Surface Tensions of Aqueous Solutions of Sodium Alkyl Sulfates in Contact with Methane under Hydrate-Forming Conditions

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This paper presents experimental data on the surface tensions of aqueous solutions of sodium alkyl sulfates (ionic surfactants) in contact with methane at a pressure of 3.90 MPa and a temperature of 275 K (i.e., a condition in which a clathrate hydrate of methane is thermodynamically stable). These data were obtained in the metastable absence of any hydrate in the experimental system (i.e., every measurement was accomplished during the induction time for hydrate formation). Three sodium alkyl sulfates appreciably different in length of the hydrophobic radicals were used—they were sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), and sodium hexadecyl sulfate (SHS). The concentration of each of these surfactants was varied over a range including the critical concentration above which the surface tension levels off. On the basis of visual observations of pendant drops of SDS solutions, we identified the critical concentration for SDS as the solubility above which a hydrated solid of SDS forms instead of the critical micelle concentration (CMC) above which micelles of SDS would form. The SDS solubility was thus determined to be (2.2 to 2.3) g·kg^{-1}, which agrees, within mutual uncertainties, with the CMC determined at a higher temperature, 293 K, either in the same pressurized methane ambience or in the air under atmospheric pressure. These results completely conflict with those reported by Sun et al. in their recent paper published in this Journal (*J. Chem. Eng. Data* **2004**, *49*, 1023−1025).

Introduction

Clathrate hydrates (abbreviated hydrates, hereafter) are crystalline solid compounds formed from water and some *guest* substances such as light hydrocarbons, carbon dioxide, and some fluorocarbons. It is generally accepted that the addition of appropriate surfactants to liquid water to be brought into contact with guest substances is effective in shortening the induction time for hydrate nucleation and/or increasing the rate of hydrate-phase growth succeeding nucleation. For example, Zhong and Rogers[1] reported drastic effects of the addition of sodium dodecyl sulfate (SDS) on hydrate formation from ethane or natural gas and suggested the usefulness of surfactants for the purpose of high-rate production of natural gas hydrates, which are to be stored and/or transported as fuel gas stocks. Zhong and Rogers[1] were probably the first to claim that the highest surfactant effects are available when the surfactant concentration in the aqueous phase exceeds the critical micelle concentration (CMC). Subsequently, hydrate researchers sometimes referred to the CMC concept in their discussions on hydrate formation in surfactant-added systems.[2−4] Another notable claim by Zhong and Rogers[1] was that the CMC for SDS under ethane hydrate-forming condition is reduced to 242 mg·kg^{-1}, which is one order lower than the existing CMC data obtained with aqueous SDS solutions in contact with ambient air.[5,6] The determination of the CMC under hydrate-forming condition by Zhong and Rogers[1] was based on their observation that the induction time for hydrate formation is leveled at concentrations above 242 mg·kg^{-1}. The second claim of Zhong and Rogers[1] was supported by two other research groups based on their separate experimental studies. Han et al.[2] observed that the gas content in the hydrates formed from natural gas and aqueous SDS solutions at a temperature of 275 K increased with an increase in the SDS concentration up to 300 mg·kg^{-1} and leveled off beyond that. From this finding, they assumed the CMC in their experimental system to be 300 mg·kg^{-1}. Using the pendant drop technique, Sun et al.[7] measured the surface tensions of SDS solutions in contact with methane at a temperature of 273.2 K and pressures ranging from 2.2 MPa to 7.2 MPa. (The clathrate hydrate of methane is thermodynamically stable at pressures above 2.65 MPa when the temperature is 273.2 K.[8]) On the basis of the obtained surface tension data, Sun et al.[7] determined the CMC for SDS to be 500 mg·kg^{-1}, which is less than a quarter of the ordinary CMC value observed in the ambient air.[5,6] That is, Zong and Rogers,[1] Han et al.,[2] and Sun et al.[7] are in mutual agreement in that the CMC for SDS exhibits an anomalous reduction under pressurized hydrate-forming conditions.

In two papers published very recently,[9,10] the above-stated CMC concept concerning hydrate formation and also the anomalous reduction in the CMC under hydrate-forming conditions were seriously disputed. On the basis of their electrical conductivity measurements with SDS solutions in contact with methane under a hydrate-forming condition (4 MPa and 275 K), Di Profio et al.[9] reported that there was no indication of micelle formation over the SDS concentration range from 0.23 g·kg^{-1} to 2.0 g·kg^{-1} and that the CMC could not be detected before the concentration was increased to ≈2.3 g·kg^{-1} at which precipitation of SDS occurred. The other paper was our own contribution.[10] Our arguments presented there are outlined below. First, the Krafft point, the critical temperature below which surfactant molecules do not form micelles but form a hydrated

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solid in a given aqueous phase, for SDS had been reported to be (281 to 289) K;[11−13] hence, it is likely that no micelles actually formed in the above-mentioned hydrate-related studies.[1−4,7] Second, our pendant-drop measurements of surface tensions of SDS solutions in the ambience of HFC-32 (CH_2F_2), a hydrate-forming hydrofluorocarbon gas, at a temperature of 279 K and pressures ranging from 0.101 MPa to 0.401 MPa (i.e., including a thermodynamic condition under which a hydrate can form) showed the SDS solubility or CMC values ranging from 1.95 $g \cdot kg^{-1}$ to 2.2 $g \cdot kg^{-1}$. That is, we did not find such a drastic reduction of the solubility or CMC even under a hydrate-forming condition.

The hydrate-based procedures that Zong and Rogers[1] and Han et al.[2] used to determine what they called the CMC (possibly the solubility of SDS) are novel and not yet accepted in the field of physical chemistry of solutions. On the other hand, Sun et al.[7] used the conventional surface-tension-based procedure, which was essentially the same as that we used in our previous study.[10] Thus, the apparent discrepancy in obtained results between the studies of Sun et al.[7] and ourselves[10] needs to be investigated. As we already discussed,[10] it is not likely that the almost 4-fold difference in the CMC or the solubility (0.5 $g \cdot kg^{-1}$ vs ∼2.0 $g \cdot kg^{-1}$) is caused by the difference in the ambient gas species—methane and HFC-32. To decide this issue, we have performed surface tension measurements with aqueous SDS solutions in contact with methane at the same pressure, 3.9 MPa, and at two different temperatures, 275 K and 293 K, which are lower and higher, respectively, than the methane + aqueous liquid + hydrate equilibrium temperature. We have also measured, at the same pressure and temperature (3.9 MPa and 275 K), the surface tensions of aqueous solutions of two other sodium alkyl sulfates, sodium tetradecyl sulfate (STS) and sodium hexadecyl sulfate (SHS), which have longer hydrophobic radicals than SDS, expecting their utility in promoting hydrate formation for some industrial purposes such as natural gas storage and the separation of hydrate-forming species from gas mixtures. The results of these measurements are presented in this paper in the form of the surface tension versus the concentration of each surfactant. Both the solubility at 275 K and the CMC at 293 K for SDS and the solubilities of STS and SHS at 275 K are also determined on the basis of the obtained surface tension data.

Experimental Section

Materials. The methane used in the experiments was a research-grade gas of 99.9 % purity (mass basis) supplied by Toyoko Kagaku Co., Tokyo. SDS of 99.5 % (mass basis) certified purity was supplied by Nacalai Tesque, Inc., Kyoto. STS and SHS were supplied by Wako Pure Chemical Industries, Ltd., Osaka, and both of them were of 98.5 % (mass basis) certified purity. Each of these surfactant chemicals was weighed on an electronic balance (A&D model ER-180A) with a 0.1-mg readability and dissolved in a known volume of deionized and distilled water to prepare each solution sample for surface tension measurements.

Apparatus. Figure 1 shows the schematic of the experimental setup used in this study. This setup is similar to what we used in our previous study[10] to measure the surface tensions of SDS solutions in contact with HFC-32 and to observe hydrate formation. However, the rectangular 1.5-L test chamber used in the previous study[10] was replaced by a much smaller, cylindrical pendant-drop cell for higher pressure use. This pendant-drop cell was composed of a cylindrical stainless steel frame, two circular polished Pyrex glass windows, and stainless steel flanges for fixing the windows to both sides of the frame. The inside dimensions of the cell were 50 mm in diameter and 10 mm in axial length (i.e., the horizontal spacing between the two windows). The cell had four ports each equipped with a Swagelok connector. These ports were used for inserting a sheathed type-T thermocouple, evacuating the cell with the aid of a vacuum pump, supplying methane from a high-pressure cylinder through a pressure-reducing valve, and inserting a stainless steel tube for hanging surfactant−solution drops for surface tension measurements. A digital pressure gauge (Valcom model VPMC-A4-4) was attached on the tubing between the pressure-reducing valve and the pendant-drop cell. This pressure gauge warrants an accuracy of 0.005 MPa. The tube for hanging pendant drops was 1.607 mm o.d., and it was vertically inserted into the cell such that each pendant drop hung from the tip was located at the midpoint inside the cell. The tip of the tube was sharply cut at right angles, and its surface over ≈10 mm from its tip was coated with Teflon to prevent pendant drops from extending over the circular edge of the tip and climbing up the tube wall. The outside diameter of the Teflon-coated portion of the tube was 1.632 mm. The other end of the tube was connected to a screw syringe, which was made of stainless steel except for a Teflon O-ring for sealing the gap between its cylinder and plunger. For controlling its temperature, the pendant-drop cell was immersed in a rectangular water bath made of transparent poly(methyl methacrylate) plates. The bath was equipped with an immersion-type cooler and a PID-controlled heater integrated with a stirrer. This allowed us to control the temperature inside the pendant-drop cell within ± 0.1 K.

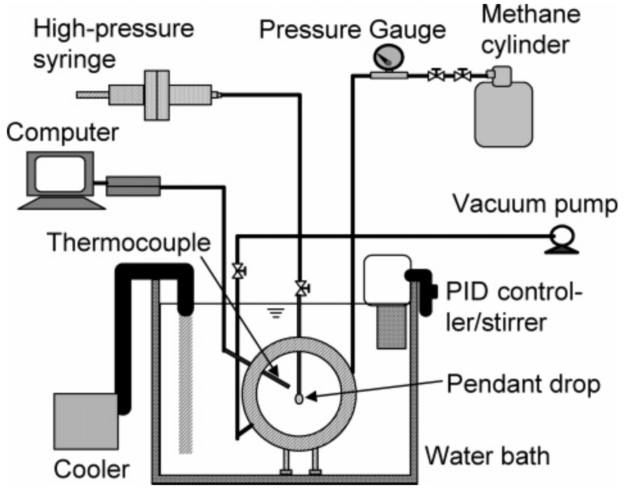

Figure 1. Schematic of the experimental setup.

Procedure. Each experiment for measuring the surface tension was commenced by charging the screw syringe with an aqueous solution of a known surfactant concentration. The subsequent operation was to evacuate the pendant-drop cell, the portion of methane supply tubing between the cell and the pressure-reducing valve, and the tubing connecting the syringe to the cell. The evacuated space was then charged with methane, adjusting its pressure to a prescribed level. The screw syringe was manipulated to form a pendant drop of the surfactant solution at the Teflon-coated tip of the stainless steel tube vertically inserted in the cell. The cell was allowed to stand for more than 2 h to ensure that the pendant drop was thermally equilibrated with its surroundings and that the adsorption of surfactant molecules over the drop surface had reached

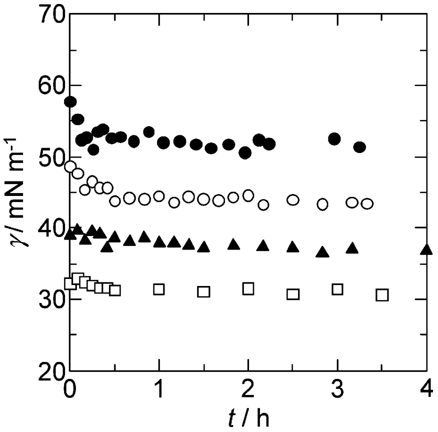

Figure 2. Chronological changes in the surface tensions of aqueous solutions with four different SDS concentrations: ●, 500 mg·kg^{-1}; ○, 1000 mg·kg^{-1}; ▲, 1500 mg·kg^{-1}; □, 2250 mg·kg^{-1}. The surface tension data obtained with pendant drops exposed to methane atmosphere (p = 3.90 MPa, T = 275 K) are plotted against their ages.

a steady state. The images of the drop were then captured by an optical system, which was assembled from a digital microscope (Keyence VH-5000), a zoom lens (Keyence VH-Z05), and a personal computer, such that the meridian profile of the drop could be viewed along a horizontal axis with the aid of diffusive back lighting. Except for one set of measurements performed at a higher temperature (293 K), the measurements were performed under a pressure−temperature condition that allowed hydrate formation: p = 3.90 MPa and T = 275 K. (The methane + aqueous liquid + hydrate three-phase equilibrium temperature T_{eq} corresponding to the pressure p = 3.90 MPa is predicted by CSMHYD[8] to be 277.3 K.) However, every measurement with a pendant drop was accomplished while no hydrate was visually detected on the drop; in other words, the drop images captured after a 2 h aging but still within the induction time for hydrate nucleation were used for evaluating the surface tension.

Data Processing and Uncertainty Evaluation. The videographic images of pendant drops were processed using the conventional "method of the selected plane"[14] with the aid of the equations by Misak[15] for the dimensionless shape factor to deduce the values of the surface tension γ. The mass densities of surfactant solutions and methane required in this calculation process were evaluated using PPOPATH,[16] on the assumption that the densities of the surfactant solutions are equal to that of pure water under each $p-T$ condition. The error analysis scheme given by Ambwani and Fort[14] was applied to the above data acquisition/processing procedure to evaluate the uncertainty of the surface tension values presented later in this paper. The combined standard uncertainty of these surface tension values was estimated to be ± 1.5 %. The γ data we obtained with pure water (with no surfactant addition) in ambient air at p = 0.101 MPa and T = 293 K using the above procedure agreed with the relevant value given by the IAPWS-prepared correlation for the surface tension of water[17] within ± 0.5 %. Thus, we judged our experimental setup and procedure to be reliable.

Results and Discussion

Time Evolution of Surface Tensions. Figure 2 exemplifies the chronological change in surface tension γ of each of four aqueous solutions with different SDS concentrations. Here, the γ data sequentially obtained with the same pendant drop of each solution are plotted against t, the age of the drop. At any level of the SDS concentration c, we recognize that γ tends to decrease in the first 30 to 90 min in t presumably due to increasing adsorption of SDS molecules on the pendant drop surface and, possibly to a lesser extent, to increasing dissolution of methane in the drop. Because we are concerned with the equilibrium surface tensions within the scope of this paper, the γ data obtained with pendant drops aged over 2 h are exclusively presented hereafter.

Table 1. Surface Tension Data Obtained with SDS Solutions in Contact with Methane or Air

	γ/mN·m^{-1}		
	methane		air
c/mg·kg^{-1}	p = 3.90 MPa T = 275 K	p = 3.90 MPa T = 293 K	p = 0.101 MPa T = 293 K
100			65.5
500	51.9		56.4
1000	43.6	38.8	48.5
1200	40.0		
1400	38.9		
1500	36.9	33.6	41.3
1750	35.0		
1800			38.5
1900	34.5		
2000	32.2	31.7	36.5
2100	32.2		35.7
2200			34.9
2250	30.9	29.5	
2300			34.2
2400			33.9
2500	30.6	29.1	34.2
3000	31.0	29.3	34.5

Surface Tensions of SDS Solutions. Table 1 summarizes the γ data obtained with SDS solutions in contact with methane at two different temperatures, T = 275 K and 293 K, but under the same pressure, p = 3.90 MPa. Table 1 also lists the γ data obtained with SDS solutions in contact with ambient air (i.e., at p = 0.101 MPa and T = 293 K). The latter data were obtained in our preceding study[10] and presented here only for comparison. The data given in Table 1 are plotted in graphical form in Figure 3 to display the pattern of change in γ with the SDS concentration c. Irrespective of the ambient gas species and the $p-T$ condition, γ monotonically decreases with an increase in c up to (2.2 to 2.3) g·kg^{-1}. With a further increase in c, we find no change in γ exceeding the range of its uncertainty. The critical concentration (c_{cr}) beyond which γ levels off should be identified as either the CMC or the solubility (c_s) beyond which SDS molecules form a hydrated solid. On the basis of the observational experiments described in the Appendix of this paper, we can safely claim that c_{cr} observed at the higher temperature, T = 293 K, is the CMC, but c_{cr} observed at the lower temperature, T = 275 K, is c_s instead of the CMC. We should note that the CMC and c_s observed under three different ambient/thermodynamic conditions are almost the same. This finding completely contradicts the claim of Sun et al.[7] that the CMC for SDS solutions in contact with methane under hydrate-forming conditions (p = 5.1 MPa and 7.2 MPa, T = 273.2 K) or under a condition slightly deviating from the hydrate-forming $p-T$ region (p = 2.2 MPa, T = 273.2 K) is reduced to 500 mg·kg^{-1}. We cannot provide any logical explanation for this contradiction.

Surface Tensions of STS and SHS Solutions. Tables 2 and 3 list the γ data obtained with STS solutions and SHS solutions, respectively, in contact with methane under a hydrate-forming thermodynamic condition, p = 3.90 MPa

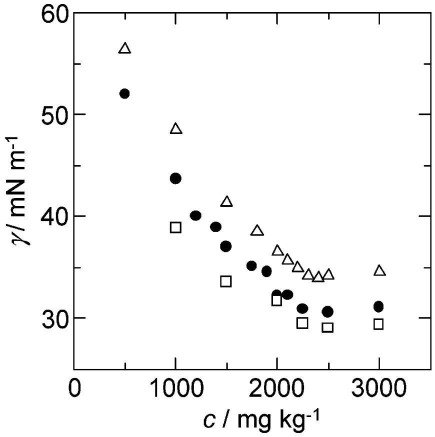

Figure 3. Variations in surface tension γ with SDS concentration c. The data obtained at three different thermodynamic conditions were collected for mutual comparison: △, $p = 0.101$ MPa and $T = 293$ K in ambient air; ●, $p = 3.90$ MPa and $T = 275$ K in methane; □, $p = 3.90$ MPa and $T = 293$ K in methane. Each γ data point was obtained with a pendant drop having been aged more than 2 h under a given condition. The data for SDS solutions in contact with ambient air (△) were reproduced from ref 10 for comparison; the other data (●, □) were obtained in this study and are detailed in Table 1. The lower temperature condition with the use of pressurized methane ($p = 3.90$ MPa, $T = 275$ K) falls in the hydrate-forming $p-T$ region, and every measurement under this condition was performed during the induction time (i.e., in the metastable absence of any hydrate). The higher and lower temperatures, $T = 293$ K and 275 K, are respectively above and below the Krafft point, T_K. Thus, the critical concentration above which γ levels off at the higher temperature is the CMC, while that at the lower temperature is the solubility beyond which SDS forms a hydrated solid instead of micelles.

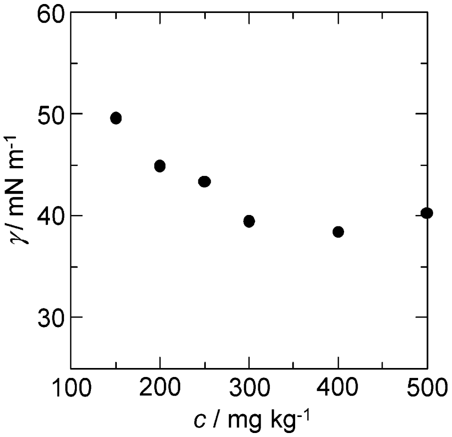

Figure 4. Variation in surface tension γ with STS concentration c. Each γ data point was obtained with a pendant drop having been aged more than 2 h in a methane ambience at $p = 3.90$ MPa and $T = 275$ K. The data shown here are detailed in Table 2.

Table 2. Surface Tension Data Obtained with STS Solutions in Contact with Methane at $p = 3.90$ MPa and $T = 275$ K

c/mg·kg^{-1}	γ/mN·m^{-1}
150	49.5
200	44.9
250	43.3
300	39.4
400	38.4
500	40.2

Table 3. Surface Tension Data Obtained with SHS Solutions in Contact with Methane at $p = 3.90$ MPa and $T = 275$ K

c/mg·kg^{-1}	γ/mN·m^{-1}
10	57.4
25	54.0
30	52.8
40	50.3
50	50.2

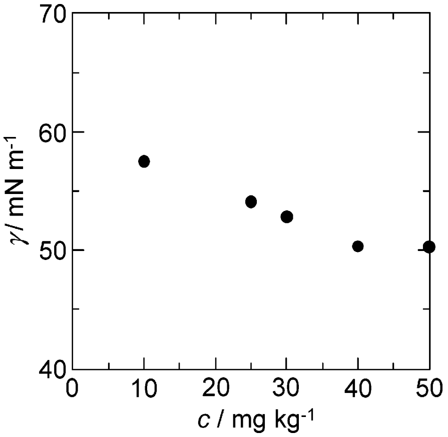

Figure 5. Variation in surface tension γ with SHS concentration c. Each γ data point was obtained with a pendant drop having been aged more than 2 h in a methane ambience at $p = 3.90$ MPa and $T = 275$ K. The data shown here are detailed in Table 3.

and $T = 275$ K. These data are plotted in Figures 4 and 5 in a form analogous to Figure 3. As expected from the longer hydrophobic radicals in these surfactants than in SDS, the solubility c_s for these surfactants is found to be much lower than that for SDS; that is, $c_s \approx 300$ mg·kg^{-1} for STS and $c_s \approx 40$ mg·kg^{-1} for SHS. The magnitude of the reduction in γ available at $c \geq c_s$ is in the order of the magnitude of c_s (i.e., the largest for SDS and the smallest for SHS).

Conclusions

We have measured the surface tensions of aqueous solutions of sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), and sodium hexadecyl sulfate (SHS) each in equilibrium with the methane-rich gas phase in the absence of methane hydrate but under a pressure−temperature condition that thermodynamically allows the formation of the hydrate. For each of the three surfactants, the solubility (the critical concentration above which the surfactant molecules form a hydrated solid) was determined on the basis of the surface tension versus concentration profile. The solubility of SDS thus determined is almost the same as that determined with the SDS solutions in ambient air. We have found no sign that the solubility, which was presumably misunderstood to be the CMC in some previous studies, is substantially reduced under hydrate-forming pressure−temperature conditions.

Appendix: Visual Observations of Pendant Drops To Determine the Krafft Point

To determine the Krafft point for SDS solutions in contact with methane pressurized to 3.90 MPa, we performed a series of visual observations of pendant drops. These observations were not for the quantitative surface tension measurements but for detecting, if any, the formation of solid phases in the drops. Hence, the direction of the lighting of the drops was varied from time to time to obtain a sharp contrast of the surfaces of possibly semitransparent solid crystals. An SDS solution adjusted at $c = 3000$ mg·kg^{-1} was used to prepare sample drops. Each

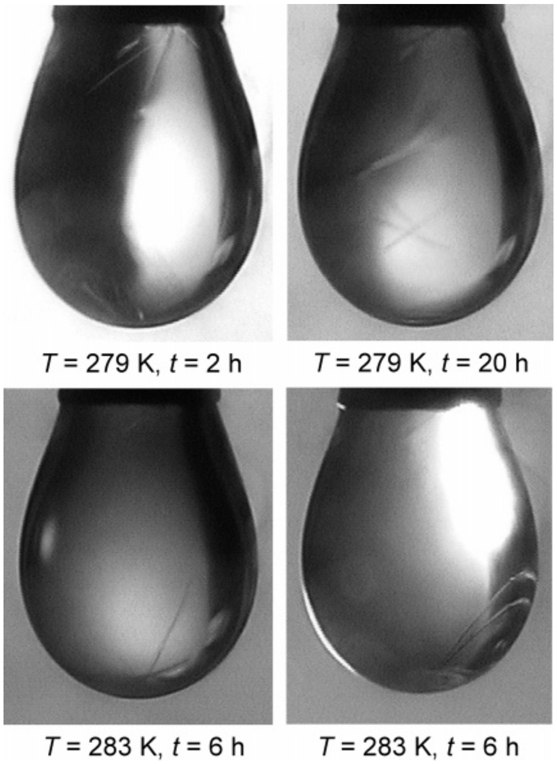

Figure 6. Snapshots of a pendant drop of an aqueous SDS solution ($c = 3000$ mg·kg^{-1}) in methane gas at $p = 3.90$ MPa. The diameter of the tube suspending the drop was 1.63 mm. Indicated below each snapshot are the system temperature T and the time t over which the drop was aged at the temperature T. The lighting direction was varied from shot to shot to best visualize the dendrites of hydrated SDS formed in the drops.

drop was first maintained in a methane ambience pressurized to 3.90 MPa and adjusted at 275 K for 1 day. The temperature was then raised stepwise to 279 K, 283 K, and finally 287 K. These three temperature levels were maintained for 20 h, 6 h and 0.5 h, respectively. Snapshots of the drop were taken from time to time at each temperature level. Figure 6 exemplifies two snapshots of a drop at each of the two temperature levels, 279 K and 283 K. In every snapshot shown here, we can recognize some dendrites grown in the drop. Because the hydrate of methane cannot form at temperatures above 277.3 K under a pressure of 3.90 MPa,[8] these dendrites must not be the hydrate of methane but a hydrated solid of SDS. We observed that the above dendrites inside the drop disappeared while the temperature was maintained at 287 K. This fact means that the Krafft point in the SDS + water + methane system under pressure of 3.90 MPa is higher than 283 K and lower than 287 K. Comparing this finding to the Krafft point data reported in the literature,[11−13] we can conclude that neither the pressure up to 3.90 MPa nor the presence of methane instead of air appreciably affects the Krafft point. This finding also indicates that the critical SDS concentration (c_{cr}) above which the surface tension γ levels off is not the CMC but the solubility c_s when $T = 275$ K, while it should be the CMC when $T = 293$ K (see Figure 3).

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