

Supercritical or Compressed CO₂ as a Stimulus for Tuning Surfactant Aggregations

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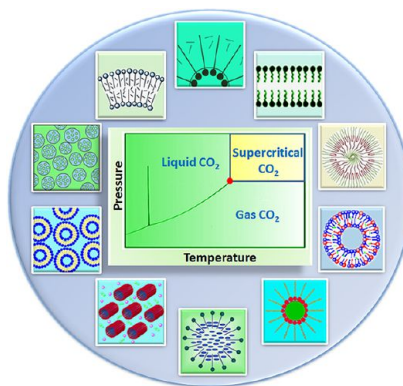
CONSPECTUS

Surfactant assemblies have a wide range of applications in areas such as the chemical industry, material science, biology, and enhanced oil recovery. From both theoretical and practical perspectives, researchers have focused on tuning the aggregation behaviors of surfactants. Researchers commonly use solid and liquid compounds such as cosurfactants, acids, salts, and alcohols as stimuli for tuning the aggregation behaviors. However, these additives can present economic and environmental costs and can contaminate or modify the product. Therefore researchers would like to develop effective methods for tuning surfactant aggregation with easily removable, economical, and environmentally benign stimuli.

Supercritical or compressed CO₂ is abundant, nontoxic, and nonflammable and can be recycled easily after use. Compressed CO₂ is quite soluble in many liquids, and the solubility depends on pressure and temperature. Therefore researchers can continuously influence the properties of liquid solvents by controlling the pressure or temperature of CO₂. In this Account, we briefly review our recent studies on tuning the aggregation behaviors of surfactants in different media using supercritical or compressed CO₂.

Supercritical or compressed CO₂ serves as a versatile regulator of a variety of properties of surfactant assemblies. Using CO₂, we can switch the micellization of surfactants in water, adjust the properties of reverse micelles, enhance the stability of vesicles, and modify the switching transition between different surfactant assemblies. We can also tune the properties of emulsions, induce the formation of nanoemulsions, and construct novel microemulsions. With these CO₂-responsive surfactant assemblies, we have synthesized functional materials, optimized chemical reaction conditions, and enhanced extraction and separation efficiencies.

Compared with the conventional solid or liquid additives, CO₂ shows some obvious advantages as an agent for modifying surfactant aggregation. We can adjust the aggregation behaviors continuously by pressure and can easily remove CO₂ without contaminating the product, and the method is environmentally benign. We can explain the mechanisms for these effects on surfactant aggregation in terms of molecular interactions. These studies expand the areas of colloid and interface science, supercritical fluid science and technology, and chemical thermodynamics. We hope that the work will influence other fundamental and applied research in these areas.



Introduction

Surfactants are an important class of molecules. They have wide applications in chemical industry, material science, biology, and enhanced oil recovery. It is well-known that surfactants have the ability to self-assemble into various morphologically different structures, such as micelles, reverse micelles, vesicles, liquid crystals, etc. Tuning the microstructures of surfactant assemblies is of great importance from both theoretical and practical points of view,

because the functions and properties of surfactant solutions and assemblies depend strongly on their microstructures. There has been much research on tuning the aggregation behaviors of surfactants by using a variety of chemical stimuli including cosurfactants, acids, salts, alcohols, etc.^{1–3} These commonly used additives are solid or liquid compounds, which suffer from economic and environmental costs, as well as contamination or modification of products by the additives. Development of simple, inexpensive, environmentally benign methods to control the aggregation

behaviors of surfactants using greener and easily removed stimuli is of great importance but is challenging.

Supercritical or compressed CO₂ is regarded as a green solvent because it is nontoxic, abundant, tunable, and non-flammable, has moderate critical temperature and pressure (31.1 °C and 7.38 MPa), and can be easily recaptured and recycled after use.^{4–6} In particular, compressed CO₂ is quite soluble in many liquids, and the solubility depends on pressure and temperature.^{7,8} Dissolution of CO₂ in liquids can change the properties of the liquid solvents considerably. Therefore, the properties of liquid solvents can be tuned continuously by controlling the pressure or temperature of CO₂. These unique features of CO₂ make it possible and promising to tune the properties of surfactant assemblies through effective, controllable, economical, and environmentally benign routes.

CO₂ has been found to be versatile in tuning the properties of a variety of surfactant assemblies: (i) switching micellization of surfactant in water, (ii) adjusting properties of reverse micelles, (iii) enhancing stability of vesicles, (iv) switching transition between different surfactant assemblies, (v) tuning properties of emulsions, and (vi) constructing novel microemulsions. These CO₂-responsive surfactant assemblies have been successfully applied in synthesizing functional materials, optimizing chemical reaction conditions, and enhancing the efficiencies of extraction and separation. In comparison with conventional solid or liquid additives, the utilization of CO₂ has some obvious advantages. First, the aggregation behaviors of surfactants can be easily adjusted by changing CO₂ pressure. Second, the tuning of the aggregation behaviors of surfactants by CO₂ is reversible, which can be realized simply by pressurization and depressurization; thus CO₂ can be regarded as a “switch” for the molecular aggregations of surfactants. Third, CO₂ can be easily removed by depressurization, which makes the postprocessing much easier in comparison with the conventional additives that usually cause contamination or modification of the products. Fourth, utilization of CO₂ is environmentally benign. In this Account, we discuss the recent progress on this interesting topic.

Switching Micellization of Surfactant in Water by CO₂

A micelle is an aggregate of amphiphilic molecules, with the nonpolar portions in the interior and the polar portions at the exterior surface, which is commonly exposed to water. The micellization of amphiphilic molecules is generally induced by increasing the surfactant concentration to be

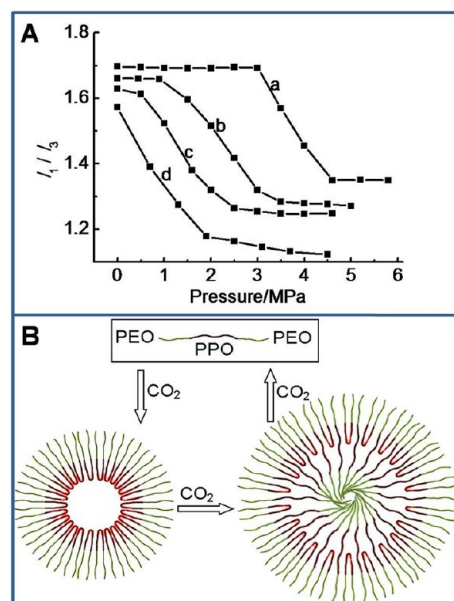


FIGURE 1. (A) I_1/I_3 ratio of pyrene's fluorescence at different CO₂ pressures in P104 solutions with initial P104 concentration of (a) 0.01, (b) 0.05, (c) 0.5, and (d) 2.0 wt %. (B) Illustration of CO₂-induced micellization: (top) Pluronic monomer; (bottom, left) micelle with a hydrophobic PPO core; (bottom right) swollen micelle with an amphiphilic PPO/PEO core. Reproduced from ref 10. Copyright 2011 Wiley-VCH.

above critical micellization concentration (cmc), adjusting temperature, or adding additives to change the cmc.⁹

CO₂ has been found to be efficient in triggering the micellization of Pluronic (PEO–PPO–PEO; triblock copolymers in which PEO represents poly(ethylene oxide) and PPO stands for poly(propylene oxide)) in water.¹⁰ Figure 1A shows the I_1/I_3 ratio of pyrene fluorescence, which is an excellent index to study the association of amphiphilic molecules, in P104 (EO₂₇PO₆₁EO₂₇) solutions at different CO₂ pressures. In the absence of CO₂, the I_1/I_3 ratio is high due to the predominantly aqueous microenvironment around pyrene. At this state, the Pluronic molecules dissolved in water do not aggregate considerably and exist in the form of individual monomers. With the addition of CO₂, the I_1/I_3 ratio suddenly decreases in a certain pressure range and finally levels off, indicating that micelles are formed at this pressure. Interestingly, even when the surfactant concentration is as low as 0.01 wt %, hundreds of times lower than the cmc, CO₂ is still efficient in inducing the micellization of Pluronic. More interestingly, the CO₂-induced micelle formed at certain pressures is different from the common micelles with hydrophobic core; that is, it has an amphiphilic core, in which hydrophobic and hydrophilic domains coexist (Figure 1B). After depressurization, the surfactant molecules return to the initial state without obvious aggregation

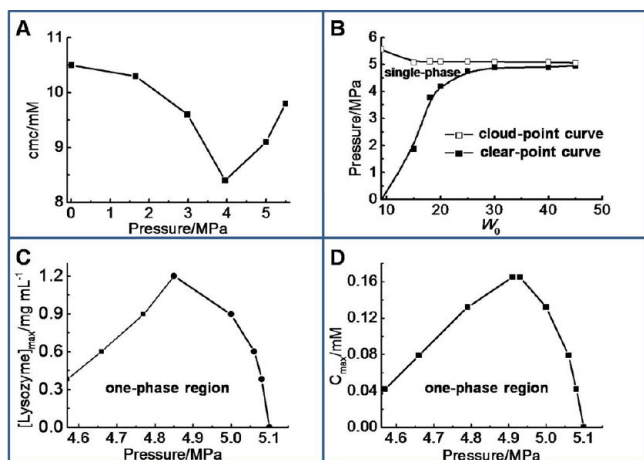


FIGURE 2. (A) The cmc values of lecithin/cyclohexane solutions at different CO₂ pressures. (B) Maximum water-to-surfactant molar ratio (W_0) in lecithin/cyclohexane solution ([lecithin] = 40 mM) at different CO₂ pressures. (C, D) Maximum lysozyme concentration (C) and PdCl₂ concentration (D) in water/lecithin/cyclohexane solution ([lecithin] = 40 mM, $W_0 = 20$) at different CO₂ pressures. The temperature is 303.2 K. Reproduced from ref 16. Copyright 2008 American Chemical Society.

(Figure 1B). Consequently, the micellization of Pluronic in water can be switched through the easy control of pressure. The main reason for CO₂ to induce the micellization is attributed to the increased hydrophobic effect in the system with the addition of CO₂, which promotes the self-assembly of surfactant molecules. Moreover, CO₂ can reduce the cloud point temperature of *p*-tert-octylphenoxy polyethylene (Triton X-100)/water micellar solutions considerably, which has been utilized for separation of phenol, vanadium ion, and gold nanoparticles from water.¹¹

Adjusting Properties of Reverse Micelles with CO₂

Surfactants can form reverse micelles spontaneously in nonpolar solvents under suitable conditions.¹² In a reverse micelle, the hydrophobic tails of surfactants extend into the exterior apolar phase, while the hydrophilic head groups point inside, forming a polar core. It has been demonstrated that the properties of reverse micelles, such as cmc, stability, micropolarity, pH, microstructure, and solubilization ability, can be controlled by CO₂ pressure.^{13–18} Figure 2A shows the cmc of lecithin (a biosurfactant) in cyclohexane at different CO₂ pressures.¹⁶ The cmc decreases with increasing pressure in the low pressure region, indicating that the addition of CO₂ is favorable to the formation of reverse micelles. However, the cmc increases with pressure after passing through a minimum value. This suggests that CO₂ affects cmc in two opposite ways. First, it can stabilize the reverse

micelles by inserting into the interfacial region of the reverse micelles, which is favorable to enhancing the formation of reverse micelles or reducing cmc value. Second, CO₂ in the solvent reduces the hydrophobicity of the solvent because CO₂ is less hydrophobic than cyclohexane, which is not favorable to reducing cmc value. At lower pressures, the first factor is dominant, while at higher pressures, the second factor becomes crucial. The competition of the two opposite factors results in the minimum in the cmc versus pressure curve.

The solubilization abilities of lecithin reverse micelles for different substances have been investigated in the presence of CO₂. Figure 2B,C,D shows the solubilization capacities of lecithin reverse micelles for water, lysozyme, and PdCl₂ at different CO₂ pressures, respectively.¹⁶ The maximum water-to-surfactant molar ratio ($W_{0,max}$) is 9 in the absence of CO₂. With the addition of CO₂, the solubilization capacity for water is enhanced significantly, and $W_{0,max}$ can reach 45 at 4.95 MPa. For lysozyme and PdCl₂, their solubilities in reverse micelles are enhanced significantly in the lower pressure region, and the solubilized biomolecule and inorganic salt can be precipitated completely at higher pressure, while the surfactant remains in the solution. Therefore, high extraction and recovery efficiencies of the salt and protein can be achieved by controlling CO₂ pressure. The extraction and fractionation of different substances by controlling the solubilization capacity of reverse micelles using CO₂ pressure have great potential for application with some unique advantages.

Enhancing Stability of Vesicles by CO₂

Vesicles are enclosed and hollow lamellar aggregates with a curved bilayer membrane comprised of amphiphilic molecules.¹⁹ The vesicular systems formed from the mixtures of anionic and cationic surfactants in aqueous solutions usually precipitate due to partial shielding of charges. It has been discovered that CO₂ can significantly enhance the stability of the vesicles in the dodecyltrimethylammonium bromide (DTAB)/sodium dodecyl sulfate (SDS) system.²⁰ A scheme for CO₂ to stabilize the vesicles is illustrated in Figure 3A. In the absence of CO₂, the surfactants precipitate immediately after mixing of the solutions of DTAB and SDS. However, in the presence of CO₂, the vesicles can be stable for 15 days. As a small molecule, CO₂ can insert into the bilayer region of the vesicles to reduce the size of the vesicles and enhance the rigidity of the membrane, thus enhancing the stability of vesicles. On the basis of this discovery, a method to prepare hollow silica spheres using tetraethyl

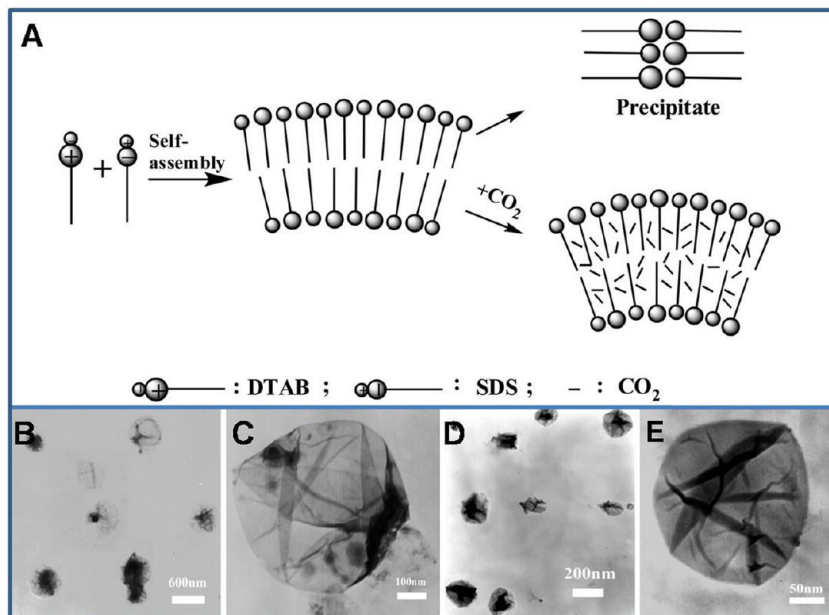


FIGURE 3. (A) Illustration of enhanced stability of DTAB/SDS vesicles by CO₂. (B–E) TEM images of silica particles prepared in DTAB/SDS aqueous solution ($C_{\text{total}} = 10.0$ mM, 1:1) at 3.50 MPa (B, C) and 6.02 MPa (D, E). Reproduced from ref 20. Copyright 2009 American Chemical Society.

orthosilicate (TEOS) as precursor and CO₂-stabilized vesicles as template has been developed. The silica hollow spheres are in the hundreds of nanometers, and their size can be controlled by the pressure of CO₂ (Figure 3B–E). Further studies show that some small hydrocarbon gases, such as methane, ethane, propane, ethylene, propylene, and isobutene, can also enhance the stability of the vesicles formed in mixed cationic–anionic surfactant solutions.²¹ This proves that the insertion of small molecules into the bilayer membrane plays a key role for enhancing vesicle stability.

Switching Transition between Different Surfactant Assemblies by CO₂

With a regular array of surfactant bilayers alternating with water layers, lamellar liquid crystals (L_a) are anisotropic and highly viscous,²² which is very different from isotropic micellar solution (L_1). Switching the $L_a \rightarrow L_1$ phase transition is a very interesting topic. For the sodium bis-2-ethylhexyl-sulfosuccinate (AOT)/water (1:1 by weight) lamellar liquid crystal, phase transition occurs at or above 413 K. The effect of CO₂ on the properties of AOT/water system (1:1 by weight) has been studied at 290.7 K. As shown in Figure 4A,²³ in the low pressure range, the viscosity of the system is very high and gradually decreases with the addition of CO₂ (photographs a–c). Interestingly, as the pressure reaches an optimum value, the sample suddenly loses its viscoelasticity and changes into a transparent fluid (photographs d and e). The phase transition from liquid crystal to fluid is reversible

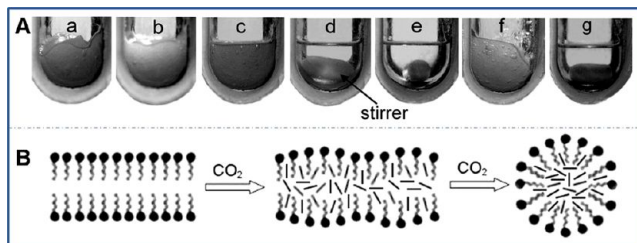


FIGURE 4. (A) Photographs of AOT/water system (1:1 by weight) at 290.7 K (a) without CO₂ and at CO₂ pressures of (b) 3.09, (c) 4.36, (d) 4.85, and (e) 5.07 MPa. Photographs f and g correspond to d after releasing of CO₂ and pressurization to 4.85 MPa again, respectively. (B) Illustration for the $L_a \rightarrow L_1$ phase transition induced by compressed CO₂. Reproduced from ref 23. Copyright 2008 Wiley-VCH.

and can be repeated by controlling CO₂ pressure. After releasing CO₂, the fluid shown in photograph d changes back into L_a phase (photograph f), and the transparent fluid forms again after CO₂ is recharged (photograph g). The results of small-angle X-ray scattering study indicate the phase transition from liquid crystal to micellar solution.

Because CO₂ is very soluble in hydrocarbons, it can insert into the hydrophobic surfactant bilayer of L_a phase, even deep inside the tail region of surfactant, changing the structure of the bilayers. With increasing pressure of CO₂, the ordering structure of L_a phase is disrupted, and a more thermodynamically stable micellar solution is formed when the pressure is high enough (Figure 4B). Liu and co-workers have used molecular dynamics simulation to investigate the CO₂-induced $L_a \rightarrow L_1$ phase transition.²⁴ The results

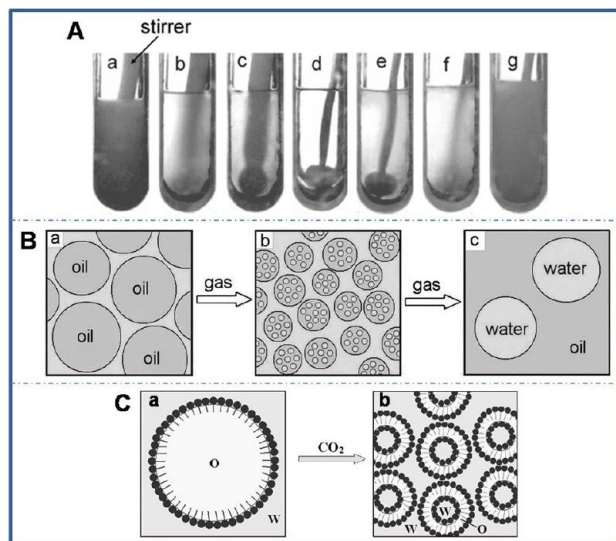


FIGURE 5. (A) Photographs of H₂O/AOT/isooctane system ([AOT] = 0.02 g/mL, $V_{\text{water}}/V_{\text{isooctane}} = 1$) at 303.2 K and CO₂ pressures of (a) 0, (b) 3.55, (c) 3.64, (d) 3.78, (e) 3.90, (f) 4.01, and (g) 4.45 MPa.²⁷ (B) CO₂-triggered (a) oil-in-water to (c) water-in-oil emulsion inversion via a (b) water-in-oil-in-water nanoemulsion in AOT/water/isooctane emulsion ([AOT] = 0.045 M, $V_{\text{water}}/V_{\text{isooctane}} = 0.11$) at 303.2 K.²⁸ (C) CO₂-induced (b) water-in-oil-in-water double nanoemulsion formed in CTAB/water/heptanes emulsion ([CTAB] = 0.04 g/mL, $V_{\text{water}}/V_{\text{heptane}} = 1$) at 303.2 K.²⁹ Copyright 2008 Wiley-VCH. Reproduced by permission of the PCCP Owner Societies.

demonstrate that the lamellar bilayer becomes loose and unstable as swollen by CO₂ and expands with more CO₂ dissolved; thus a microstructure transition occurs eventually. This is consistent with the proposed mechanism shown in Figure 4B. Moreover, it has been also shown that CO₂ can induce the micelle-to-vesicle transition in DTAB/SDS mixed surfactant aqueous solution.²⁵

Tuning Properties of Emulsions by CO₂

An emulsion is a heterogeneous system consisting of at least two immiscible liquids and is unstable thermodynamically. Tuning the properties of emulsions has been an important research topic for years, which has found wide applications in many different processes.²⁶ CO₂ has been used to tune the properties of oil/water/surfactant emulsions, such as stability, morphology, droplet size, etc.^{27–32} Figure 5A shows the photographs of a water/AOT/isooctane emulsion system at 303.2 K and different CO₂ pressures.²⁷ In the absence of CO₂, the emulsion is completely turbid upon stirring. Interestingly, the turbid emulsion becomes more and more transparent as CO₂ is added to the system under stirring, and a completely transparent emulsion is formed when CO₂ pressure reaches 3.78 MPa. Subsequently, with continuously increasing pressure, the transparent emulsion

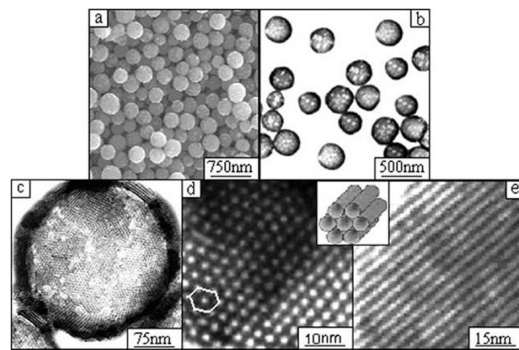


FIGURE 6. SEM (a) and TEM (b–e) images of silica obtained in a CO₂-induced nanoemulsion ([CTAB] = 0.02 g/mL, $V_{\text{TEOS}}/V_{\text{heptane}} = 1:9$, $V_{\text{oil}}/V_{\text{water}} = 1:1$, 303.2 K, 3.91 MPa). The inset between d and e is the schematic illustration of the ordered hexagonal pore channels, and the white label in d shows a hexagonal pore unit. Reproduced from ref 30. Reproduced by permission of The Royal Society of Chemistry.

changes into turbid again. After the stirrer is stopped for a certain time, the transparent emulsion shown in photograph d separates into water-rich and isooctane-rich phases, indicating the formation of thermodynamically unstable nanoemulsion. By variation of experimental conditions, multiple water-in-oil-in-water nanoemulsions²⁸ (b in Figure 5B) and double water-in-oil-in-water nanoemulsions²⁹ (b in Figure 5C) have been induced by CO₂. In comparison with the conventional nanoemulsions, the CO₂-induced nanoemulsions have the following special advantages: they can be formed in a wide range of surfactant concentrations and water-to-oil volume ratios; the transition between the macroemulsion and nanoemulsion is reversible and can be controlled by pressurization and depressurization; CO₂ can be easily removed by reducing pressure; the method is low-energy.

The CO₂-induced nanoemulsions have been utilized to synthesize various materials with controlled morphologies, such as silica,^{29,30} gold,³¹ and polymers.^{27,32} For example, the water/*n*-heptane/cetyltrimethylammonium bromide (CTAB)/CO₂ nanoemulsion has been utilized in silica synthesis.³⁰ No catalyst is required in this route because H⁺ produced by ionization of CO₂ in water can catalyze the hydrolysis reaction, which makes the process cleaner because CO₂ is nontoxic and can be released automatically after depressurization. As shown in Figure 6, the calcined sample is composed of uniform, monodisperse, hollow spherical particles with a diameter of about 280 nm, and highly ordered hexagonal pore channels exist in the shells of the hollow silica spheres. It is proposed that the nanosized oil droplets form the cores of the silica spheres, and the cylindrical micelles of the surfactant in the aqueous phase act as templates for the formation of the mesopores in silica shells.

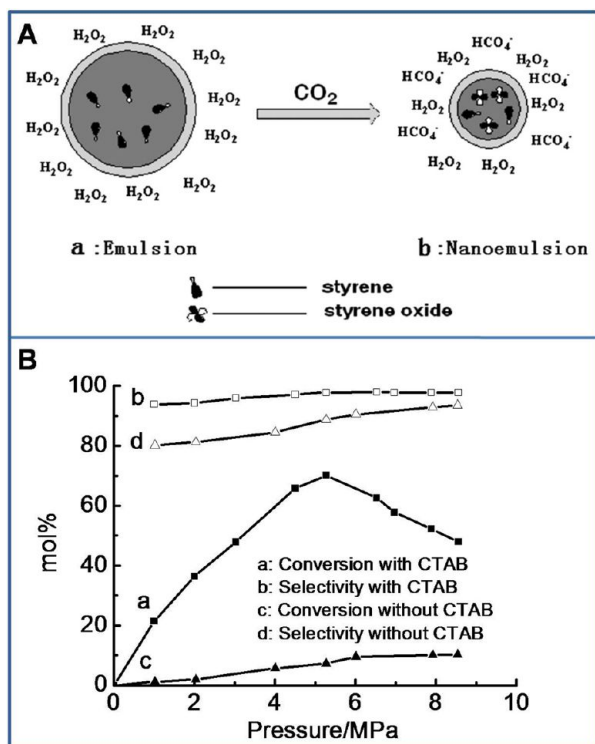


FIGURE 7. (A) Schematic illustration for the epoxidation reaction of styrene without CO₂ (a) and in CO₂-induced nanoemulsion (b). (B) The styrene conversion and the product selectivity at different CO₂ pressures with CTAB (0.055 M) (a, b) and without CTAB (c, d). The experimental conditions were $V_{\text{heptane}}/V_{\text{water}} = 4:5$, $V_{\text{total}} = 6$ mL, 4.5 M H₂O₂, 1.5 M styrene, 0.3 M KOH, 40.0 °C, 7 h. Reproduced from ref 33. Reproduced by permission of The Royal Society of Chemistry.

Therefore, the hollow silica spheres with ordered mesoporous shells are formed after removing the oil and surfactant by washing and calcination.

The unique function of CO₂ to tune the droplet size of emulsions continuously provides opportunity to study the effect of droplet size of emulsions on chemical reactions in a wide droplet size range. The styrene epoxidation in the CTAB/H₂O/n-heptane/styrene/H₂O₂ emulsion system at different CO₂ pressures has been investigated.³³ In the reaction, CO₂ acts not only as a modulator for the emulsion droplet size but also as bicarbonate source to catalyze the reaction (Figure 7A). With addition of CO₂, the conversion of styrene is gradually increased and reaches a maximum at 5.27 MPa, where the droplet size of the emulsion is the smallest (39.5 nm), and then the conversion decreases with further increasing pressure (Figure 7B). At 5.27 MPa, the conversion in the emulsion can reach 70.1%, 10 times higher than that in a surfactant-free system at the same pressure. This is because the catalytic reaction is significantly accelerated due to the smallest droplet size of the emulsion and the largest interfacial surface area. From the practical

point of view, this process is advantageous in that the reaction efficiency can be easily optimized by pressure of CO₂, and CO₂ can be used as bicarbonate source, no additional catalyst is used, and the process is greener. It is believed that the concept of tuning the efficiency of reactions in emulsions using CO₂ can also be used for some other reactions.

Constructing Novel Microemulsions with CO₂ and Ionic Liquid

A microemulsion is a thermodynamically stable dispersion of two immiscible fluids (generally organic solvent and water) stabilized by surfactants. Owing to the capacity to host a variety of polar and nonpolar species simultaneously, microemulsions have been widely applied in extraction, chemical reaction, and nanomaterial synthesis.³⁴ The formation of microemulsions with CO₂ is very attractive owing to its unusual solvent properties. Recently, a large number of reports on microemulsions formed by CO₂ and water (water-in-supercritical CO₂^{35–37} and CO₂-in-water microemulsions³⁸) have emerged.

Room-temperature ionic liquids (ILs), which are organic salts with melting points below 100 °C, have received much attention.^{39,40} They can dissolve many organic and inorganic substances, and their properties are designable to satisfy the requirements of various applications. ILs can be utilized as amphiphile self-assembly media,⁴¹ and a variety of microemulsions with ILs have been formed, including IL-in-oil and oil-in-IL microemulsions,^{42,43} IL-in-water and water-in-IL microemulsions,^{44,45} and IL-in-IL microemulsions.⁴⁶

The simultaneous utilization of CO₂ and ILs can combine the advantages of the two fluids. With surfactant *N*-ethyl perfluorooctylsulfonamide (*N*-EtFOSA) and guanidium-based ILs, IL-in-CO₂ microemulsions have been constructed.⁴⁷ A scheme for the reverse micelle in the IL-in-CO₂ microemulsion is illustrated in Figure 8A. At readily accessible pressures, the IL-to-surfactant molar ratio (W) can reach 0.8 for the CO₂/1,1,3,3-tetramethylguanidinium acetate (TMGA)/*N*-EtFOSA system, which is equivalent to a W_0 of 8 for water-in-CO₂ microemulsion considering that the molecular weights of TMGA and water are 175.2 and 18.0 g/mol, respectively. The IL domains dispersed in CO₂ can solubilize different salts, such as methyl orange, CoCl₂, and HAuCl₄, which have been utilized to synthesize gold nanoparticles (Figure 8B,C). Senapati et al. have investigated the formation of IL-in-CO₂ microemulsions via a computer simulation that demonstrates the entire process of self-aggregation at the atomic level.⁴⁸ They provide direct evidence of the existence of stable IL droplets within a continuous CO₂ phase through amphiphilic surfactants.

The CO₂-in-IL microemulsions, with IL as the continuous phase and CO₂ as the dispersed phase, have also been created recently.⁴⁹ For the 3.0 wt % N-EtFOSA/TMGA solution, the maximum amount of CO₂ solubilized in micelles, characterized by the molar ratio of CO₂ in micelles to surfactant (R_{CO_2}), can reach 12.5 at 5.7 MPa. At $R_{\text{CO}_2} = 12.5$, the micelles have an average size of 47 nm, considerably larger than the CO₂-free micelles. However, if the pressure is lower than 5.7 MPa, the CO₂-in-TMGA microemulsion cannot be formed. The mechanism for the formation of CO₂-in-IL microemulsion is illustrated in Figure 9. In the absence of CO₂, the surfactant molecules self-aggregate into “dry” micelles with the empty cores (a in Figure 9). At lower CO₂ pressures, gaseous CO₂ dissolves in the surfactant interfacial region and interacts with surfactant, as “bound CO₂”, which is incapable of expanding the micelles (b in Figure 9). As the pressure exceeds the saturation vapor pressure of CO₂, liquefied CO₂ enters into the micellar cores to form CO₂

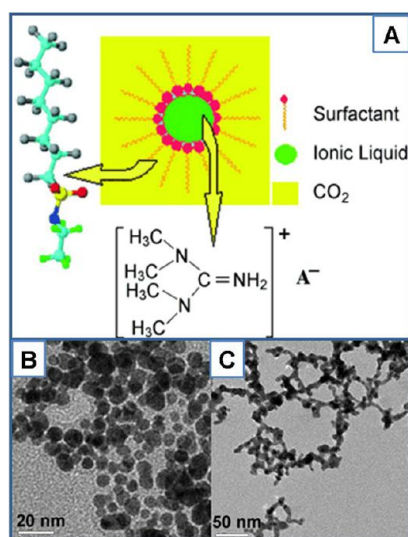


FIGURE 8. (A) Scheme for IL-in-CO₂ microemulsion. (B,C) TEM images of gold prepared in IL-in-CO₂ microemulsion ([N-EtFOSA] = 0.060 g/mL, $W = 0.41$) at 308.2 K and 20.00 MPa with the weight ratio of H₂AuCl₄ to 1,1,3,3-tetramethylguanidinium trifluoroacetate (TMGA) 0.01 (B) and 0.04 (C). Reproduced from 47. Copyright 2007 Wiley-VCH.

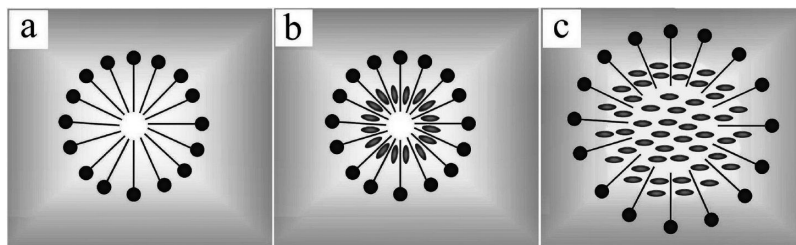


FIGURE 9. Schematic illustration for the formation of CO₂-in-IL microemulsion: (a) “dry” micelle dispersed in IL; (b) CO₂-bound micelle; (c) CO₂-swollen micelle. Reproduced from ref 49. Copyright 2011 Wiley-VCH.

domains, and the CO₂-in-IL microemulsion is formed (c in Figure 9). The CO₂-swollen micelles are “tunable”, because their size can be easily tuned by the pressure of CO₂.

A mesoporous metal–organic framework (MOF) has been synthesized in IL/supercritical CO₂/surfactant emulsion.⁵⁰ As shown in Figure 10A, MOF nanospheres (~80 nm) with highly ordered hexagonal pores were formed. The pore size and wall thickness are about 3.6 and 3.0 nm, respectively. The micropore size is 0.7 nm, determined by N₂ adsorption–desorption method. These MOF nanospheres combine advantages of both microporous and mesoporous materials and have potential applications in gas separation and catalysis. The possible mechanism to form such a novel structure of MOFs is shown in Figure 10B. The surfactant molecules self-assemble into cylindrical micelles with the fluorocarbon chain directed toward the inside of the micelles, and CO₂ exists as a core of the micelles. The IL, Zn(NO₃)₂, and 1,4-benzenedicarboxylic acid (H₂BDC) form a continuous phase (a in Figure 10B). The Zn²⁺ and BDC²⁻ in the IL form a crystalline microporous framework, leaving the micelles as cavities. Therefore, MOFs with well-ordered mesopores and microporous structured walls were formed after removal of IL, CO₂, and surfactant (b in Figure 10B).

Conclusions and Perspectives

Supercritical or compressed CO₂ can be used to tune the aggregation behaviors of surfactants in different media. The method is effective, simple, and environmentally benign, and many surfactant assemblies of different structures have been obtained. This is a new topic of colloid and interface science, and much fundamental and applied research needs to be conducted further. First, more new surfactant assemblies with special structures and functions should be designed and constructed with the aid of CO₂. Second, more applications of CO₂-tuned surfactant assemblies in different fields such as material synthesis, chemical reaction, and extraction should be explored. Third, the detailed mechanisms for CO₂ to tune aggregation behaviors of surfactants

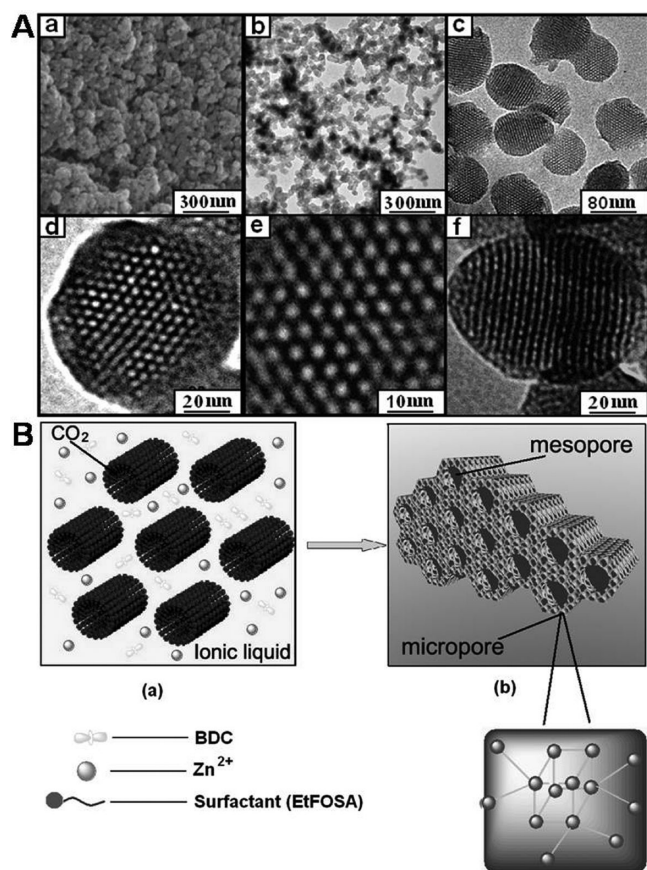


FIGURE 10. (A) SEM (a) and TEM (b–f) images of the MOF synthesized in surfactant/IL/CO₂ emulsion. (B) Schematic illustration for the formation of the MOF: (a) formation of N-EtFOSA cylindrical micelles; (b) MOF with ordered mesopores and microporous structured walls. Reproduced from ref 50. Copyright 2011 Wiley-VCH.

remain challenging. Since CO₂ is very different from the conventionally used additives, the mechanism can be very different. Particularly, microscopic insight is helpful to unravel the special effect of CO₂. The progress on these topics will contribute greatly to colloid and interface science and the related areas.

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BIOGRAPHICAL INFORMATION

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FOOTNOTES

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