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Enhanced Stabilization of Reverse Micelles by Compressed CO_2

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Abstract: The effect of compressed CO_2 on the solubilization capacity of water in reverse micelles of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in longer chain *n*-alkanes was studied at different temperatures and pressures. It was found that the amount of solubilized water is increased considerably by CO_2 in a suitable pressure range. The suitable CO_2 pressure range in which the solubilization capacity of water could be enhanced decreased with increasing W_0 (water-to-AOT molar ratio). The microenvironments in the CO_2-stabilized reverse micelles were investigated by UV/Vis adsorption spectroscopy with methyl orange (MO) as probe. The mechanism by which the reverse micelles are stabilized by CO_2 is discussed in detail. The main reason is likely to be that CO_2 has a much smaller molecular volume than the *n*-alkane solvents studied in this work. Therefore, it can penetrate the interfacial film of the reverse micelles and stabilize them by increasing the rigidity of the micellar interface and thus reducing the attractive interaction between the droplets. However, if the CO_2 pressure is too high, the solvent strength of the solvents is reduced markedly, and this induces phase separation in the micellar solution.

Keywords: alkanes · carbon dioxide · micelles · surfactants

Introduction

Reverse micelles can be defined as supramolecular self-assembled aggregates of nanoscale dimensions with hydrophobic moieties extending outward into an apolar solvent and hydrophilic groups converging inward into a polar region (a separate pseudophase) of another solvent such as water.[1] Reverse micelles have a number of applications, such as polymerizations,[2] chemical reactions,[3] electrocatalysis,[4] enzyme kinetic studies,[5] and separation and extraction of proteins.[6] The highly rigid structure of reverse micelles has also been exploited to template the production of size-controlled nanoparticles of metals[7] and alloys.[8] In addition, reverse micelle nanostructures can also be used in membrane mimetic studies to probe the water structure and the physiological activity of biological membranes and proteins.[9]

An important property of a reverse micelle is its solubilization capacity for water as microdroplets dispersed in the oil phase. The solubilization capacity of water in reverse micelles depends on many factors, such as the nature of the polar and hydrocarbon groups of the surfactant, solvent, temperature, and the presence of co-surfactant and electrolytes. It is well known that some compressed gases, such as CO_2 and ethylene, are quite soluble in a number of organic solvents, and they can reduce the solvent strength of the solvents to such a degree that the solutes can be precipitated. This process is usually referred to as the gas antisolvent (GAS) process,[10] and GAS techniques have been used in fields such as fractionation,[11] recrystallization,[12] particle generation,[13] and precipitation of nanoparticles and biomolecules from sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles.[14] The GAS effect can also induce formation of reverse micelles of PEO-PPO-PEO polymer surfactant in a good solvent because the solvent strength of solvent is reduced.[15]

Previously, we studied the effect of compressed CO_2 or ethylene on the solubilization of water in Triton X-100/cyclohexane solution.[16] Surprisingly, we found that at suitable pressures the compressed gases did not act as antisolvents; instead, they functioned as a co-surfactant that stabilized the reverse micelle and increased the water-to-surfactant molar ratio W_0 in this system. Since Triton X-100 is a nonionic surfactant, it is of interest whether this effect is applicable to solutions of ionic surfactants. AOT is the most commonly used ionic surfactant for preparing reverse micellar solutions due to its ability to solubilize large amounts of

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water in nonpolar solvents.[17] It is well established that phase separation of reverse micelles can arise from either interdroplet interactions or curvatures that are larger than the natural curvature of the interface for reverse micelles.[18] For higher alkane solvents, it is known that the decrease in solubilization capacity of water in the AOT/solvent system is due to an increase in attractive interactions between droplets.[18c] In this study, we investigated the effect of compressed CO_2 on the solubilization capacity of water in reverse micelles of AOT in *n*-alkanes with different chain lengths. It is demonstrated that compressed CO_2 also has the function of a co-surfactant that stabilizes the reverse micelles and enhances the solubilization capacity of water. We discuss the mechanism by which CO_2 stabilizes reverse micelles in detail. Co-surfactants have been used for years in applications of micellar solutions in various fields. However, the mechanism by which co-surfactants stabilize micelles is still not very clear, although much research has been carried out. A co-surfactant usually has a polar group and a nonpolar chain, and it is very difficult to separately determine their contributions to stabilizing micelles. The results of this work provide useful information for understanding the function of the nonpolar chain of a co-surfactant, which is helpful in investigating the mechanism of cosurfactants.

Results

Volume expansion coefficient: It is well known that the solubility of CO_2 in organic solvents depends on pressure and temperature, and the solvents are expanded by the dissolved gas. The volume expansion can be characterized by the volume expansion coefficient $\Delta V = (V - V_0)/V_0$, where V and V_0 are the volumes of the CO_2-saturated and CO_2-free solutions, respectively. We determined ΔV of AOT solutions with different solvents at different CO_2 pressures (Figure 1).

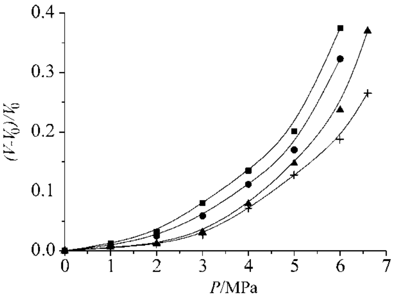

Figure 1. Dependence of volume expansion coefficient ΔV of AOT/alkane mixtures on CO_2 pressure (■ decane, ● dodecane, ▲ tetradecane, + hexadecane. $T = 30.0\,°C$, $C_{AOT} = 0.1\ mol\,L^{-1}$).

As expected, ΔV increases with pressure because the concentration of CO_2 in the solutions is higher at higher pressure. At a given pressure, ΔV decreases with increasing chain length of the solvent. This suggests that the solubility of CO_2 in alkanes decreases with increasing size of the solvent molecule.

Effect of compressed CO_2 on the solubilization capacity of water: Phase separation of microemulsions can arise by two mechanisms. One is micelle–micelle interaction. The attractive forces due to overlapping between the tails of neighboring reverse micelles cause surfactant and water to precipitate into a new surfactant-rich phase.[20] The second is the natural-curvature mechanism: relatively pure excess water precipitates when the micelle radius becomes equal to the natural curvature.[18c]

The one-phase region in a temperature versus W_0 diagram of AOT in apolar solvents can extend to large W_0 values.[21] It has been reported that the upper temperature boundary of the one-phase region results from micelle–micelle interaction. It is usually called the haze point boundary. At temperatures above the haze point boundary, a surfactant-rich and a surfactant-lean phase are present. Phase separation at the lower boundary is caused by the natural-curvature mechanism. It is called the solubilizaton curve, in reference to the solubilization of water. With decreasing temperature, water comes out of solution without surfactant. In addition, it is well established that the temperature at which the maximum solubilization of water is achieved decreases as the alkyl chain length of *n*-paraffinic solvents increases. The one-phase region shifts to lower temperature as the chain length of alkane solvents increases.[22] This implies that AOT becomes increasingly oleophilic with decreasing temperature, because the temperature of the maximum solubilization of water may be equal to the phase inversion temperature (pit). This trend is opposite to that for a nonionic surfactant in nonaqueous solutions.[21] As a result, the decrease in W_0 of an AOT/longer chain alkane system is due to the increase in the attractive interaction between neighboring reverse micelles when the temperature is equal to or above room temperature.

Figure 2 shows the dependence of W_0^{max} (the maximum solubilization capacity of water) on alkyl chain length of the solvent at 30.0 °C in the absence of CO_2. Evidently, W_0^{max} decreases as the alkyl chain length increases (i.e. from decane to hexadecane). We further checked the behavior of the phase separation of these systems at saturation of solubilization. When the water-soluble dye Methyl Orange (MO) was

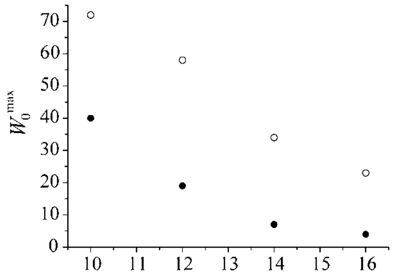

Figure 2. Maximum solubilization capacity of water as a function of alkyl chain length at 30.0 °C [$C_{AOT} = 0.1\ mol\,L^{-1}$. ● CO_2-free; ○ with compressed CO_2 at suitable pressure (see Table 1)].

added, we saw the bottom phase quickly turn orange, while the upper phase remained colorless. This indicates that the larger attractive interaction among droplets plays the major role in phase separation under these conditions in the absence of CO_2, and the result is consistent with those of other authors.[18c,23]

Figure 2 also gives W_0^{max} values in the presence of CO_2, and the corresponding pressure ranges for different systems are listed in Table 1. Only one phase exists in a system in the corresponding pressure range, whereas the phase separation occurs outside of the pressure range at W_0^{max}. For example, with decane as solvent and $W_0 = W_0^{max}$ as in Figure 2, there is one phase in the range of 4.2–5.1 MPa. All the water in the system can be solubilized in the reverse micelles. When the pressure is lower than 4.2 MPa or higher than 5.1 MPa, the system separates into two phases. In this work, maximum W_0 (W_0^{max}) means that if the W_0 exceeds W_0^{max}, there is no one-phase region in the system at any pressure (see Figure 3). Evidently, compressed CO_2 can increase W_0^{max} of AOT reverse micelles in long-chain alkanes. Table 1 also shows that compressed CO_2 can enhance the stability of reverse micelles over a wide pressure range. The pressure required to stabilize the reverse micelles increases with increasing alkyl chain length. One reason for this is that the solubility of CO_2 decreases with increasing chain length.

Table 1. Pressure range of CO_2 at maximum W_0 ($T = 30.0$ °C, $C_{AOT} = 0.1$ mol L^{-1}).

alkyl chain length	10	12	14	16
P [MPa]	4.2–5.1	4.9–6.0	5.7–6.6	6.5–7.0

Effect of pressure on W_0 in the AOT/dodecane system: Figure 3 shows that a clear increase in the water solubilization in AOT/dodecane can be achieved at 30.0 °C with the aid of compressed CO_2. We investigated W_0 as a function of pressure under these conditions.

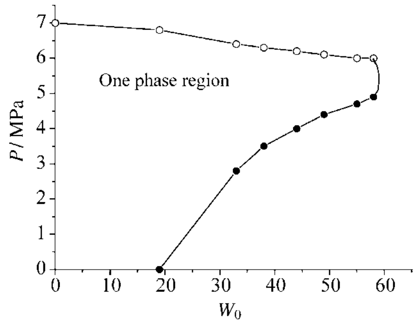

Figure 3. W_0 as a function of CO_2 pressure in AOT/dodecane system at 30.0 °C ($C_{AOT} = 0.1$ mol L^{-1}).

In the absence of compressed CO_2, phase separation occurs when W_0 exceeds 20. However, the maximum value of W_0 can reach about 58 under appropriate CO_2 pressure, which corresponds to W_0^{max}, as discussed above. In addition, the suitable pressure range of CO_2 gradually decreases with increasing W_0, and decreases sharply as W_0 approaches W_0^{max}. Figure 3 shows clearly that the microemulsion can be separated into two phases simply by decreasing or increasing the CO_2 pressure, and a homogeneous one-phase microemulsion forms again on adjusting the CO_2 pressure. Therefore, the formation and breakage of the reverse micelles can be easily controlled by means of the CO_2 pressure. The systems with other solvents exhibit similar behavior.

Table 2. Suitable pressure range of CO_2 at maximum W_0 and different temperatures.

T [°C]	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0	55.0	60.0
P [MPa]	2.0–2.6	2.4–3.8	4.3–5.2	4.9–6.0	5.6–6.3	6.1–7.0	6.6–7.3	7.4–8.4	7.5–8.3	7.7–9.4

Effect of temperature on W_0 in AOT/dodecane: We also investigated the effect of compressed CO_2 on the solubilization capacity of water in AOT/dodecane from 15 to 60 °C (Figure 4). Over a wide temperature range, W_0^{max} is much higher in the presence of compressed CO_2 than in the absence of compressed CO_2. These results further illustrate that compressed CO_2 can enhance the stability of the micelles. The suitable pressure increases with increasing temperature (Table 2) since the solubility of CO_2 decreases with increasing temperature. Interestingly, W_0^{max} gradually decreases with increasing temperature in the absence of compressed CO_2, while W_0^{max} reaches a maximum at about 35 °C in the presence of compressed CO_2.

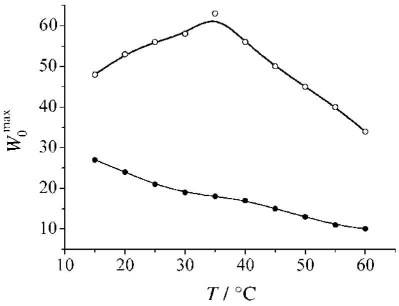

Figure 4. Maximum solubilization capacity of water in AOT/dodecane versus temperature without (●) and with (○) compressed CO_2 in suitable pressure ranges ($C_{AOT} = 0.1$ mol L^{-1}; the corresponding suitable pressure ranges are listed in Table 2).

Solvatochromic study: It is well known that the absorption maximum λ_{max} of Methyl Orange (MO) is sensitive to the polarity of its local environment, and λ_{max} shifts to longer wavelength as the polarity increases. It is one of the commonly used solvatochromic probes to study the properties of polar cores of reverse micelles both in organic solvents and supercritical fluids.[24] Our experiments indicated that MO is not soluble in dodecane/CO_2, as evidenced by the fact that the absorbance of MO in the mixed solvent is negligible. In the presence of water and the surfactant, the absorbance of MO could be observed. The λ_{max} of MO in AOT/dodecane/water with various W_0 at 5.3 MPa are listed in Table 3.

Table 3. λ_{max} of MO in AOT solution (0.1 mol L^{-1}) as a function of W_0 at 30.0 °C ($P = 5.3$ MPa).

W_0	2	5	10	20	30	40	50
λ [nm]	401.4	403.6	404.8	408.6	409.8	411.4	412.6

The λ_{max} of MO increases from 401.4 to 412.6 nm as W_0 varies from 2 to 50. This indicates increasing polarity of the reverse micelles. However, λ_{max} is much smaller than in water (464 nm). Similar results have been found in both ambient and supercritical systems,[25] where the increasing water content resulted in a small solvatochromic shift between 404 and 412 nm. The results indicate that MO exists in a low-polarity environment in these reverse micellar systems. Zhu et al.[26] performed an in-depth study of MO in Triton X-100 reverse micelles in benzene/hexane, and they also observed a much shorter wavelength maximum as compared with bulk water. They concluded that the polar outer shell of the reverse micelle was the most likely position of MO solubilization, that is, although MO was located within the polar core, it was not positioned in the water pool. In our experiments, the results obtained suggest that MO is most likely situated at the interface of the surfactant/water core, a region known to possess a polarity intermediate between those of bulk water and dodecane/CO_2.

Table 4. λ_{max} of MO in AOT/dodecane reverse micelles versus CO_2 pressure at 30.0 °C. ($W_0 = 10$, $C_{AOT} = 0.1$ mol L^{-1}).

P [MPa]	0.0	1.0	2.0	3.0	4.0	5.0	6.0
λ/nm	407.8	407.4	406.8	406.2	405.6	404.8	404.0

We expect that CO_2 pressure will affect the environment of MO in these reverse micellar systems. Table 4 lists the λ_{max} values of MO in AOT/dodecane reverse micelles at some typical CO_2 pressures with $W_0 = 10$. The λ_{max} of MO moves to shorter wavelength with increasing CO_2 pressure. This indicates that the micropolarity around MO in the reverse micelles decreases with increasing CO_2 pressure. A possible explanation for this phenomenon is that, with increasing CO_2 pressure, more and more CO_2 molecules enter the surfactant-tail regions of the reverse micelles, which leads to a more rigid interfacial film. Thus, some water dispersed at the interface of the surfactant/water core is gradually expelled. As a result, the polarity at the surfactant/water interface becomes lower with increasing CO_2 pressure. As discussed above, MO in the reverse micelles exists mainly at the interface; therefore, λ_{max} becomes shorter.

Discussion

Many experimental and theoretical studies on microemulsions[27] have suggested that penetration of a solvent into interfacial films increases as its molecular volume decreases and the aromaticity of the organic solvent increases. This penetration can increase the interfacial mixing entropy and thus stabilize the interfacial film. Solvent penetration also swells the aliphatic layer of the surfactant film and causes a higher spreading pressure at the surfactant tail/solvent interface and hence a more curved interface (smaller droplet size). In contrast, less penetration of solvent into the surfactant film with increasing solvent chain length results in a more flexible interface and a greater natural radius R^0 than that of short-chain solvents. The attractive interaction between droplets is thus increased due to "sticky" collisions between droplets.[28]

The effect of the molar volume of the solvent on the solubilization capacity of water has been described for AOT reverse micelles in a series of liquid alkanes at atmospheric pressure.[18] For the alkanes from pentane to hexane, W_0^{max} increases with increasing alkyl chain length, as the solvent penetrates the tail of the surfactant less effectively with increasing solvent molecule size. A decrease in solvent penetration into the tail causes a decrease in interfacial curvature and thus an increase in W_0^{max}. Phase separation in the systems is induced by the curvature effect whenever the radius of droplets approaches R^0. As the solvent chain length is increased further, the solvent becomes so large that it penetrates the tail of the surfactant poorly and is not effective in shielding the intermicellar interaction. Thus the attractive interdroplet interaction starts governing the system. The solubilization capacity is limited by a smaller critical droplet radius R^c, and thus a decrease in the solubilization capacity is observed.

For AOT the general trend is that as the chain length of the solvent increases from hexane to hexadecane, the alkanes become poorer solvents for the surfactant,[29] and AOT is insoluble in supercritical CO_2.[30] Therefore, it is not expected that the addition of compressed CO_2 could increase the solubility of AOT in mixtures of CO_2 and longer chain alkanes. For example, our experiments showed that for an AOT solution (0.1 mol L^{-1}), the surfactant precipitated from dodecane at a CO_2 pressure of about 7.0 MPa (Figure 3). Since the decrease in the solubilization capacity with increasing molecular size of the solvent in these systems is due to an increase in the attractive interactions between droplets, we speculate that addition of compressed CO_2 can weaken the attractive interaction and thus increase the solubilization of water. The size of the larger solvent molecules is not favorable for their penetration of the tails of the surfactants. For example, decane can only penetrate the AOT tail to a distance of 0.24 nm, much shorter than the tail length of 0.8 nm.[31] We propose that CO_2, a small and linear molecule, can penetrate into the surfactant tail region and thus push the surfactant head groups together, though the cohesive energy density of CO_2 is lower than that of an

AOT tail, especially at lower pressures. Suitable penetration of compressed CO_2 may increase the rigidity of the surfactant film, which decreases the attractive interaction between droplets effectively, and lead to a larger critical droplet radius R^c. This argument is supported by the fact that the solubilization enhancement by compressed CO_2 is more significant for a longer chain alkane (Figure 2). In other words, CO_2 is more effective in stabilizing reverse micelles when the molecular size of the solvent is larger. The reason is that the larger alkane cannot sufficiently penetrate the interfacial film.

To obtain more information, we also investigated the effect of compressed CO_2 on the solubilization of water in systems with benzene, toluene, or cyclohexane as solvent at 30.0 °C, in which phase separation is induced by the natural-curvature mechanism.[18c,22a] It was found that compressed CO_2 could not increase the solubilization of water in these systems. This further supports the proposal that in the long-chain solvents, CO_2 decreases the attractive interaction between droplets because it penetrates the tails of the surfactant molecules.

Since the penetration of CO_2 results in enhanced spontaneous curvature, and greater spontaneous curvature leads to a smaller natural radius R^0, we expected that the reverse micelles would likely expel excess water into a second phase with increasing CO_2 pressure. We checked the behavior of the phase separation of AOT/dodecane/water ($C_{AOT} = 0.1\,mol\,L^{-1}$, $W_0 = 50$, $T = 30.0\,°C$) system over a wide range of CO_2 pressure. In the absence of CO_2 there were two phases in the system, and we saw the bottom phase turn orange when water-soluble MO was added to the system, while the upper phase remained colorless. On addition of compressed CO_2, the solution gradually became one homogeneous phase with orange color. When the CO_2 pressure was above the upper phase-separation pressure, phase separation was observed again, and the upper phase was pale yellow, while the small-volume phase at the bottom was deep red. When the CO_2 pressure was increased further, the volume of the bottom phase gradually increased until the upper phase turned colorless. We also conducted similar experiments using the oil-soluble dye Sudan IV. In this case, when the pressure exceeded the upper phase-separation pressure, the red color could be observed in both phases, and the color in the upper phase was deeper than that of the bottom phase, that is, both phases were oil-continuous at higher pressures.

To our surprise, these phenomena indicate that water precipitated with AOT when the CO_2 pressure was high enough. Johnston et al.[32] proposed that a third factor influences W_0^{max} in addition to repulsive penetration of the tails and intermicellar interactions. It is the attractive interaction between the oil and the tails of the surfactant, which may be described qualitatively by regular solution theory. The free energy of mixing of the oil and the surfactant tails is related to the square of the difference of their solubility parameters. When their solubility parameters are the same, solvation of the tails is most favorable. In this case, we speculate that a higher pressure of CO_2 reduces the solvent strength of the mixture of CO_2/dodecane to a great extent, which may make the mixed solvent incapable of shielding the overlapping of the tail regions of adjacent reverse micelles effectively and preventing the tails from entangling with each other. In other words, as the CO_2 pressure increases, more and more CO_2 dissolves in the mixed solvent and penetrates the tails of surfactants, and at the same time dodecane is likely to be expelled from the tail region, but the attractive interaction between the mixed solvent and the tails should not be strong enough to stabilize reverse micelles, and the antisovelnt effect of CO_2 plays an important role under these conditions. This is also evidenced by the fact that AOT can be precipitated even in the absence of water ($W_0 = 0$) when the CO_2 pressure is above 7.0 MPa, as shown in Figure 3.

In addition, the presence of salinity in reverse micelles decrease the attractive interaction among droplets by making the interfacial layer more rigid due to closer packing of polar groups,[33] so that the degree of interpenetration of droplets is reduced during collision. On increasing the CO_2 pressure, carbonic acid can form in the micelle cores, as a result of the ionization of CO_2. However, the solubilization of water in AOT reverse micelles is hardly influenced by weaker acids, such as CH_3COOH, whereas the solubility and solubilization curves become lower on increasing the acid strength ($HClO_4$ and HCl).[34] In our experiments, we investigated the effect of HCl in various concentrations on the solubilization of water in systems consisting of AOT and longer chain alkanes in the absence of compressed CO_2. The results showed that HCl could not increase the solubilization capacity of water, although it could vary the pH of the water core. Therefore, the effect of the formation of carbonic acid on the solubility of water is not the main reason for the solubilization enhancement of water.

The effect of CO_2 on the stability of the reverse micelles is more complex than that discussed above. For example, besides the functions discussed above, the CO_2 in the organic phase reduces the viscosity of the solvent, which may stabilize the reverse micelles because micelle–micelle collision times are shorter at lower viscosity; CO_2 may reduce the interfacial tension because it exists in the organic phase, in the film of the reverse micelles, and on the interface of the surfactant and solvent, which promotes the formation of the reverse micelles.

A conventional co-surfactant usually contains both a polar group and a hydrocarbon chain, and it is very difficult to clarify their functions, while the gas used in this work is small, nonpolar molecule that solely has the function of the hydrocarbon chain in a co-surfactant. The results of the present study provide some useful information for gaining insight into the mechanism of co-surfactants. For example, they suggest that the nonpolar chain of a co-surfactant between the tails of surfactants can stabilize reverse micelles, as the phase separation is governed by micelle–micelle attractive interactions.

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Conclusion

The effect of compressed CO_2 on the solubilization capacity of water in reverse micelles of AOT in longer chain *n*-alkanes has been studied under different conditions. It was demonstrated that the amount of solubilized water is increased considerably by CO_2 in suitable CO_2 pressure ranges. A possible reason is that CO_2 penetrates the interfacial film of the reverse micelles and results in a more rigid, hardened interfacial film, which reduces the attractive interactions between the droplets. When the pressure exceeds a certain value, the solvent strength of the CO_2/alkane mixed solvent becomes too weak, which is unfavorable for stabilizing reverse micelles, and precipitation of AOT occurs at high pressure even in the absence of water. In this case, the antisolvent effect of CO_2 is dominant, and the reverse micelles are broken.

Experimental Section

Materials: AOT (sodium bis-2-ethylhexyl sulfosuccinate, 99% purity) was purchased from Sigma. Decane, dodecane, tetradecane, and hexadecane (99% purity) were supplied by Acros. Benzene, toluene, cyclohexane, Methyl Orange (MO), and Sudan IV were produced by Beijing Chemical Reagent Factory (A.R. Grade). CO_2 (99.995% purity) was supplied by Beijing Analytical Instrument Factory. All reagents were used without further purification. Double-distilled water was used.

Determination of water solubilization: The experiments were based on the fact that the solutions were clear and transparent if the water was all solubilized; otherwise, they were hazy or turbid. The apparatus and procedures were similar to those reported previously for studying polymer solutions[15] and the Triton X-100/cyclohexane system.[16] It consisted mainly of a high-pressure viewing cell with a volume of 40 cm^3, a constant-temperature water bath, a high-pressure syringe pump (DB-80), a pressure gauge, a magnetic stirrer, and a gas cylinder. The temperature of the water bath was controlled by a HAAKE D8 temperature controller. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT, Model 93) and an indicator, which was accurate to ±0.025 MPa in the pressure range of 0–20 MPa.

As an example, we describe the experimental procedures involving compressed CO_2, because those in the absence of CO_2 were relatively simple. In a typical experiment, the air in the viewing cell was replaced by CO_2, and a solution of AOT in the solvent of interest (5 mL) and the desired amount of double-distilled water were loaded into the high-pressure viewing cell. The cell was placed into the constant temperature water bath. After thermal equilibrium had been reached the stirrer was started and solution was hazy and turbid. CO_2 was charged into the cell slowly until the hazy and turbid liquid solution became transparent and completely clear, which was an indication of the solubilization of all the water. In this work, the trace amount of water dissolved in the solvent (oil/CO_2) was corrected when calculating W_0, the molar ratio of water to AOT, that is, the amount of water in the solvent has been subtracted.

UV/Vis experiment: The absorption spectra of MO in the reverse micelles were studied by UV spectroscopy. The apparatus and procedures were similar to those reported previously.[15,16,19] It consisted of a gas cylinder, a high-pressure pump, a pressure gauge, a UV/Vis spectrometer, a temperature-controlled high-pressure UV sample cell, valves, and fittings. The UV/Vis spectrophotometer was produced by Beijing General Instrument Company (Model TU-1201, resolution: 0.1 nm). The sample cell was composed mainly of a stainless steel body, two quartz windows, a stirrer, and a temperature-controlling system. The optical path length and the inner volume of the cell were 1.32 cm and 1.74 cm^3, respectively. In the experiment, the sample cell was flushed with CO_2 to remove the air. The desired amounts of aqueous MO solution of suitable concentration and the AOT solution were charged into the sample cell. After thermal equilibrium had been reached, CO_2 was compressed into the UV cell to the desired pressure. The UV spectrum under equilibrium conditions was recorded, which was confirmed by the fact that the UV spectra recorded were independent of equilibration time. Generally, about 30 min was required for the system to reach equilibrium after the required pressure was reached, and the spectrum of each solution was recorded five times.

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