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# Microemulsions in supercritical $CO_2$ utilizing the polyethyleneglycol dialkylglycerol and their use for the solubilization of hydrophiles

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## Abstract

Novel polyethyleneglycol dialkylglycerol surfactants, 3-methyl-penta ethyleneglycol-2-octyl-1-pentylglycerol ($CH_3(OCH_2CH_2)_5OCH_2CHO((CH_2)_7CH_3)CH_2O(CH_2)_4CH_3$), 3-methylpentaethyleneglycol-2-pentyl-1-octylglycerol ($CH_3(OCH_2CH_2)_5OCH_2CHO((CH_2)_4CH_3)CH_2O(CH_2)_7CH_3$), 3-methylpentaethyleneglycol-2-(2-ethylhexyl)-1-octhylglycerol ($CH_3(OCH_2CH_2)_5OCH_2CHO(CH_2CH(C_2H_5)(CH_2)_3CH_3)CH_2O(CH_2)_7CH_3$), 3-methylpentaethyleneglycol-2-(2-ethylhexyl)-1-(2-ethylhexyl)glycerol ($CH_3(OCH_2CH_2)_5CH_2CHO(CH_2CH(C_2H_5)(CH_2)_3CH_3)CH_2OCH_2CH(C_2H_5)(CH_2)_3CH_3$), were synthesized to evaluate the solubility and the possibility for the formation of stable microemulsions in supercritical $CO_2$. The surfactants synthesized in this study were satisfactorily dissolved in supercritical $CO_2$. However, the quantity of water, which can dissolve into the same system, was very little. It has also become obvious that small water droplets in $CO_2$ microemulsions stabilized by synthesized surfactants have an ability to incorporate hydrophiles, water-soluble dyes, at the same system.

*Keywords:* Supercritical fluid; Carbon dioxide; Microemulsion; Surfactant; Dye

## 1. Introduction

The possibility for the utilization of supercritical (SC) fluid has widely been investigated in both academic and industrial fields. In particular, SC–$CO_2$ is an attractive alternative to both water and organic solvent because it is inexpensive, essentially nontoxic, nonflammable, requires relatively gentle critical conditions ($T_C = 31.1$ °C, $P_C = 7.38$ MPa), and can easily be recaptured and recycled after use. However, SC–$CO_2$ is a poor solvent for a wide range of hydrophiles because of its low permittivity [1]. The most current technique to dissolve hydrophiles in SC–$CO_2$ is to make an addition of a small amount of entrainer to increase the polarity and therefore solvent power. However, an increase in the solubility of hydrophiles is not necessarily sufficient for this SC–$CO_2$ entrainer medium.

Our strategy is to dissolve the hydrophiles in a SC–$CO_2$/microemulsion system that involves dispersing small amounts of water in SC–$CO_2$. Water-in-oil microemulsions (or reverse micelles) have the property of enclosing small amounts of water in their interior thereby providing a stable aqueous microenvironment, the so-called water-pool, in non-aqueous media [2]. Reverse micelles have attracted considerable interest, because of this characteristic solubilization property and the high potential for experimental and industrial application. For example, reverse micelles have been

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widely applied in the field of the chemical reactions of solubilized substances such as artificial photosynthesis [3,4] and for the synthesis of fine-grains [5–7]. Catalysis and carrier function of reverse micelles should also be taken into consideration for future applications. Unfortunately, the preparation of stable microemulsion in SC–$CO_2$ has considerable difficulty compared to that in organic media because of the solubility of surfactant molecule. In fact, Consani and Smith have reported that over 130 commercially available surfactants are insoluble or only slightly soluble in SC–$CO_2$ and neither do they attract and nor retain significant amounts of water [8]. At present, fluorinated surfactants synthesized by Johnston and co-workers [9–13] and DeSimone and co-workers [14–16] seem to have the highest solubility in SC–$CO_2$. In our previous study, we have also applied the fluorinated surfactant to SC–$CO_2$ system for the formation of the stable microemulsion and for the solubilization of water-soluble dyes in the same system [17–19]. Further, other surfactants, ethylene glycol derivatives, were also examined for the same purpose [20–22]. In those studies, surfactants used were satisfactorily dissolved in SC–$CO_2$ and water-soluble dyes also solubilized in the same system. However, some disadvantages remain. For example, fluorinated surfactants are not commercially available, expensive and may have an undesirable environmental impact. In addition, microemulsions obtained by ethylene glycol derivatives required significant amounts of entrainer for the solubilization of water and water-soluble dyes. In order to raise the potential of the application of microemulsions in SC–$CO_2$ to academic and industrial fields, the preparation of suitable surfactants must be necessary.

The purpose of the present study is the preparation of stable water/$CO_2$ microemulsions for the solubilization of hydrophiles in SC–$CO_2$. In order to achieve this purpose, we have synthesized novel $CO_2$-philic surfactants. In the first half of this paper, synthesis of the novel surfactants and their solubility in SC–$CO_2$ were described. In the second half of this paper, solubilization of the polar substances in the same system was evaluated using conventional water-soluble dyes.

## 2. Experimental

### 2.1. Materials

Diethylene glycol (Nacalai Tesque Co., Ltd.), sodium hydride (Nacalai Tesque Co., Ltd.), tetrahydrofuran (Nacalai Tesque Co., Ltd.), chloromethyloxirane (Nacalai Tesque Co., Ltd.), 1-pentanol (Nacalai Tesque Co., Ltd.), 1-bromooctane (Nacalai Tesque Co., Ltd.), 1-octanol (Nacalai Tesque Co., Ltd.), 1-bromopentane (Nacalai Tesque Co., Ltd.), *t*-butyl alcohol (Nacalai Tesque Co., Ltd.), 1-bromo-2-ethylhexane (Tokyo Chemical Industry Co., Ltd.), and 2-ethyl-1-hexanol (Nacalai Tesque Co., Ltd.) were all used as received. Pentaethyleneglycol *n*-octyl ether was obtained from Nikko Chemicals Co., Ltd., and was used without further purification. Initial water content of pentaethyleneglycol *n*-octyl ether molecule was found through the Karl Fisher titration method to be 0.3% (w/w). The dyes used were 1,2-dihydroxyanthoraquinone (DA) and 3,4-dihydroxy-9,10-dioxo-2-anthoraquinonesulfonic acid sodium salt (DDA). These dyes were obtained from Aldrich Chemical Co. Inc., and were used as received.

The flow chart for the synthesis of surfactants was summarized in Scheme 1. The detailed procedure is as follows.

#### 2.1.1. Synthesis of pentaethyleneglycol nomomethyl ether (*1*)

Diethylene glycol (29.08 g, 0.27 mol) dissolved in 50 ml of THF was slowly injected into 50 ml of THF solution that contains NaH (1.97 g, 0.082 mol) in an ice bath and stirred at 333 K for 30 min. Diethylene glycol chloroethyl methyl ether (10.0 g, 0.055 mol) in 50 ml THF was then slowly injected and the mixture was refluxed at 348 K for 11 days. After reflux, the product was extracted with several portions of $H_2O/CH_2Cl_2$ and combined organic fractions were dried over $Na_2SO_4$ and evaporated to dryness. Solid product was re-extracted with several portions of $H_2O$/benzene and combined aqueous phase was extracted with $CH_2Cl_2$. Collected organic fractions were dried over $Na_2SO_4$ and evaporated to dryness (yield 6.31 g, 45.7%).

(**1**) $^1$H NMR: $\delta = 3.36$ (s, 3H, $-OCH_3$), 3.61–3.65 (m, 20H, $-OCH_2CH_2-O-$).

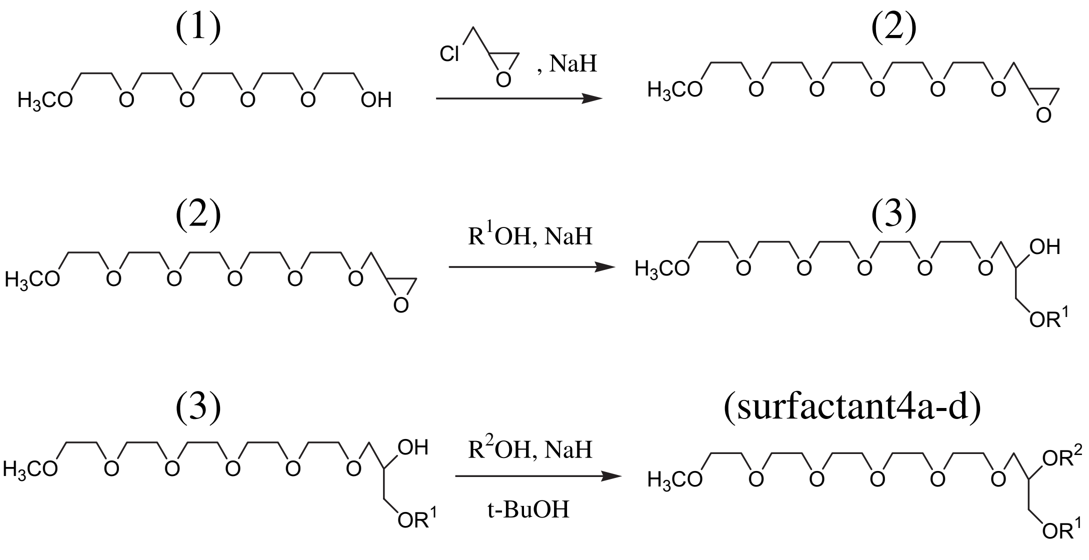
#### 2.1.2. Synthesis of pentaethyleneglycol glycidylmethyl ether (*2*)

Chloromethyloxirane (32.14 g, 0.35 mol) was dissolved in NaOH (13.90 g, 0.35 mol)/TBAB (0.62 g, 0.0019 mol) mixture. Pentaethyleneglycol nomomethyl ether (4.66 g, 0.019 mol) was then slowly injected in the solution and was allowed to react at 313 K for 5 h. After the reaction, the product was filtered with celite and extracted with several portions of $H_2O/CH_2Cl_2$. Collected organic fractions were dried over $Na_2SO_4$ and evaporated to dryness (yield 3.08 g, 51.6%).

(**2**) $^1$H NMR: $\delta = 2.61$ (dd, 1H, $J = 7$ Hz), 2.78 (t, 1H, $J = 7$ Hz), 3.12–3.23 (m, 1H), 3.36 (s, 3H, $-OCH_3$), 3.42 (d, 1H, $J = 8$ Hz), 3.44 (d, 1H, $J = 8$ Hz), 3.48–3.80 (m, 20H, $-OCH_2CH_2-O-$).

#### 2.1.3. Synthesis of 3-methylpentaethyleneglycol-1-pentylglycerol (*3*)

NaH (0.27 g, 0.011 mol) was dissolved in 1-pentanol (5.00 g, 0.057 mol). Pentaethyleneglycol glycidylmethyl ether (1.00 g, 0.0033 mol) was then slowly injected at 343 K and was allowed to react at 353 K for 30 h. After



| Surfactant- | 4a | 4b | 4c | 4d |
|---|---|---|---|---|
| $R^1$ | $(CH_2)_4CH_3$ | $(CH_2)_7CH_3$ | $(CH_2)_7CH_3$ | $CH_2CH\ (C_2H_5)\ (CH_2)_3CH_3$ |
| $R^2$ | $(CH_2)_7CH_3$ | $(CH_2)_4CH_3$ | $CH_2CH\ (C_2H_5)\ (CH_2)_3CH_3$ | $CH_2CH\ (C_2H_5)\ (CH_2)_3CH_3$ |

Scheme 1.

the reaction, the contents were cooled to room temperature and were neutralized with 1 N HCl (11.30 ml). The product was extracted with several portions of $H_2O/CH_2Cl_2$. Combined organic fractions were dried over $Na_2SO_4$ and the solvent was evaporated. The residue was purified with silica gel chromatography (benzene:ethyl acetate:methanol = 3:2:1) to give the corresponding 3-methylpentaethyleneglycol-1-pentylglycerol (yield 1.02 g, 81.0%).

(**3**) $^1H$ NMR: $\delta = 0.85–0.96$ (t, 3H, 7 Hz, $-CH_3$), 1.22–1.38 (m, 6H, $-CH_2-$), 1.59–1.63 (m, 2H, $-OCH_2-$), 3.36 (s, 3H, $-OCH_3$), 3.40–3.44 (m, 2H, $-OCH_2-R-$), 3.46–3.57 (m, 5H, $-OCH_2CHO-CH_2-O-$), 3.63–3.65 (m, 20H, $O-CH_2CH_2O-$).

### *2.1.4. Synthesis of 3-methylpentaethyleneglycol-2-octyl-1-pentylglycerol (**surfactant-4a**)*

3-Methylpentaethyleneglycol-1-pentylglycerol (0.50 g, 0.0011 mol)/*tert*-butyl alcohol (5 ml) was slowly injected in NaH (0.27 g, 0.011 mol)/*tert*-butyl alcohol (50 ml) mixture at 333 K. 1-Bromooctane (0.86 g, 0.0057 mol)/*tert*-butyl alcohol (5 ml) was then slowly added. The mixtures were refluxed at 363 K for 70 h and were extracted with several portions of $H_2O/CH_2Cl_2$. Combined organic fractions were dried over $Na_2SO_4$ and the solvent was evaporated. The residue was purified with silica gel chromatography (benzene:ethyl acetate = 1:2) to give the corresponding 3-methylpentaethyleneglycol-2-octyl-1-pentylglycerol (**surfactant-4a**, yield 0.58 g, 75.8%).

(**4a**) $^1H$ NMR: $\delta = 0.82–0.92$ (m, 6H, $-CH_3$), 1.22–1.39 (m, 12H, $-CH_2-$), 1.53–1.61 (m, 4H, $-O-C-CH_2-$), 3.67 (s, 3H, $-OCH_3$), 3.41–3.60 (m, 9H), 3.62–3.69 (m, 20H, $-OCH_2CH_2-O-$).

### *2.1.5. Synthesis of 3-methylpentaethyleneglycol-1-octylglycerol*

NaH (0.27 g, 0.011 mol) was dissolved in 1-octanol (7.00 g, 0.054 mol). Pentaethyleneglycol glycidylmethyl ether (1.00 g, 0.0033 mol) was then slowly injected at 70 °C and was allowed to react at 353 K for 23 h. After the reaction, the contents were cooled to room temperature and were neutralized with 1 N HCl (11.30 ml). The product was extracted with several portions of $H_2O/CH_2Cl_2$. Combined organic fractions were dried over $Na_2SO_4$ and the solvent was evaporated. The residue was purified with silica gel chromatography (benzene:ethyl acetate:methanol = 3:1:0.7) to give the corresponding 3-methylpentaethyleneglycol-1-octylglycerol (yield 1.12 g, 79.0%).

$^1H$ NMR: $\delta = 0.83–0.94$ (t, 3H, 7 Hz, $-CH_3$), 1.19–1.39 (m, 12H, $-CH_2-$), 1.58–1.63 (m, 2H, $-OCH_2-$), 3.36 (s, 3H, $-OCH_3$), 3.39–3.43 (m, 2H, $-OCH_2-R-$), 3.45–3.53 (m, 5H, $-OCH_2CHO-CH_2-O-$), 3.59–3.68 (m, 20H, $O-CH_2CH_2O-$).

### 2.1.6. Synthesis of 3-methylpentaethyleneglycol-2-pentyl-1-octylglycerol (**surfactant-4b**)

3-Methylpentaethyleneglycol-1-octylglycerol (0.50 g, 0.0011 mol)/*t*-butyl alcohol (5 ml) was slowly injected in NaH (0.27 g, 0.011 mol)/*t*-butyl alcohol (50 ml) mixture at 333 K. 1-Bromopentane (0.86 g, 0.0057 mol)/*t*-butyl alcohol (5 ml) was then slowly added. The mixtures were refluxed at 363 K for 70 h and were extracted with several portions of $H_2O/CH_2Cl_2$. Combined organic fractions were dried over $Na_2SO_4$ and the solvent was evaporated. The residue was purified with silica gel chromatography (benzene:ethyl acetate = 1:1) to give the corresponding 3-methylpentaethyleneglycol-2-pentyl-1-octylglycerol (**surfactant-4b**, yield 0.50 g, 87.9%).

(**4b**) $^1$H NMR:$\delta = 0.82–0.91$ (m, 6H, $-CH_3$), 1.22–1.37 (m, 12H, $-CH_2-$), 1.49–1.60 (m, 4H, $-O-C-CH_2-$), 3.36 (s, 3H, $-OCH_3$), 3.39–3.58 (m, 9H), 3.63–3.71 (m, 20H, $-OCH_2CH_2-O-$).

### 2.1.7. Synthesis of 3-methylpentaethyleneglycol-2-(2-ethylhexyl)-1-octhylglycerol (**surfactant-4c**)

3-Methylpentaethyleneglycol-1-octylglycerol (0.60 g, 0.0014 mol)/*t*-butyl alcohol (5 ml) was slowly injected in NaH (0.33 g, 0.014 mol)/*t*-butyl alcohol (50 ml) mixture at 333 K. 1-Bromo-2-ethylhexane (1.98 g, 0.010 mol)/*t*-butyl alcohol (5 ml) was then slowly added. The mixtures were refluxed at 363 K for 5 days and were extracted with several portions of $H_2O/CH_2Cl_2$. Combined organic fractions were dried over $Na_2SO_4$ and the solvent was evaporated. The residue was purified with silica gel chromatography (benzene: ethyl acetate = 1:1) to give the corresponding 3-methylpentaethyleneglycol-2-(2-ethylhexyl)-1-octhylglycerol (**surfactant-4c**, yield 0.60 g, 79.6%).

(**4c**) $^1$H NMR: $\delta = 0.81–0.90$ (m, 9H, $-CH_3$), 1.19–1.51 (m, 21H, $-CH_2-$ and $-CH-$), 3.36 (s, 3H, $-OCH_3$), 3.41–3.50 (m, 4H, $-O-CH_2-R$), 3.48–3.61 (m, 5H, $O-CH_2-CHO-CH_2-O-$), 3.58–3.69 (m, 20H, $-OCH_2CH_2-$).

### 2.1.8. Synthesis of 3-methylpentaethyleneglycol-1-(2-ethylhexylglycerol)

NaH (0.27 g, 0.011 mol) was dissolved in 2-ethyl-1-hexanol (6.76 g, 0.052 mol). Pentaethyleneglycol glycidylmethyl ether (1.00 g, 0.0033 mol) was then slowly injected at 343 K and was allowed to react at 353 K for 21 h. After the reaction, the contents were cooled to room temperature and were neutralized with 1 N HCl (11.30 ml). The product was extracted with several portions of $H_2O/CH_2Cl_2$. Combined organic fractions were dried over $Na_2SO_4$ and the solvent was evaporated. The residue was purified with silica gel chromatography (benzene:methanol = 7.5:1) to give the corresponding 3-methylpentaethyleneglycol-1-(2-ethylhexylglycerol) (yield 0.87 g, 61.3%).

$^1$H NMR: $\delta = 0.81–0.92$ (m, 6H, $-CH_3$), 1.20–1.54 (m, 9H, $-CH_2-$ and $-CH-$), 3.36 (s, 3H, $-OCH_3$), 3.39–3.43 (m, 2H, $-O-CH_2-R$), 3.51–3.60 (m, 5H, $O-CH_2-CHO-CH_2-O-$), 3.63–3.66 (m, 20H, $-OCH_2CH_2-$).

### 2.1.9. Synthesis of 3-methylpentaethyleneglycol-2-(2-ethylhexyl)-1-(2-ethylhexylglycerol) (**surfactant-4d**)

3-Methylpentaethyleneglycol-1-(2-ethylhexylglycerol) (0.84 g, 0.0019 mol)/*t*-butyl alcohol (5 ml) was slowly injected in NaH (0.46 g, 0.019 mol)/*t*-butyl alcohol (50 ml) mixture at 333 K. 1-Bromo-2-ethylhexane (2.76 g, 0.014 mol)/*t*-butyl alcohol (5 ml) was then slowly added. The mixtures were refluxed at 363 K for 4 days and were extracted with several portions of $H_2O/CH_2Cl_2$. Combined organic fractions were dried over $Na_2SO_4$ and the solvent was evaporated. The residue was purified with silica gel chromatography (benzene:ethyl acetate = 3:2) to give the corresponding 3-methylpentaethyleneglycol-2-(2-ethylhexyl)-1-(2-ethylhexylglycerol) (**surfactant-4d**, yield 0.83 g, 78.7%).

(**4d**) $^1$H NMR: $\delta = 0.81–0.93$ (m, 12H, $-CH_3$), 1.19–1.48 (m, 18H, $-CH_2-$ and $-CH-$), 3.38 (s, 3H, $-OCH_3$), 3.40–3.53 (m, 4H, $-O-CH_2-R$), 3.48–3.61 (m, 5H, $O-CH_2-CHO-CH_2-O-$), 3.59–3.72 (m, 20H, $-OCH_2CH_2-$).

## 2.2. Procedure

The phase behavior of microemulsions in SC–$CO_2$ and the solubilization of dyes in the same system were evaluated using high-pressure reaction apparatus as described before [17]. The main component of the apparatus was a stainless steel viewing cell (4.6 $cm^3$ total volume) containing a 3 cm diameter optical window, which was 1.5 cm thick. In all experiments, prescribed amounts of the surfactant, water and dyes were loaded into the bottom of the cell before commencing. Liquid $CO_2$ from a cylinder was compressed via a pressurizing pump and caused to flow to the reaction cell until the pressure reached the desired value. The contents of the cell were stirred using a Teflon-coated bar driven by an exterior magnet. Phase boundaries of mixtures were confirmed by visual inspection through optical windows. In each experiment, pressures at the cloud point were accumulated by several measurements. Average pressures observed at each cloud point were converted to the density through Ely–Haynes–Bain method [23]. Solubilization of the dye in the system was confirmed by optical observations with Multichannel Spectrophotometer MCPD-100 (Otsuka Electronics Co., Ltd.) to determine the visible absorption of the system. In this paper, the quantity of solubilized water in the system was expressed as the molar ratio of water to surfactant, that is, $w = [H_2O]/[\text{surfactant}]$.

## 3. Results and discussion

Fig. 1 shows phase boundary of the **surfactant-4a**/$CO_2$ system as a function of $CO_2$ density. A clear one phase region is given at the right side of each plot. For comparison, the solubility of the pentaethyleneglycol *n*-octyl ether in SC–$CO_2$ is also shown. The pentaethyleneglycol *n*-octyl ether is known as a $CO_2$-philic surfactant that has been presented by Johnston and coworkers [24]. The structure of the pentaethyleneglycol *n*-octyl ether molecule is similar to the **surfanctant-4a** except the presence of the side chain. Therefore the solubility of the pentaethyleneglycol *n*-octyl ether in SC–$CO_2$ is a good measure to evaluate the solubility of the surfactants synthesized in this study. As shown in Fig. 1, the solubility of **surfactant-4a** in SC–$CO_2$ increased with increasing $CO_2$ density. These behaviors well agree with that of the pentaethyleneglycol *n*-octyl ether molecule. An increase in the solvent power obviously relates to the solubility of these surfactants. However, the solubility of **surfactant-4a** in the system at a definite $CO_2$ density is quite different from that of the pentaethyleneglycol *n*-octyl ether. The amount of **surfactant-4a** that can dissolve in SC–$CO_2$ is 3-hold high compared to the pentaethyleneglycol *n*-octyl ether. It is interesting to note that **surfactant-4a** shows high solubility in SC–$CO_2$ even without the addition of any entrainer. High solubility of **surfactant-4a** in this system may relate to the end group of the molecule. Alternatively, the side chain of the surfactant molecule may play an important role in the dissolution behavior of **surfactant-4a**. Dealing with the first issue of an effect of the end group of the molecule, the terminal $CH_3$ group in **surfactant-4a** may reduce the opportunity of cohesion between the molecules. As a result, **surfactant-4a** would show higher solubility in SC–$CO_2$ compares to pentaethyleneglycol *n*-octyl ether. The second factor to be considered is an effect of the side chain of the surfactant molecule. As is generally known, the solubility of the surfactant in SC–$CO_2$ is remarkably enhanced when suitable entrainer is present in the system. The most current entrainer would be a kind of alcohol. As is obviously shown from the structure of **surfactant-4a**, the side chain is composed of pentyl group and is bonded with ether bond. Therefore the role of the pentyl group in **surfactant-4a** molecule may correspond to pentyl alcohol as an entrainer. In addition, chain length of the side chain would be suitable to interact with the surfactant tail more tightly.

In the surfactant/entrainer/$CO_2$ system, two possibilities are generally considered as a role of an entrainer. One is the role of the co-surfactant, which concentrates at the surfactant interface. Mitchell et al. demonstrated that entrainers operate by inserting itself between surfactant tails and reducing tail–tail interactions [25,26]. On the other hand, DeGennes et al. reported that the entrainer acts on the surfactant interface itself to reduce interfacial tension, which promote the formation of flexible microemulsion [27,28]. The validity of those proposals may be evaluated with the results in this study. As mentioned above, the side chain that equivalents to pentyl alcohol as an entrainer is bonded with the center of **surfactant-4a**. Further **surfactant-4a** shows higher solubility in SC–$CO_2$ compared to pentaethyleneglycol *n*-octyl ether. From these results the role of entrainer seems not to be adsorption on the interface of the surfactant but insertion between surfactant tails to exhibit the ability as a co-surfactant in this system.

Fig. 2 compares effects of temperature on phase boundary of **surfactant-4a** or **-4b**/$CO_2$ system. In this case, a clear one phase region is given at the upper side of each plot. As shown in Fig. 2, the difference in the temperature has negligible influence on the solubility of **surfactant-4a** and **-4b**. Further, the difference in the solubility between them was not observed. As shown in Scheme 1 the difference in chemical structures between **surfactants-4a** and **-4b** may be ignored because alkyl tail and side chain of those surfactants are freely replaced by

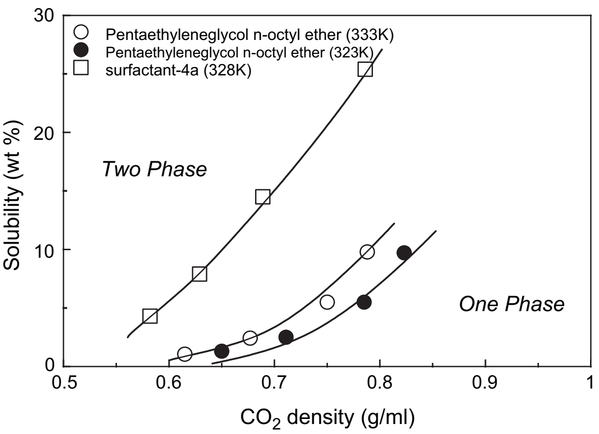


Fig. 1. Phase boundaries of the surfactant/$CO_2$ system.

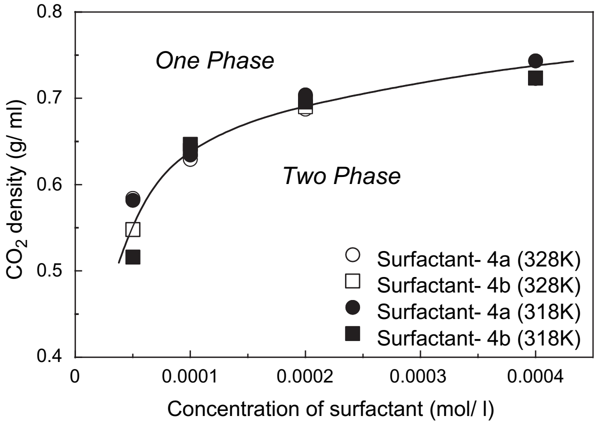


Fig. 2. Effects of temperature on phase boundaries of the surfactant/$CO_2$ system.

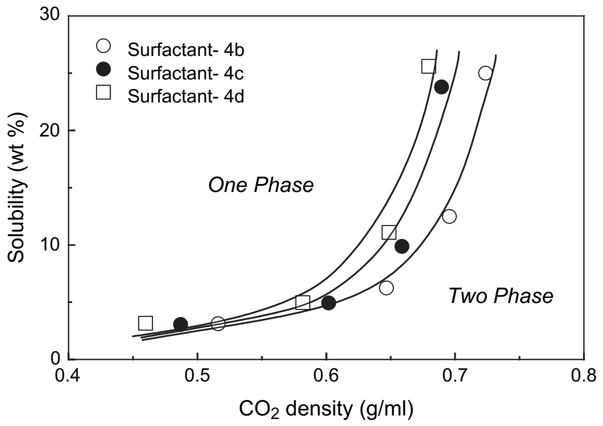


Fig. 3. Effects of the side chain of the surfactant molecule on phase boundaries of the surfactant/$CO_2$ system at 313 K.

a rotation of molecular chain. Since the difference in the chain length between the alkyl tail and the side chain is slight, affinity of the surfactant molecule to $CO_2$ would be equivalent. Fig. 3 shows the results of similar investigation at the time of using **surfactant-4b**, **-4c** and **-4d**. The effect of alkyl branch of the side chain in the surfactant molecule could be evaluated by comparing their solubility. As shown in Fig. 3, the solubility of **surfactant-4c** that contains one ethyl branch in the side chain is equivalent or slightly lower than that of **surfactant-4b**. The similar tendency was seen observed in the relation between **surfactant-4a** and **-4b**. Branched hydrocarbon group seems to be unfavorable for the solvation with $CO_2$ molecule.

Fig. 4 shows the solubility of water in **surfactant-4a**/$CO_2$ system. For comparison, the solubility of water in pure $CO_2$ at the same temperature is also shown as a dotted line. The total amount of water solubilized in the system is higher than that in pure $CO_2$, indicating that introduced water is partially stabilized as the water droplets. **Surfactant-4a** seems to have an ability to form water in $CO_2$ microemulsion. $CO_2$ density that is necessary to solubilize water in the system increased with increasing the $w$ value. These results well agree with our previous data examined with fluorinated surfactants [17]. However, the maximum $w$ value without phase separation in this system was very low. Clear one phase was never obtained at more than $w = 2$, suggesting that **surfactant-4a** molecule was saturated with water around $w = 2$. From these results, the majority of introduced water in this system may be bound with polyoxyethylene chain of the surfactant molecule. As a result, there is very little quantity of water which can exist as free water. These results may also relate to the terminal group of the surfactant molecule. Different from surfactants synthesized in this study, the surfactant which contains terminal OH group in a molecule could take in a lot of water in the interior of aggregates. On the other hand, the interior of aggregates with **surfactant-4a** may not have an ability to form the larger water droplet because of the repulsion of the terminal $CH_3$ group.

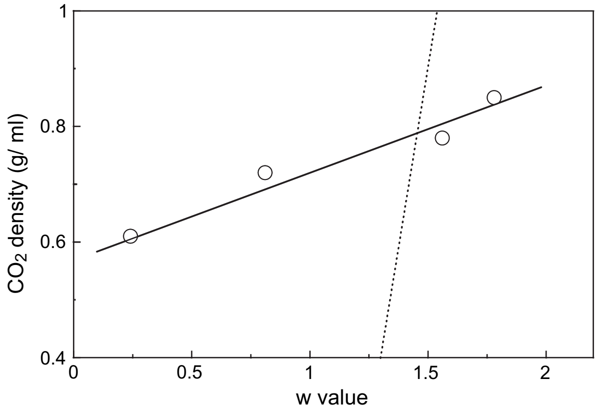


Fig. 4. Solubility of water in surfactant/$CO_2$ system.

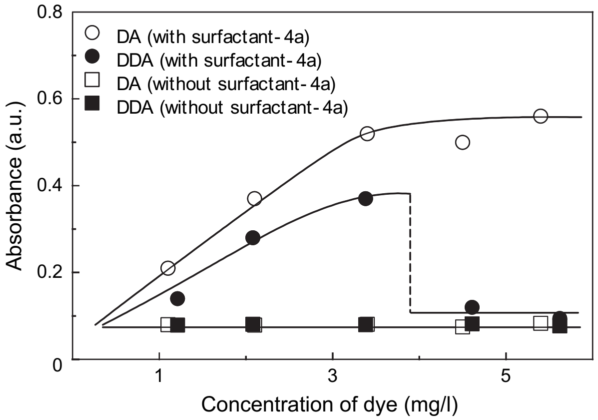


Fig. 5. Solubility of dyes in the surfactant/$CO_2$/water system. Temperature: 313 K, $CO_2$ density: 0.7 g/ml, $w = 1.5$, [**surfactant-4a**]: 0.2 mM.

Fig. 5 compares the variation of the absorbance of two kinds of dyes from the **surfactant-4a**/$CO_2$ system. In

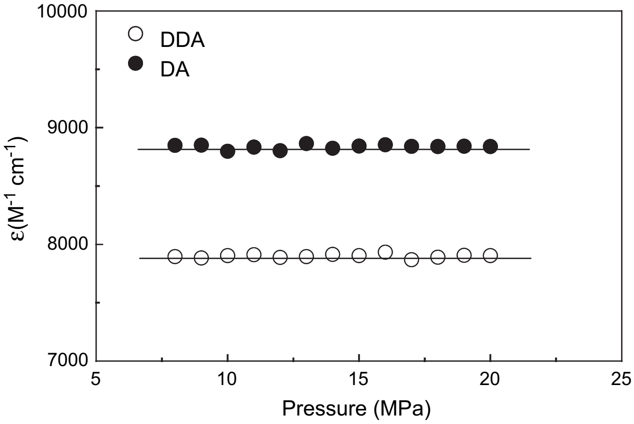


Fig. 6. Variations of molar extinction coefficient of 1,2-dihydroxyanthoraquinone (DA) and 3,4-dihydroxy-9,10-dioxo-2-anthoraquinonesulfonic acid sodium salt (DDA) in **surfactant-4a**/$CO_2$/water system as a function of $CO_2$ density. Temperature: 313 K, $w = 1.5$, [**surfactant-4a**]: 0.2 mM.

this case, the absorbance of each dye was recorded at the wavelength of their maximum absorption. For comparison, the absorbance from a similar system without **surfactant-4a** was also shown. As shown in Fig. 5, the absorbance of both dyes from the system without **surfactant-4a** showed zero dye absorbance, indicating that dyes did not dissolve in the system. When **surfactant-4a** is added in the system, an increase in the concentration of the dye results in an increase in the absorbance irrespective of the dye used. The introduced dyes seem to be apparently solubilized in SC–$CO_2$ media. However, the variation of the absorbance of these two dyes in comparatively high concentration is quite different. The absorbance from DDA disappeared at a higher concentration of the dye, although the absorbance from DA leveled off at a higher concentration of the dye. These results may be explained with their solubilizing behaviors into the system or the differences in the functional group in the dye molecule. In the former case, the microemulsion in this system may not have the large scale water droplet as mentioned before. Therefore almost all introduced dye would not be solubilized in free water in the water droplet but is solvated with the polyoxyethylene chain of the surfactant molecule. After the surfactant molecule is saturated with the introduced dye, it may be difficult to dissolve surplus dyes in this system in which bulk-like water does not exist. In addition, $SO_3Na$ group in DDA molecule might be equivalent to an addition of a strong electrolyte to a colloidal system. As a result, all the dye in the system may have precipitated with the surfactant according to the same phenomenon similar to flocculation. In the system containing DA, on the other hand, flocculation does not occur because there is no component that corresponds to an electrolyte and only the superfluous dyes precipitate.

Fig. 6 shows the variation of molar extinction coefficient ($\varepsilon$) of dyes as a function of $CO_2$ density. As shown in Fig. 6, $\varepsilon$ of both dyes seems to be constant regardless of $CO_2$ density. These results are different from those of $CO_2$ soluble substances. Rice et al. reported [29] that $\varepsilon$ of a specimen in SC–$CO_2$ was greatly dependent on the $CO_2$ density. The shift or the change of the spectrum would cause the apparent $CO_2$ density dependency of $\varepsilon$ because the variation of the density results in the variation of the solvent power. Therefore, dissolution of the solute into $CO_2$ of different pressure would correspond to the dissolution into different kinds of solvents. Dissolution of the dye in this case, on the other hand, was attained by dissolution of the surfactant into SC–$CO_2$ because the dye itself was solvated with a part of the polyoxyethylene chain of the surfactant molecule. As a result, dissolution condition of the used dye was not changed even if the surrounding environment was changed.

## 4. Conclusion

Solubility of novel polyethyleneglycol dialkylglycerol surfactants in SC–$CO_2$ has been investigated. Four kinds of surfactants synthesized in this study showed high solubility in SC–$CO_2$ even without the addition of any entrainer. We found that alkyl side chain within the synthesized surfactants had an important role as a co-surfactant to increase their solubility in SC–$CO_2$. Water and water-soluble dyes were also solubilized in the same systems. However, their amount in the system was little compared to those of general microemulsion systems. We concluded that the problem in the limitation of solubilization could be improved by further modification of the terminal group of the surfactant molecule.

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