

Enhancement of the Solubilization Capacity of Water in Triton X-100/Cyclohexane/Water System by Compressed Gases

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Abstract: The effect of compressed CO₂ and ethylene on the properties of Triton X-100/cyclohexane/water systems was studied at different temperatures and pressures. Surprisingly, it was discovered that the compressed gases had the functions of co-surfactants. At suitable pressures, the water-to-surfactant molar ratio (W_0) was enhanced significantly by the dissolution of the gas in the solution. The microenvironment in the reverse micelles was investigated by UV-visible spectroscopy by using methyl orange (MO) as a probe.

The influence of *n*-hexane, Na₂CO₃, NaHCO₃, H₂C₂O₄, and CaCl₂ at various concentrations on the solubilization of water in the absence of compressed gases was also investigated in order to obtain some information about the mechanism of the interesting phenomenon. This new route to stabilize reverse micelles may have poten-

tial applications to other similar systems. Moreover, the results of this work provide some useful information to get insight into the mechanism of co-surfactants, because a conventional co-surfactant usually contains both polar group and hydrocarbon chain, and it is very difficult to clarify the functions these two groups, while the gases used in this work are small non-polar molecules, which solely have the function of the hydrocarbon chain in a co-surfactant.

Keywords: carbon dioxide · cyclohexane · micelles · surfactants · Triton X-100

Introduction

In nonpolar media certain surfactants assemble to form reverse micelles in which the polar head groups of the amphiphiles cluster to form a micelle core and hydrophobic tails are extended into the organic bulk phase. The reverse micelles so-formed can solubilize a large quantity of water to form water pool in the center of the micelles.^[1] Reverse micelles of various kinds have been studied extensively,^[2] including those formed in supercritical solvents,^[3] and those with non-aqueous polar domains.^[4] Reverse micelles can be used in many processes, such as in chemical and biological reactions,^[5] extraction and fractionations,^[6] and preparation of fine particles.^[7] It is not surprising that many excellent papers have been published in the literature.

It is well known that some compressed gases, such as CO₂ and ethylene, are quite soluble in a number of organic solvents, and that 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 a gas antisolvent process (GAS).^[8] GAS techniques have been used in different fields, for example, fractionation,^[9] recrystallization,^[10] particle generation,^[11] formation of reverse micelles of the copolymer (EO)₂₇(PO)₆₁(EO)₂₇ (P104) in *p*-xylene by reducing the solvent power when the temperature is above the phase inversion temperature,^[12] and precipitation of the nanoparticles and biomolecules from sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles.^[13]

Stabilization of reverse micelles and controlling water-to-surfactant molar ratio (W_0) of reverse micelles are crucial for various applications. This can be achieved by adding co-surfactants such as short-chain alcohols^[14] or esters.^[15] Scientists and engineers have used co-surfactants and studied the mechanism for many years. However, the mechanism is still not completely clear. In this paper, we find a novel function of compressed CO₂ and ethylene. They have the functions of co-surfactants in that they can stabilize the reverse micelles of Triton X-100 (CH₃C(CH₃)₂CH₂C(CH₃)₂C₆H₄-(OCH₂CH₂)_{9,5}OH), which is a typical nonionic surfactant, in cyclohexane and enhance the solubilization of water significantly. We expect that this new way to stabilize microemulsion can apply to more nonpolar solvent-surfactant systems. Meanwhile, we think the results of this work provide some useful information to gain insight into the mechanism

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of cosurfactants, because the conventional co-surfactants usually contain both polar group and hydrocarbon chain, and it is very difficult to clarify the functions of these groups, while the gases used in this work are small nonpolar molecules. Therefore, we get some clearer evidence about the function of nonpolar chain of co-surfactants.

Experimental Section

Materials: Triton X-100 was obtained from Farco Chemical, Hong Kong. Cyclohexane and methyl orange (MO) were produced by Beijing Chemical Reagent Factory (A.R. Grade). CO₂ (99.995% purity) and ethylene (99.9%) were supplied by Beijing Analytical Instrument Factory. All the reagents were used without further purification. Double distilled water was used.

Determination of water solubilization: The experiments were based on the fact that the solution is clear and transparent if the water was completely solubilized, otherwise the solution was hazy or milky.^[16] The apparatus and procedures were similar to those reported previously for studying polymer solutions.^[12] It consisted mainly of a high-pressure view cell with a volume of 40 cm³, 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.

In a typical experiment, the air in the view cell was replaced by CO₂ (or ethylene, depending on which of them was used). The solution of Triton X-100 in cyclohexane (5 mL) and the desired amount of double distilled water were loaded into the high-pressure view 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 milky. CO₂ was charged into the cell slowly until the hazy and milky liquid solution became transparent and completely clear, which was an indication of the solubilization of all the water,^[12,16] and the bluish translucent appearance of a system was not considered as the onset of solubilization. It was estimated that the uncertainties of phase separation pressure measurement was ± 0.1 MPa.

UV-visible measurements: The absorption spectra of MO in the reverse micelles was studied by UV spectroscopy. The apparatus and procedures were similar to those reported previously.^[12,17] It consisted of a gas cylinder, a high-pressure pump, a pressure gauge, an UV-visible spectrometer, a temperature-controlled high-pressure UV sample cell, and valves and fittings. The UV-visible 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 cm³, respectively. In the experiment, the sample cell was flushed with CO₂ to remove the air. The desired amounts of MO aqueous solution of suitable concentration and Triton X-100 in cyclohexane were charged into the sample cell. After thermal equilibrium had been reached, CO₂ was compressed into the UV cell to the desired pressure. The UV spectrum at equilibrium condition was recorded, which was confirmed by the fact that the UV spectra recorded were independent of equilibration time. Generally, about 30 minutes were required for the system to reach equilibrium after suitable pressure was reached, and the spectrum of each solution was recorded four times.

Results and Discussion

Volume expansion coefficient: It is well known that the solubility of a gas in a liquid depends on pressure and temperature, and the liquid is expanded by the gas dissolved. The volume expansion can be characterized by volume expansion

coefficient $\Delta V = (V - V_0) / V_0$, in which V and V_0 are the volumes of the CO₂-saturated and CO₂-free solutions, respectively. The dependence of ΔV of Triton X-100/cyclohexane on the pressure of CO₂ and ethylene is demonstrated in Figure 1. As expected, ΔV increases with pressure, because the concentration of CO₂ in the liquid is increased.

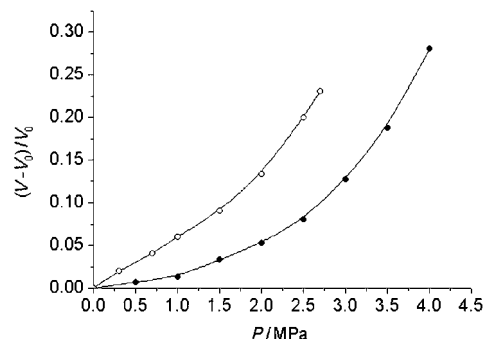


Figure 1. Dependence of volume expansion coefficient ΔV of Triton X-100/cyclohexane mixture on pressure of the gases (● CO₂ $c_{TX} = 0.31$ mol L⁻¹ $T = 20.0^\circ\text{C}$; ○ ethylene $c_{TX} = 0.31$ mol L⁻¹ $T = 25.0^\circ\text{C}$).

The effect of CO₂ pressure on the solubilization of water:

Other authors have described the phase diagram of Triton X-100/cyclohexane/water systems at 20°C^[18] and 30°C.^[15] The solubilization of water into the organic phase by the nonionic surfactant was very poor, although the uptake of water became appreciable when alcohols were added.^[14]

In our experiments, W_0 is below 1.0 at 20.0°C, which agrees with that reported by other authors.^[14] However, the value of W_0 can reach about 10.5 when appropriate amount of compressed CO₂ was added. Figure 2 shows the value of

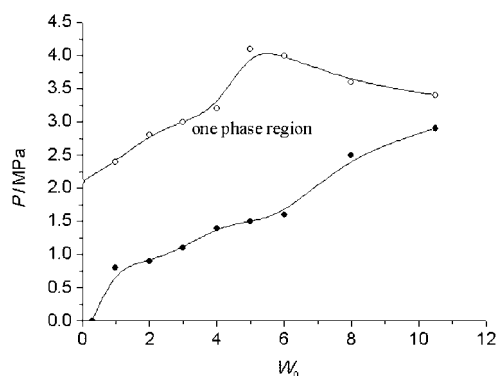


Figure 2. W_0 as a function of CO₂ pressure at 20.0°C ($c_{TX} = 0.31$ mol L⁻¹).

W_0 as a function of pressure at 20.0°C. In this work, the trace amount of water dissolved in the solvent (cyclohexane/CO₂) was corrected when calculating W_0 ; that is, the amount of water in the solvent was subtracted. Stable microemulsions are formed between the two curves. The system separates into two phases outside this microemulsion region.

It can be seen from Figure 2 that the surfactant can form reverse micelles with various W_0 values in the suitable CO₂ pressure range, although the W_0 is very small in the absence

of CO₂. This indicates that an evident increase of the solubilization capacity of the reverse micelle can be achieved by adding compressed CO₂. The pressure range is relatively narrow as the amount of the solubilized water is very large ($W_0=10.5$). The instability of the reverse micelle above the upper pressure boundary results mainly from the fact that the solvent power of the solvent is too weak to dissolve the surfactant at the higher pressure, because CO₂ is very poor solvent for Triton X-100 and its solubility in cyclohexane increases with increasing of CO₂ pressure, as can be seen from Figure 1. This argument was confirmed by our experiments. The precipitation of the surfactant was observed at the higher pressures. The effect of compressed CO₂ on the solubilization of water at a lower Triton X-100 concentration (0.16 molL⁻¹) was also investigated at this temperature. Similarly, pronounced increase of W_0 was observed, and the maximum value of W_0 could reach 6.0 at 20.0 °C.

Figure 2 also shows clearly that the W_0 and phase separation in Triton X-100/cyclohexane systems can be controlled by CO₂ pressure. In our experiments, as expected, the microemulsion could be separated into two phases simply by decreasing or increasing pressure of CO₂, and a homogeneous one-phase microemulsion was formed again by adjusting CO₂ pressure. Therefore, formation and breakage of the reverse micelles could be easily controlled by tuning pressure of CO₂.

Effect of temperature on the solubilization of water: For nonionic surfactants, temperature affects the solubility of surfactant in oil, due in part to the break of hydrogen bonds between surfactant head groups,^[19] and the hydrophilic interactions of nonionic surfactant are more profoundly influenced by temperature than are the lipophilic interactions.^[20] In this work, the effect of temperature on the solubilization of water in water/Triton X-100/cyclohexane systems without and with compressed CO₂ was also investigated; the results are shown in Figure 3 and Table 1 lists the pressure range in which stable reverse micelles can be formed at different W_0 values. In a wide temperature range, the maximum W_0 is

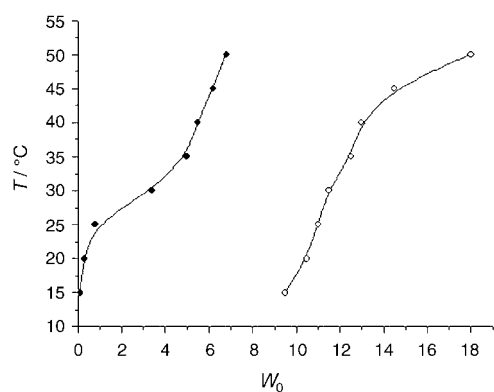


Figure 3. Effect of temperature on the solubilization of water in water/Triton X-100/cyclohexane systems with (○) and without (●) compressed CO₂ ($c_{TX}=0.31$ molL⁻¹).

Table 1. Pressure range of CO₂ at maximum W_0 ($c_{TX}=0.31$ molL⁻¹).

T [°C]	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0
P [MPa]	2.3–3.3	2.9–3.4	3.1–3.5	3.4–3.8	3.8–4.1	3.9–4.3	4.0–4.4	4.8–5.1
W_{0max}	9.5	10.5	11.0	11.5	12.5	13.0	14.5	18.0

much higher in the presence of compressed CO₂ than that in the absence of compressed CO₂.

Solvatochromic probe studies: The absorption maximum (λ_{max}) of methyl orange (MO) is sensitive to the polarity of its local environment, and the 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.^[21,22] The absorption spectra of MO in a dry Triton X-100/cyclohexane reverse micelle system has been determined by Zhu et al.^[21] They reported that the absorption maximum (λ_{max}) of MO remained at 417 nm in a wide range of surfactant concentration, which was slightly lower compared to that in pure Triton X-100 (422.5 nm). This suggests that cyclohexane penetrates the interior of the micelle aggregates. Moreover, λ_{max} of MO in the dry reverse micelle of Triton X-100 and hexanol in cyclohexane is much lower (411 nm).^[23] This indicates that the property of the solvent may affect the micropolarity of reverse micelle considerably.

MO is insoluble in cyclohexane.^[21] Our experiments indicated that it was not soluble in cyclohexane/CO₂ mixture either, as evidenced by the fact that the absorbance of MO in the mixed solvent was negligible. The absorption spectra of MO in a dry Triton X-100/cyclohexane (here “dry” means that no water is added to the system) reverse micelle system as a function of CO₂ pressure were firstly observed and the λ_{max} values are given in Table 2. The λ_{max} determined in the

Table 2. The λ_{max} of MO in Triton X-100/cyclohexane dry reverse micelles versus CO₂ pressure at 20.0 °C ($c_{TX}=0.31$ molL⁻¹).

P [MPa]	0	1.0	2.0
λ_{max} [nm]	417.0	414.0	410.5

dry micelle in the absence of CO₂ is the same as that reported by other authors.^[21] It can be seen from Table 2 that the λ_{max} of MO move to shorter wavelength with the increasing pressure of CO₂. This indicates that the interior micropolarity of the dry micelle decreases with the increase of the CO₂ pressure. A possible explanation for this phenomenon is that more CO₂ can penetrate into the aggregates with the increase of CO₂ pressure. In other words, with the increasing of CO₂ pressure, more and more CO₂ enter the polar cores of the dry reverse micelles, which reduces the polarity of the cores.

The λ_{max} of MO in the Triton X-100/cyclohexane/water system with various W_0 and at 1.6 MPa are listed in Table 3.

Table 3. The λ_{max} of MO in 0.31 molL⁻¹ Triton X-100 solution as a function of W_0 at 20.0 °C ($P=1.6$ MPa).

W_0	0.5	1.0	2.0	3.0	5.0	6.0
λ_{max} [nm]	415.0	417.0	418.5	421.0	421.0	421.0

The λ_{\max} of MO increases from 415 nm to 421 nm as W_0 varied from 0.5 to 3.0. However, when W_0 is in the range of 3.0–6.0, λ_{\max} is independent of W_0 . The possible explanation of these phenomena is that formation of a water pool in the aggregates starts at $W_0=3.0$. The MO probe is located in the polar core of Triton X-100 reverse micelle and embedded between the oxyethylene chains, but outside the water pool. Water added to the reverse micelles first hydrates the oxyethylene chains of Triton X-100 and then forms water pool. Similar mechanism has been discussed by different authors for various reverse micelles.^[23,24]

Our experiments demonstrated that the λ_{\max} of MO decreased from 421 nm to 419 nm as the CO_2 pressure increased from 1.6 MPa to 3.0 MPa at $W_0=5.0$. In addition, λ_{\max} at $W_0=10$ and 3.0 MPa was also 419.0 nm, which is shorter than 421 nm. These results further suggest that MO is mainly embedded between the oxyethylene chains and the penetration of CO_2 . Therefore, increasing the size of the water core does not change the local environment of the probe considerably.

Possible mechanism: Generally, the solubilization capacity of water in reverse micelles can be interpreted based on a consideration of the R ratio, which compares the balance of the individual cohesive energies of the functional groups present at the interface.^[20] Addition of compressed CO_2 will decrease the solvent power of an organic solvent,^[8,25] which should result in a decrease of the value of R ratio. As a result, the single-phase region will shift to higher temperature and thus decrease the solubilization of water in this system, because the experimental temperatures are well below the phase-inversion temperature in cyclohexane.^[26] In other words, the solubilization capacity should be reduced if CO_2 solely weakens the solvent strength. In order to further provide evidence for this argument, we studied the effect of n -hexane, which is a poor solvent for Triton X-100^[27] and can reduce the solvent power of cyclohexane for Triton X-

Table 4. The solubilization of water in the reverse micelle of Triton X-100 in mixed solvent of cyclohexane and n -hexane ($c_{\text{TX}}=0.31 \text{ mol L}^{-1}$, $T=30.0^\circ\text{C}$).

$V_{\text{hex}}/V_{\text{cyclo}}$	0:100	1:99	1:39	1:19	1:9	1:4	1:3	1:1
W_0	3.4	3.4	3.1	2.5	1.0	0.5	0.3	0

100, with the maximum W_0 at 30.0°C ; the results are listed in Table 4. Evidently, the maximum W_0 decreases with addition of n -hexane. This further suggests that enhancement of solubilization ability by CO_2 does not originate from an anti-solvent effect, because addition of a poor solvent reduces the W_0 .

On the basis of thermodynamic principles, it can be deduced that CO_2 distributes between organic continuous phase and the micelle phase. Dissolution of CO_2 in the water core can change its pH and ionic strength, because CO_2 can be ionized in water. To obtain some information about whether this factor affects the solubilization capacity or not, we conducted some experiments to study the effect

of Na_2CO_3 , NaHCO_3 , $\text{H}_2\text{C}_2\text{O}_4$, and CaCl_2 at various concentrations on the solubilization of water in the absence of compressed CO_2 . The results showed that these electrolytes could not increase the solubilization capacity of water, although they could vary the pH and ionic strength of the water cores. This is similar to the conclusion that weak acid (CH_3COOH) hardly influenced the solubility diagram in tetrachloroethylene solution of a polyoxyethylene nonylphenyl ether ($n=8$).^[28] Therefore, it is likely that the enhancement of water solubilization in Triton X-100/cyclohexane reverse micelles by CO_2 does not result from the change of pH or ionic strength of the water cores.

The ability of reverse micelles to solubilize water depends on droplet size and the interdroplet interaction.^[29] However, in the system studied in this work the phase separation is mainly caused by the micelle–micelle interactions, because the experimental temperatures are lower than the phase-inversion temperature.^[30] Therefore, it is likely that the decrease of the attractive interdroplet interaction by addition of CO_2 is the dominant factor for the enhancement of solubilization capacity.

Effect of CO_2 on the properties is very complex, because it distributes between the organic continuous phase, the interfacial film of the reverse micelles, and the polar cores. To our knowledge, it is very difficult to explain the interesting and anomalous phenomenon above. However, on the basis of the above experimental results and discussions, and the information extracted from the related papers and books by other authors, we deduce that CO_2 influences the stability of the reverse micelles in several ways:

- 1) The CO_2 in the organic phase reduces the solvent strength of the solvent, which should reduce the ability to solubilize water as discussed above.
- 2) 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 the lower viscosity.
- 3) CO_2 is a small molecule and it can insert itself between surfactant tails; this leads to a more rigid, hardened interfacial film, and consequently to stabilize the micelles due to reduction of tail–tail interaction
- 4) CO_2 may reduce the interfacial tension, because it exists in the organic phase, in the film of the reverse micelles, and on interface of the surfactant and solvent, which promotes the formation of the reverse micelles.

The first factor is not favorable to the solubilization of water as discussed above, while all the others favor the enhancement of the stability of the reverse micelles. In a suitable pressure range, the last three factors are dominant, and W_0 becomes larger. Therefore, the compressed gas has the functions of cosurfactants at suitable pressures.

To further aid evidences for the above arguments, the same type of experiment was performed with compressed ethylene, and the results are shown in Figure 4. Evidently, ethylene can also enhance the ability of the reverse micelle to solubilize water at room temperature. We believe the mechanism is similar.

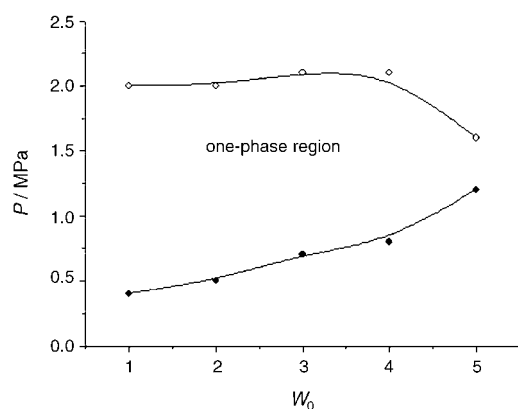


Figure 4. W_0 as a function of ethylene pressure range at 25.0°C ($c_{\text{TX}} = 0.31 \text{ mol L}^{-1}$).

Conclusions

In this work, we have studied the effect of compressed CO_2 and ethylene on the properties of Triton X-100/cyclohexane/water systems, and the main results are summarized as follow.

In a wide temperature range, the maximum W_0 is much higher in the presence of compressed CO_2 at suitable pressures than that in the gas-free solution. The microemulsion could be separated into two phases simply by decreasing or increasing pressure of CO_2 , and a homogeneous one-phase microemulsion can be formed again by adjusting CO_2 pressure. At 1.6 MPa, the λ_{max} of methyl orange gradually increases from 415 nm to 421 nm with an increase in the W_0 value from 0.5 to 3.0, while λ_{max} is independent of W_0 at higher W_0 values. At a fixed W_0 the λ_{max} decreases with increasing pressure. These results suggest that formation of water pool in the aggregates starts at $W_0 = 3.0$ and the probe is located in the polar core of Triton X-100 reverse micelle and embedded between the oxyethylene chains, but outside the water pool, and that CO_2 can penetrate into the reverse micelles. Compressed ethylene can also enhance the ability of the reverse micelle to solubilize water at room temperature. They both have the function of co-surfactants in that they can stabilize the reverse micelles. In contrast, *n*-hexane, a poor solvent for Triton X-100 with larger size, reduces the W_0 considerably.

The stability of the Triton X-100/cyclohexane reverse micelles depends mainly on the interdroplet interaction, because the experimental temperatures are well below the phase-inversion temperature. It is likely that compressed CO_2 or ethylene could enhance the stability of the micelles by decreasing the attractive interaction between the droplets.

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