Highly Methyl-Branched Hydrocarbon Surfactant as a CO₂-philic Solubilizer for Water/Supercritical CO₂ Microemulsion

Masanobu Sagisaka*, Kotaro Kudo, Shota Nagoya and Atsushi Yoshizawa

Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University (Bunkyo-cho 3, Hirosaki, Aomori 036-8561, JAPAN)

Abstract: To develop an efficient and fluorine-free solubilizer for a water/supercritical CO₂ microemulsion (W/CO₂ μ E), in this study, a highly methyl-branched alkyl, isostearyl group was focused on as a CO₂-philic tail, and the custom-made isostearyl surfactant, sodium 2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl sulfate (SIS1) was synthesized. The surface tension (γ) of an aqueous SIS1 solution was measured at ambient pressure as a function of surfactant concentration, and it was found to be 25 mN/m at concentrations of > 1.5 mM. A low γ value can generally be reached only by a fluorocarbon surfactant, which implies that SIS1 has an excellent solubilizing power for the W/CO₂ μ E, similar to some fluorocarbon surfactants reported previously. Visual observations of the SIS1/W/CO₂ mixtures revealed the formation of transparent single phases without separated water, identified as W/CO₂ μ E. The μ E was well-stabilized at pressures > 210 bar and temperatures > 55 °C. At 75 °C and 370 bar, SIS1 was found by spectral measurements using a water-soluble UV-light absorber to solubilize water contents up to a maximum water-to-surfactant molar ratio (W_0) = 50. The achievement of W_0 = 50 in a W/CO₂ μ E system has not been reported previously in similar hydrocarbon surfactant/W/CO₂ systems, and this demonstrates that a highly methyl-branched alkyl group can act as a good CO₂-philic group for a W/CO₂ -type surfactant.

Key words: supercritical carbon dioxide, microemulsion, surfactant, reversed micelle, solubilizing power

1 INTRODUCTION

The emission of volatile organic compounds (VOCs) and effluent waste streams pose threats to the environment. Carbon dioxide is one of the few solvents not regulated as a VOC by the US Environmental Protection Agency (EPA). Furthermore, liquid or supercritical carbon dioxide (scCO₂) represents a cheap, nontoxic, nonflammable and environmentally responsible alternative to conventional VOC solvents. CO₂ has other important advantages in that it is readily available from renewable resources, and it is recyclable and biocompatible. It is also unique as a solvent (apart from water) it is 100% biorecyclable through photosynthetic pathways. The critical point is readily accessible (31.1 °C and 73.8 bar), so that the variation of solvent density with temperature and pressure offers flexibility in solvent power, which is not so readily achieved with normal solvents. Rapid solvent removal and recycling are also possible by controlling evaporation and condensation. Recently, efforts have been made to promote the use of scCO₂ and

to develop suitable formulations for a whole range of industrial processes. As scCO₂ can dissolve certain low-molecular-weight and nonpolar materials, it is already routinely employed as a solvent routinely for various commercial processes, such as coffee decaffeination, chromatography, extraction, organic synthesis, polymerization, and nanomaterial processing¹⁾. Therefore, scCO₂ offers great opportunities for applications in a variety of domains.

ScCO₂ containing reversed micelles with encapsulated aqueous cores, in other words, a W/CO₂ microemulsion (W/CO₂ μ E), can be assumed to be a "universal solvent." The universal solvent is an organized fluid that combines the desirable characteristics of scCO₂ with the solution properties of bulk water, and it can be used to overcome the problems in the use of typical W/O μ Es for chemical industries²⁾.

For the W/CO₂ μ E to be a viable green technology, the amount of surfactant used should be as small as possible, whereas a larger W/CO₂ interfacial area and a larger

*Correspondence to: Masanobu Sagisaka, Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, Bunkyo-cho 3, Hirosaki, Aomori 036-8561, JAPAN

E-mail: sagisaka@cc.hirosaki-u.ac.jp

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amount of dispersed water are preferable to enhance efficiencies in those applications. One approach to meet these requirements is to explore or develop a highly efficient solubilizer for W/CO₂ μ E. Since 1990, considerable effort has been directed towards the development of surfactants that stabilize W/CO₂ μ Es^{3–20}. In earlier studies, several fluorinated surfactants were found to dissolve in CO₂ to have a high activity at the W/CO₂ interface, suggesting the feasibility of forming W/CO₂ μ Es^{21–25}. However, fluorinated surfactants, specially having long fluorocarbon chains $\geq$ C8, should be avoided in chemical industrial applications from the viewpoints of environmental and economic concerns.

The development of inexpensive and environmentally acceptable CO₂-philic hydrocarbon surfactants has also been conducted^{3–9}. However, most commercial and known hydrocarbon surfactants are insoluble and inactive in scCO₂ systems^{3–8}. In this regard, it became apparent that conventional surfactant-design theory cannot be applied to W/CO₂ systems directly and that CO₂-philicity is not directly comparable to oleo-philicity. Therefore, advancing molecular-design theory for CO₂-philic surfactants has required new directions and paradigms.

To date, only a few hydrocarbon surfactants have been reported to stabilize a W/CO₂ μ E. One of these successful surfactants is the nonionic TMN-6 (Fig. 1)^{9–11}, which has highly branched alkyl tails and $\sim$ 8 oxyethylene units. TMN-6 was reported to solubilize water up to a water-to-surfactant molar ratio, W_0 , of 30. Custom-made anionic surfactants with highly branched double or triple tails (sodium bis(3,5,5-trimethyl-1-hexyl)sulfosuccinate^{12–14}) or (sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate^{15–17}) were also found to be soluble in scCO₂ and to yield transparent, single-phase W/CO₂ μ Es (Winsor-IV W/CO₂ μ E or IV μ E) with W_0 less than

15. Note that the commercial analogue of these surfactants, Aerosol-OT (sodium bis-(2-ethyl-1-hexyl)sulfosuccinate, AOT) is inactive and insoluble in scCO₂ and is ineffective at stabilizing W/CO₂ μ Es. On the other hand, ester and ether groups have been reported to increase solubility in scCO₂ as effectively as methyl branches, and highly CO₂-philic and W/CO₂-interfacially-active copolymers with those groups have been developed and used for emulsification and polymerization^{18–20}. Unfortunately, an efficient and cost-effective hydrocarbon stabilizer for W/CO₂ μ Es, like the AOT used commonly for W/O μ Es^{26, 27}, has not yet been found.

As described above, a hydrocarbon surfactant can be rendered CO₂ compatible by having multiple methyl groups, lessening the need for environmentally hazardous (non-biodegradable) and expensive fluorocarbon chains¹⁵. This finding has the potential to encourage new academic studies and enhance the commercial viability of hydrocarbon surfactants as CO₂-philic solubilizers.

Recently, a highly methylated isostearyl unit was found to be strongly CO₂-philic²⁸. This study focused on the group as a non-fluorous CO₂-philic and strongly hydrophobic tail for an efficient CO₂-philic solubilizer. The hydrocarbon surfactant, sodium 2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl sulfate (SIS1, Fig. 1) was synthesized, and its solubilizing power and aggregation behavior in scCO₂ were examined in this study.

2 EXPERIMENTAL

2.1 Materials

We synthesized and purified the isostearyl surfactant SIS1 in our laboratory, as described in Sec. 2.2. Ultrapure water with a resistivity of 18.2 M Ω cm was obtained from a Millipore Milli-Q Plus system. CO₂ of 99.99% purity (Nippon Ekitan Co. Ltd.) was used without further treatment.

Isostearyl alcohol FO-180 was provided by Nissan Chemical Industries. *p*-Toluenesulfonic acid, sodium hydrogen carbonate, sodium sulfate, ethanol, hexane and isopropanol were purchased from Wako Pure Chemical Industries; pyridine, from Kanto Kagaku; sulfur trioxide/pyridine complex, from Acros Organics; and silica gel 60 (63–210 μ m), from Kanto Kagaku. These were used directly without further treatment. A 0.1 wt% aqueous solution of the water-soluble UV-absorber sodium *p*-toluenesulfonate (SpTS) was prepared by neutralization of aqueous *p*-toluenesulfonic acid solution with sodium hydrogen carbonate.

2.2 Synthesis

Isostearyl alcohol FO-180 (30.11 g, 111.5 mmol) and SO₃/pyridine complex (26.5 g, 16.6 mmol) were mixed in pyridine (220 mL), and the resultant solution was stirred at 50°C for 1 day. After the reaction was complete, an

Fig. 1 Chemical structures of SIS1 and TMN-6.

aqueous sodium bisulfate solution (21 g NaHCO₃ in 100 mL water) was slowly poured into the residue at 0°C (in an ice bath), and then, the mixture was stirred at 50°C for 10 min. The reaction mixture was added to isopropanol and washed with brine several times. The organic phase was dried with Na₂SO₄, and then, evaporated. Finally, purification by silica gel column chromatography with ethanol/*n*-hexane (1:10) mixture as the eluent, afforded SIS1 as a white solid (yield: 15.65 g, 37.7%): ¹H-NMR (500 MHz, CDCl₃, TMS), (δH/ppm): 0.76-1.79 (multiplet (m), 35H, aliphatic-*H*), 3.85-4.05 (m, 2H, -OCH₂); IR (KBr) ν_{max}/cm⁻¹: 2955, 1476, 1364, 1246, 1067, 971, 834, 587; Elemental analysis for C₁₈H₃₇O₄Na: found C, 57.7; H, 10.0; S, 8.6. Calcd C, 58.0; H, 10.0; S, 7.0.

2.3 Apparatus

2.3.1 Surface tension measurement

Surface tensions of aqueous surfactant solutions were measured using a Wilhelmy tensiometer (CBVP-Z, Kyowa Interface Science) equipped with a platinum plate. The measurements were performed at 35 ± 0.1°C until constant values of the surface tension of the aqueous surfactant solutions were obtained; the experimental error was less than 0.1 mN/m. The critical micelle concentration (CMC) was obtained from the point of intersection of the curves in the graph of surface tension versus logarithm of the surfactant concentration.

2.3.2 Visual observation and spectral measurement of SIS1/water/scCO₂ mixtures

A high-pressure vessel with an optical window and a moveable piston inside the vessel was used to observe the phase behavior of surfactant/water/scCO₂ mixtures with varying pressure and temperature but constant composition. A detailed description of the experimental apparatus is shown in Fig. 2.

In order to examine the formation of aqueous cores in W/CO₂ μEs, UV-visible absorption spectroscopy measurements were performed using SpTS as a trace marker for aqueous core, on a double-beam spectrometer (Hitachi High-Technologies, Co., U-2810), with a quartz window pressure cell (volume: 1.5 mL), which was connected to the experimental apparatus. The cell was made of stainless steel (SUS316), and it had three quartz windows with a thickness of 8 mm. Each window had an inner diameter of 10 mm; the windows were positioned so as to provide a perpendicular 10-mm optical path. Each window was attached to the stainless steel body of the cell using PTFE Kel-F packing. The windows were fastened tightly to the steel body, thereby compressing the packing between the stainless steel parts and the quartz window and providing excellent sealing (tested up to 400 bar). The temperature of the cell was controlled by circulating water from a thermostat bath. Spectroscopic measurements were performed and the resulting absorption spectra of the cell windows

Fig. 2 Schematic representation of the experimental apparatus.

were compared with those of a standard quartz cell for an aqueous SpTS solution at ambient pressure; it was observed that both the spectra were in good agreement with each other.

The measurements of the water/surfactant/scCO₂ systems were performed at temperatures of 35–75°C and pressures lower than 400 bar. In addition to a raw water-to-surfactant molar ratio (W_0), the parameter W_0^c was used to express the true water-to-surfactant molar ratios in the W/CO₂ μ E droplets. The solubility of water in scCO₂ was calculated as follows^{21–25}:

$$W_0^c = \frac{[\text{water}]_0 - [\text{water}]_s}{[\text{surfactant}]_0} = W_0 - \frac{[\text{water}]_s}{[\text{surfactant}]_0} \quad (1)$$

where $[\text{water}]_0$ is the number of moles of water in the system, $[\text{water}]_s$ is the number of moles of water soluble in the background CO₂, and $[\text{surfactant}]_0$ is the number of moles of surfactant. The value of $[\text{water}]_s$ was obtained from literature data^{29,30}. The densities of CO₂ were calculated using the Span-Wagner equation of state (EOS)³¹. Pre-determined amounts of surfactant and CO₂ (20.0 g), where the molar ratio of surfactant to CO₂ was fixed at 8×10^{-4} , were loaded into a variable-volume high-pressure optical cell. Then, water or an aqueous MO solution (3 mmol L⁻¹), was added to the optical cell through a six-port valve until the clear single-phase Winsor-IV W/scCO₂ μ E (IV μ E) solution became a turbid macroemulsion (E) solution or a precipitated hydrated surfactant. The surfactant molar concentration was in the range 10–20 mmol L⁻¹ (for example, 16.7 mmol L⁻¹ at 45°C and 350 bar) as the inner volume of the cell was varied by changing experimental pressure and temperature.

During spectroscopic measurements, the scCO₂ mixture was stirred and circulated between the optical vessel and the quartz window cell until a constant absorbance was attained. The circulation was then discontinued; the valves between the vessel and the quartz window cell were closed, and the measurement was performed. The physical properties of the continuous phase of scCO₂ were assumed to be equivalent to those of pure CO₂.

3 RESULTS

3.1 Interfacial Properties of SIS1 in Water

Surface tension γ of an aqueous SIS1 solution was studied as a function of concentration to determine the CMC and the surface tension at CMC (γ_{CMC}). The parameter γ_{CMC} is especially important in predicting the solubilizing ability of the surfactant in scCO₂^{32–36}; this is because (1) the water/air and water/CO₂ interfacial properties of the surfactant are correlated, and (2) a microemulsion generally forms at an interfacial tension below 1 mN/m³⁷.

Figure 3 shows the aqueous surface tensions of the highly methyl-branched hydrocarbon surfactants, SIS1 and

Fig. 3 Change in aqueous surface tension as a function of the logarithm of surfactant concentration at 35°C and 1 bar.

TMN-6, at various concentrations at 35°C. The surface tension data of TMN-6 was taken from reference¹¹ as a control. The surface tension was found to decrease as a function of concentration; however, it was invariant above the concentration indicated by the arrow in Fig. 3. The threshold concentrations were defined as the CMC. The area per SIS1 or TMN-6 molecule at the surface, A , was also calculated using the Gibbs equation and the slope of γ versus logarithm of the surfactant concentration below the CMC. The values of CMC, γ_{CMC} , and A are listed in Table 1. A comparison between SIS1 and TMN-6 revealed that the CMC and A of SIS1 were almost 1.7 and 1.5 times larger than those of TMN-6, resulting from the larger sulfate head group having mutual electrostatic repulsion and/or the bulkier isostearyl CO₂-philic tail. On the other hand, the ability to lower the surface tension of SIS1 was slightly higher than that of TMN-6, as shown by the γ_{CMC} values of 25 for SIS1 and 26 for TMN-6. This implies that SIS1 has a greater ability to lower the W/scCO₂ interfacial tension, and consequently, has a higher solubilizing power for W/CO₂ μ Es^{32–36}. This result demonstrates that a highly methyl-

Table 1 Interfacial properties of SIS1 and TMN-6 in water at 35°C and 1 bar.

	CMC* ¹ /(mol L ⁻¹)	γ_{CMC} * ² /(mN m ⁻¹)	A * ³ / Å ²
TMN-6 * ⁴	8.8×10^{-4}	26	70
SIS1	1.5×10^{-3}	25	103

*¹ Critical micelle concentration. *² Surface tension at CMC. *³ Area occupied by one surfactant molecule. *⁴ The data for TMN-6 were taken from the earlier paper^[11].

branched hydrocarbon like the isostearyl group can yield quite low surface energy at water surface, which was generally considered to be attainable by only fluorinated surfactants^{32–36}.

3.2 Solubilizing power of SIS1 for W/scCO₂ μ E

Formation of a transparent and single-phase W/CO₂ μ E, that is, a μ E of the Winsor-IV type (IV μ E)³⁸, was examined by visual observation using apparatus shown in Sec. 2.3. SIS1 was soluble in scCO₂ after vigorous stirring for several hours at the highest experimental temperature and pressure (75°C and 400 bar). If after loading water into the SIS1/CO₂ mixture and subsequent stirring for several hours, a clear single-phase was obtained, this study identified it to be IV μ E. With decreasing pressure, the IV μ E was found to be a turbid E-phase at the phase boundary pressure of IV μ E-E. The E-phase turned into two-phases (2 ϕ)

Fig. 4 Phase boundary pressures and densities between clear and turbid phases of SIS1/W/scCO₂ mixtures with different raw water-to-surfactant molar ratios, W_0 ($=[\text{surfactant}]_0/[\text{water}]_0$). The clear and turbid phases appeared at pressures higher and lower than the boundaries, respectively. Surfactant-to-CO₂ molar ratio ($[\text{SIS1}]/[\text{CO}_2]$) was fixed at 8×10^{-4} .

without stirring.

Figure 4 shows the phase boundary pressures and densities between IV μ E and E (or 2 ϕ) as a function of the temperature for the SIS1/W/scCO₂ mixtures with various W_0 values. At pressures and densities higher than the phase boundaries, a transparent single-phase IV μ E was observed. At pressures lower than those represented by the symbols, a turbid E-phase was formed. In the case of SIS1, at a temperature lower than 55°C, the appearance of the mixture with a high W_0 was translucent even at 400 bar, the highest pressure that the high-pressure apparatus can accept, and the phase boundaries could not be determined correctly. Therefore, IV μ E was suggested to be unstable at the lower temperatures. At temperatures of $\geq 55^\circ\text{C}$, however, visual observation suggested SIS1 to yield the transparent single phase with W_0 up to ~ 70 at > 300 bar. Though temperatures and pressures available for the SIS1 transparent single phase were almost similar to those for TMN-6, the attainable W_0 in the single-phase was much higher than that in case of TMN-6 (i.e. maximum $W_0 = 30$), as reported in earlier papers^{9–11}.

The correct evaluation of the solubilizing power of a surfactant in scCO₂, along with the attainable W_0 in IV μ E, is difficult by visual observation alone, because the identification of a tiny amount of separated water by human eye is difficult. To measure the solubilizing power of SIS1 accu-

Fig. 5 UV-visible absorption spectra of the clear SIS1/W/scCO₂ mixtures with different content (W_0) of aqueous SpTS solution at 75°C and 370 bar. The SpTS concentration ($[\text{SIS1}]/[\text{CO}_2]$) were fixed at 0.1 wt% and 8×10^{-4} , respectively.

rately, UV-vis spectra of SIS1/scCO₂ mixtures with aqueous 0.1 wt% SpTS solution at 75°C and 370 bar were recorded. Although SpTS is almost insoluble in pure scCO₂, the mixture formed a transparent single phase, which indicates that SIS1 was able to solubilize a SpTS solution in scCO₂, independent of the presence of SpTS.

Figure 5 shows the UV-visible absorption spectra of SpTS/SIS1/W/scCO₂ mixtures at different W_0 . Without SpTS solution ($W_0 = 0$), no absorption peak was observed in the mixture at wavelengths between 290 and 340 nm. On the other hand, loading a SpTS solution into the SIS1/scCO₂ mixture generated the absorption peak of SpTS at wavelengths ranging from 305 to 340 nm, and the peak grew as the solution content increased, suggesting the swelling of the reverse micelles as found in other W/CO₂ μ E systems^{39–41} and/or an increase in number of the μ E droplets. When the maximal absorbance at 318 nm reached ~ 0.14 , the peak did not grow even if more amount of SpTS solution was added.

From the spectra of Fig. 5, the change in the absorbance at 318 nm was plotted as a function of W_0 and W_0^c , as shown in Fig. 6. If it is assumed that all the added SpTS solution is solubilized in IV μ Es, a linear relationship is to be expected between the absorbance and $W_0^{39–41}$. According to expectation, a linear function was obtained until $W_0 = 50$ as shown in Fig. 6. The linear relationship and the appearance of the transparent single phase demonstrate that the μ E disperses SpTS proportionally up to the maximum W_0 (the maximum solubilizing capacity). When W_0 was in-

Fig. 6 Change in the absorbance at 318 nm in the SIS1/W/scCO₂ mixtures as a function of W_0 (or W_0^c), based on the results shown in Fig. 5. The SpTS concentration in water was 0.1 wt%. The experimental pressure, temperature, and [SIS1]/[CO₂] ratio were 370 bar, 75°C, and 8×10^{-4} , respectively.

creased above the $W_0^{\max}$ capacity, the absorbance gradually decreased with increasing W_0 . This suggests that IV μ Es gradually transforms into two separated phases, as Winsor-II W/CO₂ μ E. The Winsor-II W/CO₂ μ E is a W/CO₂ μ E with separated excess water, as found previously⁴² with the fluorinated AOT-analog di-HCF4 using high-pressure SANS.

Through visual observation and spectral measurement, the attainable W_0 of SIS1 was found, surprisingly, to be at least 50 at 75°C, which is the highest solubilizing capacity in a hydrocarbon surfactant/W/CO₂ μ E systems ever reported^{3–20}. This is an exciting result leading to a new approach to design efficient fluorine-free surfactants. Highly CO₂-philic surfactants can be mainly achieved by a low hydrophilic/CO₂-philic balance (HCB)⁴³, a high critical packing parameter (CPP)^{44, 45}, and weak interactions between tail-tail, tail-head, and head-CO₂ (expressed by Winsor ratio^{46, 47}). As compared with TMN-6, SIS1 has an isostearyl tail that is not only more CO₂-philic but also bulkier, with the sulfate head group being more CO₂-phobic/oleo-phobic. These properties could play an important role in realizing lower HCB, larger CPP, and weaker tail-head and head-CO₂ interactions. These W/CO₂ μ E stabilizing advantages indicate the excellent solubilizing power of SIS1.

4 CONCLUSION

Most hydrocarbon surfactants are insoluble in scCO₂ and have solubilizing powers of less than 10 in $W_0^{3–8}$. Even a commercial hydrocarbon surfactant TMN-6 having a high solubilizing power of $W_0 = 30$ needs high temperatures of $> 55^\circ\text{C}$ and high pressures of > 210 bar to form a W/CO₂ μ E^{9–11}. For the application of a W/CO₂ μ E to chemical industries, a high solubilizing power and mild pressures (~ 100 bar) and temperatures ($\sim \text{rt.}$) have been desired. In this study, a highly methyl-branched isostearyl group as a CO₂-philic part and the novel hydrocarbon surfactant, sodium isostearyl sulfate (SIS1) were employed. As expected from the excellent performance of SIS1 in lowering the air/water interfacial tension, it was successfully found to act as an excellent CO₂-philic solubilizer and to achieve the attainable $W_0 = 50$ for W/CO₂ μ E. Unfortunately, a W/CO₂ μ E still needed high pressures (> 210 bar) and temperatures ($> 55^\circ\text{C}$). To obtain a W/CO₂ μ E at lower pressures and temperatures requires the following: (1) an increase in CO₂-philicity of reversed micelle, (2) a decrease in attractive interactions between the micelles, or (3) tuning of the solvent power of CO₂ to make it more similar to that of a hydrocarbon solvent. These three requirements could be achieved by the addition of a suitable cosurfactant/cosolvent or by tuning the number and position of methyl-branches in the CO₂-philic tail. Further studies will advance surfactant design theory to develop cheap and environmental-benign

W/CO₂ μEs suitable for mild conditions.

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