system. Temperature: 328 K, density of CO_2: 0.707 g/ml, water content: 30 μl, [PFPE]: 6×10^{-5} mol/l, λ_{max}: 553 nm.

Table 1
Solubility test of ionic dyes in the PFPE surfactant/CO_2/water system at 328 K. Density of CO_2: 0.707 mg/l, water content: 30 μ/l, [PFPE]: 6×10^{-5} mol/l.

Dye	Structure	Solubility
Acid dye		
C.I. Acid Red 249	Monoazo	–
C.I. Acid Red 52	Anthraquinone	+
C.I. Acid Red 82	Anthraquinone	+
C.I. Acid Green 9	–	+
Reactive dye		
C.I. Reactive Yellow 17	Monoazo	+
C.I. Reactive Yellow 57	–	+
C.I. Reactive Red 3	Anthraquinone	–
Direct dye		
C.I. Direct Orange 26	Diazo	–
C.I. Direct Blue 71	Triazo	–
C.I. Direct Violet 51	Triazo	–
C.I. Direct Yellow 86	Triazo	–
Basic dye		
C.I. Basic Blue 3	Thiazine	+
C.I. Basic Yellow 28	Methine	+
C.I. Basic Red 29	Monoazo	+
C.I. Basic Blue 47	Anthraquinone	+

an identical charge. Therefore, anionic dyes in the interior of small water-pool may have an opportunity to take electrostatic repulsion and to stick out to outer CO_2 media. At the present stage, the differences in the solubility between anionic dyes cannot be explained clearly with the limited results, but the above-mentioned factors or their compounded factors may control the solubility of the dye in this system.

In this way, the PFPE surfactant prepared in this study has a potential to retain polar substances in SC-CO_2 by the formation of micellar aggregates. Moreover solubilization of solutes in this system seems to be related to the characteristics of the aggregates. However, experimental data obtained in this study still provides indirect information about the formation of micellar aggregates. Direct observation of the system with suitable techniques such as X-ray scattering and light scattering would be necessary for the further evaluation of the characteristics of micellar aggregates and solubilization of solutes.

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