ACS OMEGA

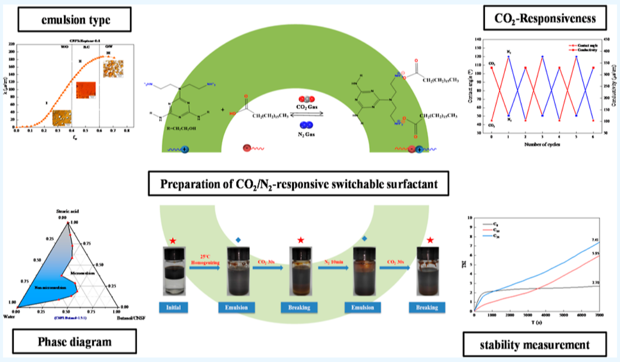
http://pubs.acs.org/journal/acsodf
Article

Study of Phase Separation and Reversibility in CO_2-Responsive Superamphiphile Microemulsions

Liyuan Cai,*[†] Jingchun Wu,[†] Miaoxin Zhang, Keliang Wang, and Zhao Yang

Cite This: *ACS Omega* 2024, 9, 44293−44303
Read Online

ABSTRACT: Phase separation of microemulsions occupies a key position in many applications, such as oil recovery, nanomaterial synthesis, and chemical reactions. Achieving an intelligent response is crucial to microemulsion development and application. For this reason, in this study, CO_2-responsive superamphiphilic molecules were developed as rapidly switchable oil-in-water microemulsions. These superhydrophilic molecules with linear structures were produced by electrostatic interaction of stearic acid and amino-trimethyltriazine COSM-1 in a 1:1 molar ratio. The introduction of n-butanol as a cosurfactant in the CO_2-responsive microemulsion system resulted in the spontaneous formation of stable microemulsions. The effect of the addition of n-butanol on the carbon dioxide-responsive microemulsion system was investigated, and the optimum amount of n-butanol was determined by optimization. After exposure to CO_2 for 30 s, the superhydrophilic molecules decomposed into inactive components at the interface, leading to a complete phase separation of the microemulsion into oil and water phases. The system was purged with N_2 at 60 °C for 10 min to remove the CO_2, and the phase separation system was transformed into a clear microemulsion, which was then evaluated for its properties. The rapid response and complete demulsification of these surface CNFS superamphiphiles to CO_2 suggest that they have promising applications in product separation, microemulsion recovery, and enhanced crude oil recovery.



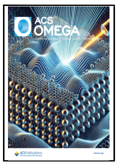
1. INTRODUCTION

Microemulsions are optically isotropic dispersions that consist of at least two immiscible liquids capable of coexisting in a single-phase region due to the presence of amphiphilic compounds.[1] Surfactants are commonly required to stabilize microemulsions.[2] Surfactant-based microemulsions (SBMEs) have been recognized for their numerous advantages as reaction media.[3]

Microemulsions possess attributes such as small size, bidirectional wetting, and high surface activity, providing unique advantages in increasing the volume of micronanovoids, enhancing permeability, and improving efficiency in the mechanism of micronanovoid displacement.[4] This technology shows promising potential in enhancing oil and gas recovery.[5] Currently, both domestic and international research on microemulsion oil displacement technology has made significant progress, leading to the development of various microemulsion systems tailored to different reservoir characteristics.[6]

At present, there have been many advances in the research of microemulsion formulation in foreign laboratories, and microemulsion systems applicable to various oil fields have been prepared.[7] In order to pursue ultralow interfacial tension, a large amount of surfactant and cosurfactant is usually required in the formation process of a microemulsion system, so the microemulsion system is called surfactant-based microemulsion (SBME).[8] Through the continuous research of microemulsion systems, more and more scholars found that surfactant is not a necessary component for microemulsion formation.[9] This led to the introduction of surfactant-free microemulsions (SFMEs), which, as the name suggests, are transparent and stable dispersions of oil, water, and "amphiphilic solvents" rich in nanodroplets.[10] CO_2-stimulated response is essentially a form of pH adjustment, but unlike traditional acid−base adjustment mechanisms, CO_2 can be removed by simple bubbling of inert gases such as nitrogen/helium or air.[11] CO_2-stimulated responsive microemulsions are also essentially a form of pH adjustment, but unlike traditional acid−base adjustment mechanisms, CO_2 can be removed by simple bubbling of inert gases such as nitrogen/helium or air, and there are no acid−base neutralization products left in the system.[12] They fall into two

Received: May 23, 2024
Revised: October 8, 2024
Accepted: October 8, 2024
Published: October 24, 2024



https://doi.org/10.1021/acsomega.4c04779

main categories, depending on the system composition: CO_2-responsive SBME and CO_2-responsive SFME.[13]

A CO_2-stimulated ringing SBME system containing 1-butyl-3-methylimidazole triazolium salt, cyclohexane, 1-hexadecyl-9-methylimidazolium salt, and *n*-decanol has been used previously, with 1-butyl-3-methylimidazole triazolium salt as the polar phase and 1-hexadecyl-9-methylimidazolium salt as the surfactant.[14] After continuous passage of CO_2 into the system for 5 min, the absorption of CO_2 by the triazole led to an increase in the anionic volume, which in turn induced changes in molecular rigidity and interactions, resulting in the formation of a turbid emulsion, and the turbid emulsion was restored to a clear and transparent microemulsion after passage of N_2 at 50 °C for 1 h.[15] However, CO_2 could only induce the transformation of the SBME into a clear emulsion and did not show any obvious phase separation.[16] Dodecyl tertiary amine ($C_{12}A$) was then introduced as a cosurfactant to stabilize the microemulsion properties, and heptane/sodium dodecyl sulfate (SDS)-*n*-butanol/water was introduced to form the O/W microemulsion.[17] Upon the introduction of CO_2, $C_{12}A$ reacted with carbonic acid dissolved in water to form ammonium bicarbonate and combined with SDS through electrostatic interaction to form an oil-soluble ion pair $C_{12}AH + C_{12}H_{25}SO_4^-$, resulting in the inability of SDS in the system to maintain an ultralow interfacial tension, and the microemulsion was thus demulsified. After the introduction of N_2 at 50 °C for 1 h, $C_{12}AH^+$ returned to the deprotonated state, releasing SDS back to the oil−water interface, and the microemulsion was formed again.[18] The microemulsion can be obtained by alternating CO_2/N_2 several times, and the droplet size is maintained at 15−20 nm, showing good reversibility and recyclability.[19] Ionic liquid surfactants have also received extensive attention as surfactant components in the formation of microemulsion systems, mainly including *N*-alkyl-*N*,*N*-dimethylethylamine cations and nitrogen-containing heterocyclic anions such as imidazolium, triazolium, and pyrazolium with *n*-pentanol and water to construct microemulsions. When CO_2 was introduced, the nitrogen-containing heterocyclic anions reacted with CO_2 to form ammonium bicarbonate and carbamate to increase the ionic strength of the system, and the salting-out effect destabilized the SBMEs, resulting in complete separation of oil and water and achieving efficient chemical reaction, product separation, and microemulsion recovery.[20]

Superamphiphiles were formed as a CO_2-responsive substance by mixing two environmentally friendly and inexpensive commercial reagents: oleic acid (HOA) and poly(propylene glycol)-bis(2-aminopropyl ether) in a molar ratio of 1:1.18.[21] The resulting responsive amphiphiles were used as a novel surfactant for the preparation of CO_2-responsive microemulsions by mixing them with 1-butanol, heptane, and water.[22] After 20 s of bubbling CO_2 gas at room temperature, the amphiphile dissociated into a surfactant-free component, and the stable microemulsion underwent complete phase separation.[23] This phase separation can be easily reversed by drumming in *N*,*N*,*N*-tributylpentylamine at 60 °C, and stable O/W microemulsions can be regained within 10 min, with three cycles having no significant effect on the rate of response to CO_2 or the stability of the microemulsions.[24] Another switchable hydrophilic solvent, *N*,*N*,*N*-tributylpentylamine (TBPA), which is practically immiscible with water but hydrophilic and miscible with water in the presence of CO_2, was used to prepare SFMEs using *N*,*N*-dimethylcyclohexylamine (DMCHA) as the oleophile and *N*,*N*-dimethylethanolamine (DMEA) as the amphiphilic solvent, and the CO_2/N_2 hydrophilicity switching property of DMCHA was successfully exploited to prepare CO_2-responsive O/W microemulsions.[25] The CO_2-responsive SFME was successfully prepared by using DMCHA with CO_2/N_2 hydrophilicity switching.[26] It is proposed that a conversion system from SBME to SFME can be prepared by mixing sodium oleate (NaOA), isopropanol (IPA), oleic acid (HOA), and water under CO_2 stimulation.[27] When the concentration of the amphiphilic solvent IPA is low, CO_2 can induce the emulsion breakage of SBME by inducing the conversion of sodium oleate to oleic acid; when the concentration of the amphiphilic solvent is high, the SBME is not emulsified but converted to the SFME.[28] A microemulsion system based on ionic liquids also exhibits such a change due to the formation of stable SFME when the concentration of cosurfactant in the system is high. The study of the CO_2-responsive SFME system is still in its infancy, and its in-depth mechanism of action and practical application are still involved,[29] so there are still many issues that deserve to be investigated. It is easy to see that the pH change due to the introduction of CO_2 is very narrow, and the molecules that can achieve CO_2 response are weak acids and bases.[30]

In addition, multi-responsive microemulsion systems for combinations of CO_2 with other stimuli have not yet been investigated, providing an opportunity for future research into CO_2-stimulation-responsive microemulsion systems.[31] The most pressing consideration is to reduce the cost of microemulsions.[32] Currently, the concentration of microemulsions applied in the field is high, which makes the amount of surfactant large, and it must also be considered that the microemulsion has a certain degree of adsorption on the surface of the rock after entering the formation, both of which increase the cost of extraction significantly.[33] How to construct the microemulsion system with the appropriate ratio and make the synergistic effect of each component is the key to reducing the cost.[34] Stearic acid is a kind of fatty acid widely found in nature; almost all fats and oils have varying content of stearic acid, which is higher in animal fats and more widely available and has a certain degree of economic practicality.[35] Stearic acid is used in the cosmetics industry to emulsify two types of skin care products, snow creams and cold creams, to form stable microemulsion systems.[36]

In this article, stearic acid is used to form CO_2-stimulation-responsive superamphiphilic molecules with aminotrimethyltriazine compounds, which can form CO_2-responsive microemulsion systems with crude oil. The formulation preference, microemulsion properties, and CO_2 stimulation response mechanism of the formed microemulsion systems are investigated. In this work, stable O/W emulsions are formed from CNFS superamphiphiles, which undergo complete demulsification after a few seconds of CO_2 administration. Considering the potential applications in thick oil extraction and pipeline transport, emulsions were prepared using simulated oils of crude oil mixed with paraffin as the oil phase. It is noteworthy that CO_2 removal by N_2 bubbling resulted in the reformation of stable microemulsions. We further demonstrate that emulsification and demulsification are mainly due to the reversible assembly and disassembly of CNFS by the removal of CO_2 or bubbling. We also investigated the emulsifying effect of CNFS superamphiphiles on different fractions of crude oils, and the results showed that the stability of the microemulsion system formed by CNFS superamphiphiles varied among different fractions of oil phases, which further demonstrated that our developed superamphiphile CNFS had a certain degree of

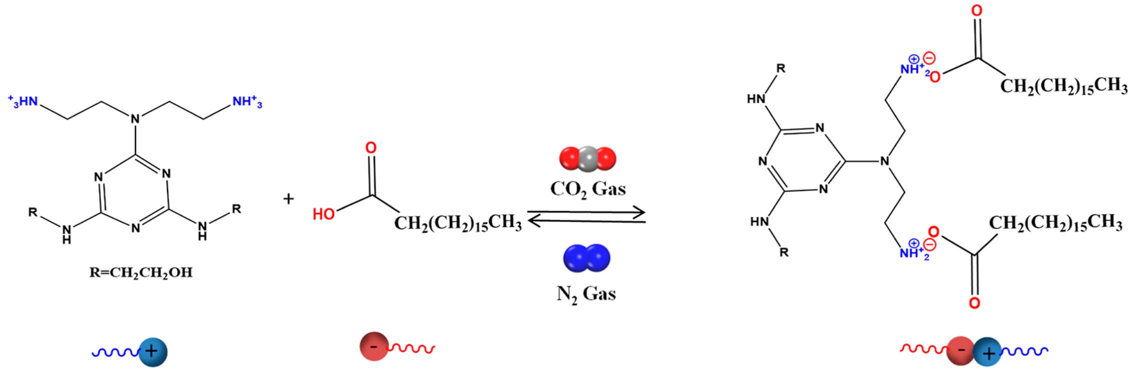


Figure 1. Synthetic route.

emulsifying effect on crude oils with fractions of C_8−C_{24}. The rapid response of the CNFS superamphiphiles to CO_2 and their complete emulsion breakage make them potentially useful for separation of reaction products and recycling of microemulsions, as well as for enhancing crude oil recovery.

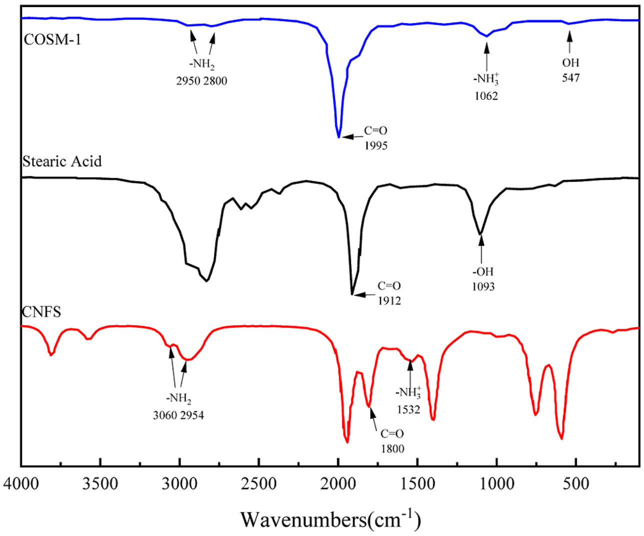


Figure 2. FTIR spectra of COSM, CNFS, and stearic acid.

2. EXPERIMENTAL SECTION

2.1. Materials. The purity of the aminotrimethyltriazine used in this study was >99.99% (HPLC). It was developed in-house in the laboratory and named COSM-1. The stearic acid (HPLC ≥ 98%), *n*-butanol (ACS grade), and heptane (ACS grade) used were supplied by Aladdin Biochemical Technologies Ltd. The gas products used in this study were carbon dioxide (HPLC ≥ 99.99%) and nitrogen (HPLC ≥ 99.99%) supplied by Wuhan Zhongxin Ruiyuan Gas Co. The deionized water collected by the purification equipment had a resistivity of more than 18.2 MΩ cm and a conductivity of less than 0.055 μs/cm. The aromatic content of the aviation kerosene used was less than 20%, with the content of bicyclic aromatic hydrocarbons (BAHs) not exceeding 3%. The olefin content was less than 2−3%, and the crystallization point of the *n*-alkane content of the fuel oil used was not higher than −50 °C ~ −60 °C. A mixture of crude oil with a viscosity of 9.6 mPa s at 45 °C provided by Daqing Oilfield and aviation kerosene was used for the experiments. The water used was simulated formation water with a mineral content of 6778 mg/L, which was configured in the laboratory.

2.2. Preparation of CO_2/N_2-Responsive Switchable Surfactant. The CO_2/N_2-responsive supramolecular amphiphilic molecule CNFS was formed by self-assembly through electrostatic interaction between carboxyl and amine groups using stearic acid mixed with the amine-based triazine compound COSM-1 in the ratio of 1:1. The synthetic route is shown in Figure 1. The product was a viscous light yellow liquid at room temperature. The products obtained from the preparation were characterized by three means: FTIR (Nicolet iS20 FTIR, Thermo Fisher Scientific, Waltham, MA, USA), ^{1}HNMR (picoSpin 45, Thermo Fisher Scientific, Waltham, MA, USA), and mass spectrometry (Agilent 7850 ICP−MS, Agilent Technologies China Ltd., Beijing, China).

2.3. Conductivity Method for Determining the Emulsion Type. The ratios of CNFS to heptane were fixed as 1:1, 7:3, 8:2, and 9:1, respectively; water was added dropwise to the system, and the change in conductivity was recorded to obtain a plot of conductivity of the microemulsion system as a function of the mass fraction of water in the system; and the single-phase zones of the microemulsions were divided into three microzones, W/O, B.C., and O/W, based on the results of the conductivities at different ratios of the emulsifiers and oil phases.

2.4. Pseudoternary Phase Diagram. The phase vanishing points of the microemulsion regions of the proposed ternary system of CNFS + *n*-butanol + heptane + distilled water with the mass ratios of CNFS to *n*-butanol of 1:1, 1.5:1, 2:1, 2.5:1, and 3:1 at 60 ± 1 °C were determined, the phase diagrams of the microemulsion regions of the proposed ternary system were plotted, and the relative areas of the microemulsion regions of the proposed ternary system for the different mass ratios of CNFS to n-butanol were calculated from the plotted phase diagrams. The relative areas of the microemulsion regions for different mass ratios of CNFS to *n*-butanol were calculated from the plotted phase diagram of the proposed ternary system. Based on the three-phase diagram, the 15% CNFS + 10% *n*-butanol + 60% water + 25% heptane microemulsion was selected for further investigation of physicochemical properties and applications.

2.5. CO_2-Responsiveness of the Microemulsion. The CO_2-sensitive microemulsion was formulated as 15% CNFS +10% *n*-butanol +60% water +25% simulated oil and emulsified using a digital high-speed homogenizer with stirring at 12,000 rpm for 30 s. The microemulsion was stabilized for 10 min, and the appearance of the emulsion was observed. The emulsion was

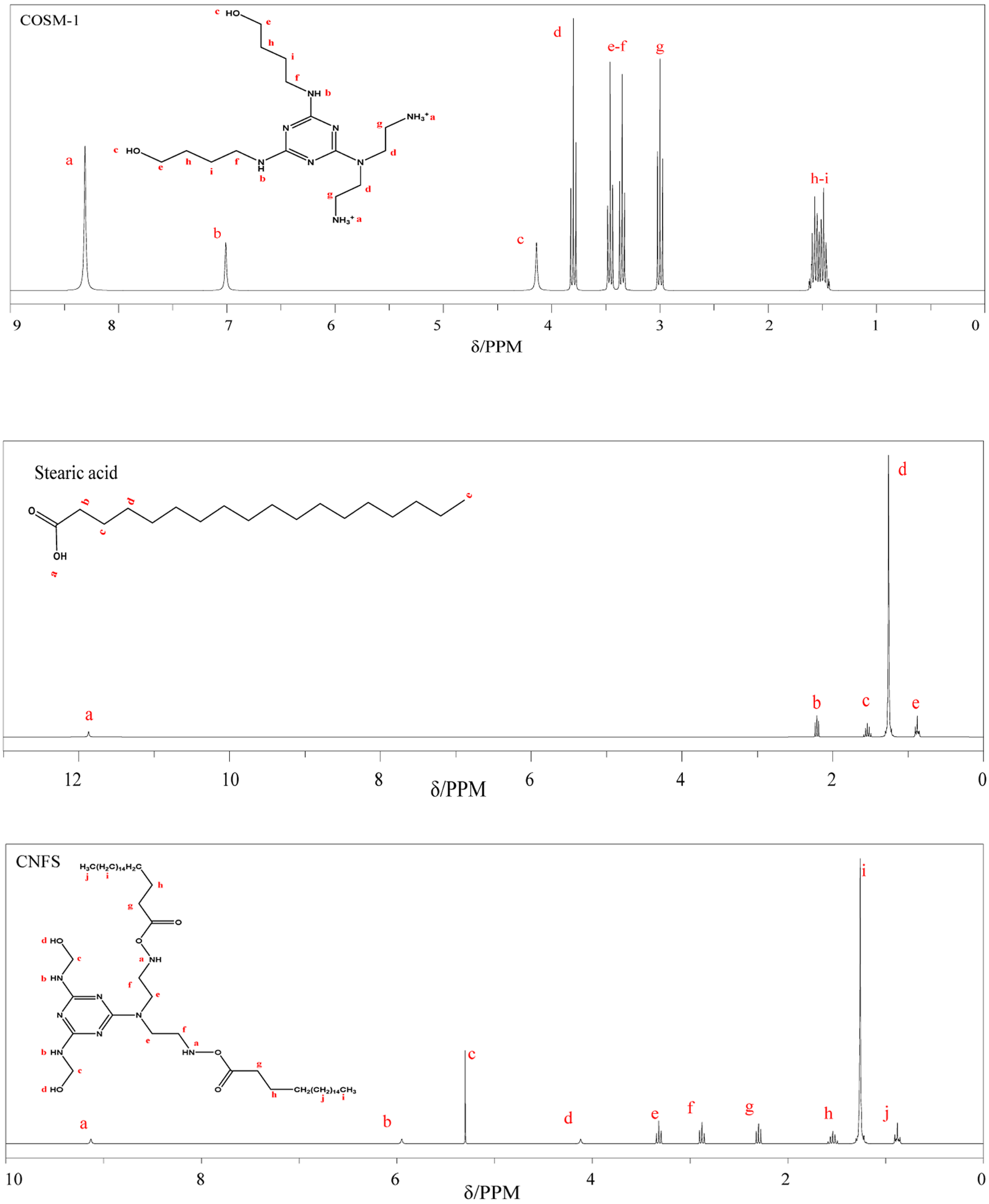


Figure 3. ^{1}H NMR spectra of COSM, CNFS, and stearic acid.

stabilized for 10 min to observe the appearance of the microemulsion; CO_2 was passed into the microemulsion at a rate of 100 mL/min for 30 s and then allowed to stand for 10 min to observe the appearance of the emulsion, which was emulsified using a digital high-speed homogenizer at 60 °C, and then N_2 was passed into the system for 10 min at 100 mL/min. The operation was repeated 3 times according to the above steps to investigate the CO_2 switching performance of water/simulated crude oil emulsions, and CO_2 was continued to be introduced into the system until complete emulsion breakage in the final cycle; photographs were taken at the end of each step to record the results. The surface tension (DCAT25, DataPhysics), pH, conductivity (CM-41X, Halcion Testing Technology, Tianjin, China), and contact angle (OCA25, DataPhysics Instruments, Baden-Württember, Germany) of the system when CO_2 was introduced or removed were measured for 3 cycles. The change in particle size (Zetasizer NanoZs90, Malvern Panalytical, UK) before and after the response of the microemulsion system was analyzed using a laser particle sizer.

2.6. Microemulsion Stability Measurement. The particle size change and migration phenomenon of emulsion droplets can be analyzed by using the multiple light scattering technique to clarify the stability and emulsion breakage process of the CO_2-responsive microemulsion system. The emulsification speed was fixed at 1000 rpm, the emulsification time was 30 s, and the emulsification temperature was 60 °C. The microemulsions were prepared using oil phases with different carbon chain lengths, and the microemulsions were removed from the sample bottles and analyzed using a stability analyzer, which outputs backscattered light intensity curves and stability kinetic indices (Turbiscan Lab, Formulaction, France), to investigate the effects of oil phases with different carbon chain lengths on the stability of the microemulsions.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Structure Characterization. In this work, novel superamphiphilic CO_2-responsive molecules were formed by electrostatic interactions between the carboxyl group of stearic acid and the amine group of triazine compound COSM-1. The self-assembled superamphiphiles were structurally characterized by FTIR and 1H NMR. Figure 2 shows the FTIR spectra of the assembled superamphiphiles and the responsive precursor component COSM-1. Upon interaction with the amine group of the triazine-chemically synthesized COSM-1, the carboxyl peak at 1912 cm^{-1} in stearic acid was shifted to 1800 cm^{-1}, while the hydroxyl group at 1093 cm^{-1} disappeared, and the surface neutral acid was completely converted into its ionized counterpart, forming an ideal superamphiphilic molecule. For the superamphiphilic molecule constructed by mixing stearic acid with COSM-1 in a 1:1 molecular ratio, $-NH_2$ in COSM-1 is expected to accept a proton from $-COOH$ to form $-NH_3^+$, which generates a new vibrational absorption peak of $-NH_3^+$ at 1532 cm^{-1}.

The electrostatic adsorption between stearic acid and COSM-1 shown in the FTIR spectra was further confirmed by 1H NMR, as shown in Figure 3. When a $-NH_2$ group in COSM-1 receives a proton and is converted to $-NH^+_3$ in the resulting supramolecule, a new nitrogen-on-activated proton peak appeared at 8.31 ppm, reflecting the unreacted 1.50 ppm $-NH_2$ peak and the average chemical shift of the new $-NH^+_3$ peak in the 8−10 ppm range. This single peak becomes broader due to the reduced exchange rate of unstable protons in the superamphiphile. Due to the positive charge of the quaternary ammonium cation, which reduces the local electron density, the ^1H chemical shift of the adjacent alkyl group in the superamphiphile molecule is shifted toward the lower field, indicating protonation of the terminal ammonia site. Conversely, the peak position of the methylene group close to the carbonyl group in the superamphiphile molecule is shifted upward due to the increase in local electron density. In addition, the expected amide peaks were not found in the full spectra. In summary, the transfer of H^+ from stearic acid to COSM-1 was confirmed, resulting in the conversion of $-COOH$ to $-COO^-$ and one of the amide groups to $-NH^+_3$. This result confirms that the superamphiphilic molecule is formed by an electrostatic interaction.

The relative molecular masses of the CNFS were calculated to be about 865, and the peaks with the highest abundance were all $[M - 2H^+ + 2H^+4]^+$; the fragmentation of the mass spectra is shown in Table 1. The relative molecular mass of the CNFS molecule decreased by about 2 after the loss of two H^+, and the relative molecular mass of the CNFS molecule increased by about 1 after the gain of one H^+ fragment, which was in accordance with the expected structure. The mass spectra are shown in Figure 4, and the elemental analyses are shown in Table 2. Elemental analysis shows that product CNFS contains 65.24% carbon, 10.72% hydrogen, 12.95% nitrogen, and 11.09% oxygen, as expected.

Table 1. Fragmentation Analysis of CNFS

products	mass-to-charge ratio (m/z)	corresponding ion peaks
CNFS	273.1709	$[M + 2H]^+$
	282.3715	$[M - 2H]^-$
	892.5453	$[M - 2H + 2H]^+$

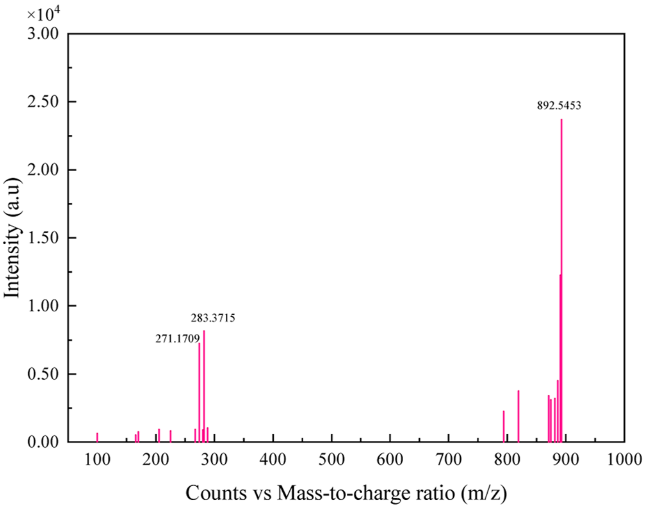
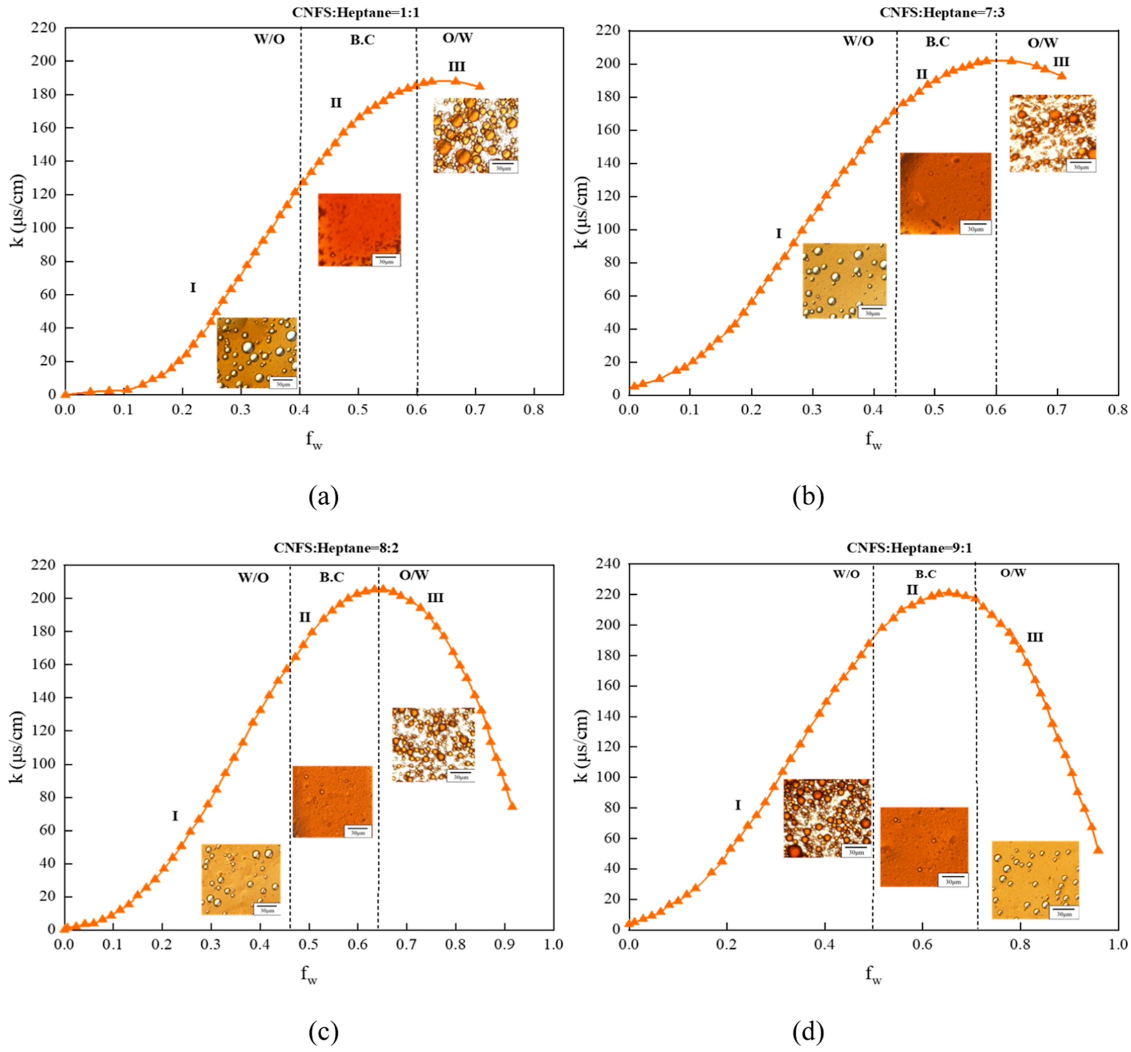


Figure 4. Mass spectra of CNFS.

Table 2. Elemental Analysis of CNFS

elemental analysis (%)			
C	H	N	O
65.24	10.72	12.95	11.09

3.2. Conductivity Method for Determining the Emulsion Type. The shift in the microenvironment of the system can be inferred using the change in conductivity, and therefore, the method can be used to classify the type of microemulsion. The mass ratio of CNFS and heptane was fixed as (a) 1:1, (b) 7:3, (c) 8:2, and (d) 9:1, respectively, and water was added dropwise to the system, and the change of conductivity was recorded. Figure 5 shows the relationship between the conductivity of the CNFS/n-butanol/oleic acid/heptane/water microemulsion system and the change of the mass fraction of water in the system under the conditions of different emulsifiers and the ratio of the oil phase. Taking CNFS:heptane = 8:2 as an example, the conductivity grows very slowly when the water content is initially low, and the conductivity of the system at this time originates from the percolation phenomenon of the reverse-phase microemulsion droplets. When $20\% \leq f_w < 50\%$, the conductivity appeared to have a linear and rapid increase; this is because with the increase of water content in the system of microemulsion droplets increasing in number, frequent viscous collisions between each other to form a water channel for charge transfer, which led to an increase in conductivity, continued to increase the water content, that is, $50\% \leq f_w \leq 65\%$, and the conductivity was again a nonlinear growth. At this time, due to further increase in water content, the droplet number continued to increase, and the system conductivity originated from the phenomenon of reverse phase microemulsion droplet filtration. The number of droplets continues to increase, so that the small, narrow water channel expansion, conductivity enhancement, and the system in the oil and water are continuous phases of an intermediate



(a) (b)

(c) (d)

Figure 5. Conductivity of the CNFS/*n*-butanol/heptane/water system varies with the mass fraction of water, where the masses of fixed CNFS and heptane are (a) 1:1, (b) 7:3, (c) 8:2, and (d) 9:1, respectively.

transition-state structure for the B.C.-type microemulsion. Finally, when $f_w \geq 65\%$, conductivity with the increase in water content continues to decline, the water becomes a continuous phase, and the O/W microemulsion droplets are gradually diluted; the collision frequency decreases, leading to a decrease in the value of the conductivity this time. The system is an O/W microemulsion. According to the conductivity results under different emulsifier and oil phase ratios, the single-phase zones of microemulsions can be divided into three microzones: W/O, B.C., and O/W.

3.3. Pseudoternary Phase Diagram.

The addition of alcohol can change the hydrophilic and lipophilic equilibrium values of surfactant and adjust the polarity of water and oil.[37] However, when the addition of alcohol in the system is not the more, the better; from Figures 6 and 7, we can see that with the change of the ratio of CNFS and *n*-butanol, the relative area of the microemulsion region has a significant change, and with the gradual increase of the ratio of CNFS and *n*-butanol, the relative area of the microemulsion region first increases and then decreases. The addition of cosurfactant is involved in supporting the distribution ratio and arrangement of surfactant molecules in the oil—water interfacial film, thus changing the interfacial properties of the system.[38]

The addition of alcohol also plays the role of softening the oil—water interfacial membrane, which is conducive to the formation of the microemulsion region. Through the experimental analysis that can be obtained in the system of n-butanol added to the existence of the optimum ratio, when the CNSF/*n*-butanol = 1.5:1, the relative area of the microemulsion region is the largest, so the system formulation of the CNSF/*n*-butyl mass ratio selected is 1.5:1, so this proportion of the formulated system is considered for the subsequent study.

3.4. CO_2-Responsiveness of the Microemulsion.

In order to study the switching response performance of the system for research, at 25 °C, the CNFS/*n*-butanol/water/simulated oil system is homogenized to form a stable emulsion, and then to the system at a rate of 100 mL/min, CO_2 30 s passes through the system after standing 10 min and can be found in the oil and water two-phase relayered; the oil—water interface is gradually clear, as shown in Figure 8. It is proven that the response of CNFS to CO_2 is more sensitive; the initial protonation generates an amine-group cation, which will be bonded with another molecule or its own carboxylate anion by electrostatic action to achieve the intermolecular or intramolecular salt bridge bond, and the hydrophobicity of the surfactant becomes greater, which makes it transfer to the oil phase. When N_2 is introduced into the oil—water mixture at 60 °C for 230 min, it can be observed that

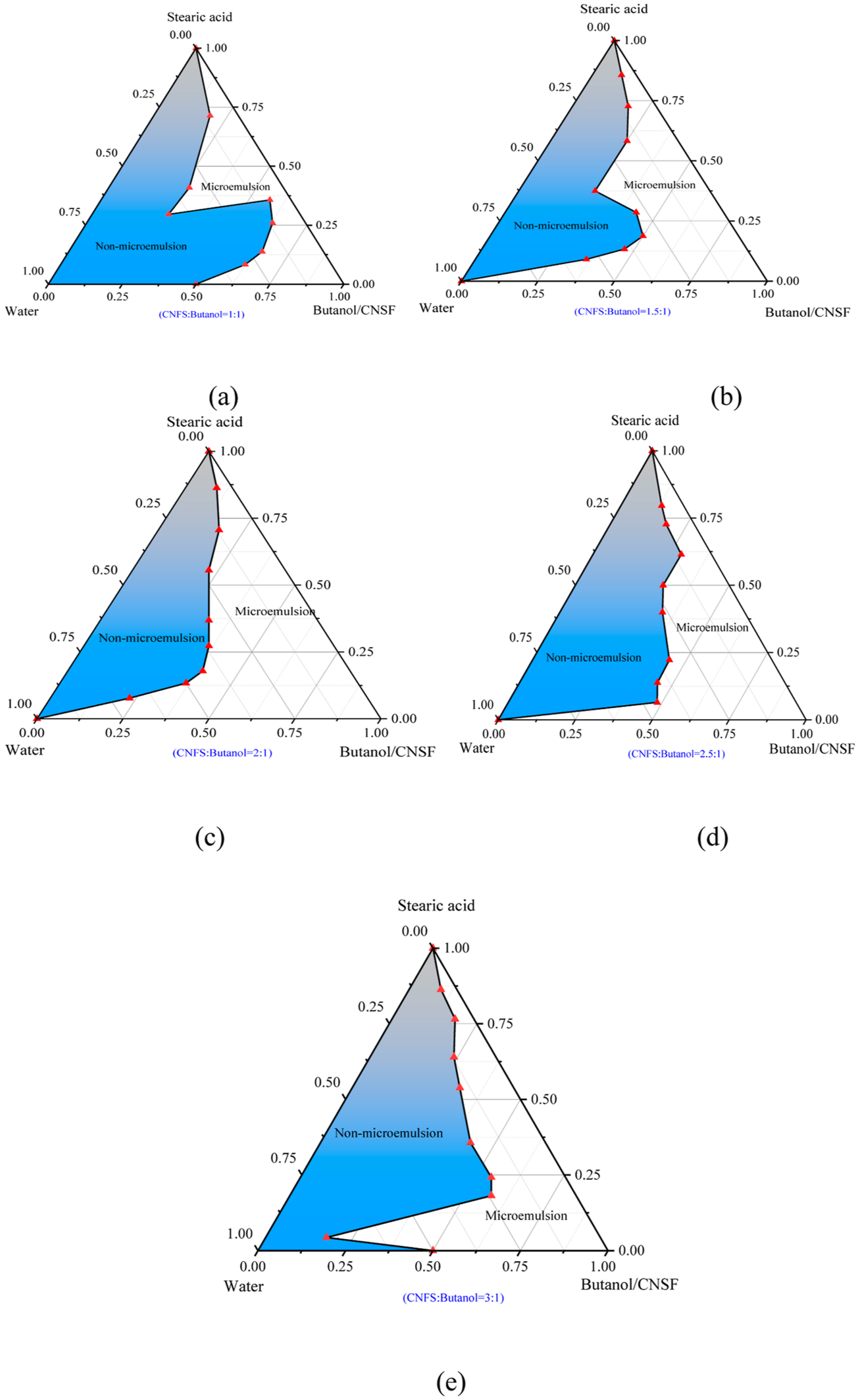


Figure 6. Phase diagram of the microemulsion region of the proposed ternary system with different CNFS/*n*-butanol mass ratios: (a) 1:1, (b) 1.5:1, (c) 2:1, (d) 2.5:1, and (e) 3:1.

the oil−water boundary is no longer regular, and the oil−water two-phase mixing can be used to form an emulsion again with the use of a homogenizer. The introduction of N_2 accelerates the release of CO_2, and the amine group ions are deprotonated and separated from the hydrophilic carboxylate anion, so that their water solubility becomes larger and the surfactant transfers back

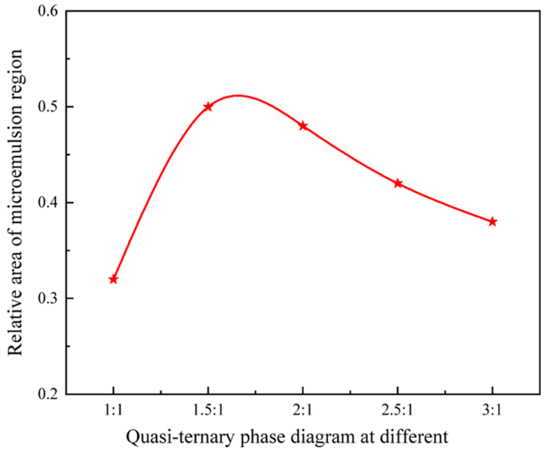


Figure 7. Relative areas of microemulsion regions of the phase diagram of the proposed ternary system with different CNFS/*n*-butanol mass ratios (pure water).

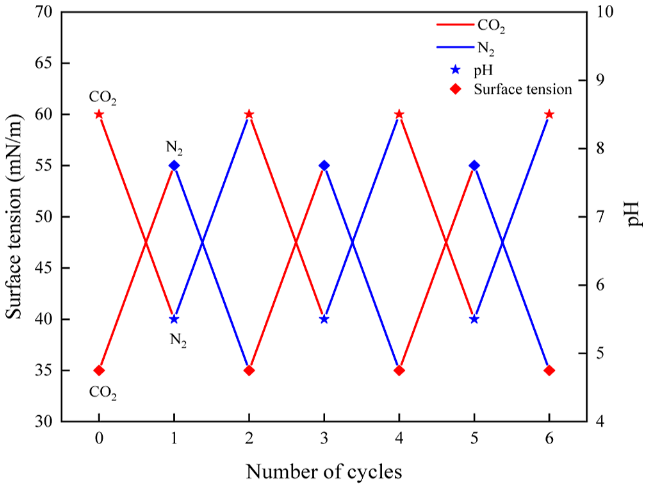


Figure 9. Changes of surface tension and the pH value of CNFS solution before and after the passage of CO_2/N_2.

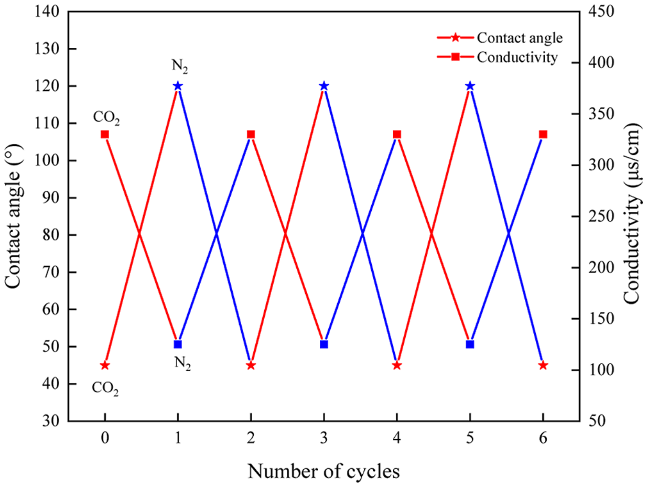


Figure 10. Changes in the contact angle and conductivity of CNFS solution before and after passing CO_2/N_2 into the solution.

to the aqueous phase. The above process of breaking the emulsion can be repeated several times.[39]

CNFS is an effective CO_2-switching surfactant that exhibits good reversibility of stimulus response in terms of surface tension, pH, conductivity, and contact angle during CO_2 application and removal. The surface tension of the CNFS aqueous solutions all showed a significant increase after the passage of CO_2, as shown in Figure 9, indicating that the surface activity of the surfactant deteriorated after the passage of CO_2. The initial pH was 8.5; with the passage of CO_2 into the solution, the pH changed to 6.36 with the increase in aeration time, as shown in Figure 10; the conductivity decreased significantly with the passage of CO_2, and the conductivity value returned to the initial state after the passage of N_2 to remove CO_2. The contact angle of the droplets on the surface of the oil-wet core discs increased significantly from 45° to 120° with the passage of CO_2, and after the passage of N_2 to remove CO_2, the contact angle would return to close to the initial state. All three cycles showed the same trend of change.

This is because, before and after the introduction of CO_2, there is such a big difference in water solubility. After all, CNFS has a hydrophilic carboxylate group, and its water solubility is better; however, after the introduction of CO_2 into the aqueous solution, due to the fact that the tertiary amine group is more sensitive to CO_2, the quaternary ammonium cation is generated by the protonation of the tertiary amine group,[40] which will be connected with another molecule or its carboxylate anion by electrostatic interaction to achieve the inter- or intramolecular salt bridge connection. Therefore, the hydrophilicity of surfactant molecules is greatly reduced, and the water solubility of CNFS is reduced, which makes the aqueous solution of CNFS turbid or even viscous. When N_2 was poured into the solution at 60 °C to remove CO_2, the quaternary ammonium cation was first deprotonated back to tertiary amine and disconnected from the hydrophilic carboxylate anion, the water solubility of CNFS was restored, and the aqueous solution returned to the transparent state again.

Microstructures of the microemulsions after the bubbling of CO_2 were investigated by DLS, as shown in Figure 11. For example, the DLS result showed that the droplet size of the initial CNFS microemulsion was about 28.91 nm. Upon injection of CO_2, the droplet size increased to 2359.47 nm due to the destruction of the W/O microemulsion. When the

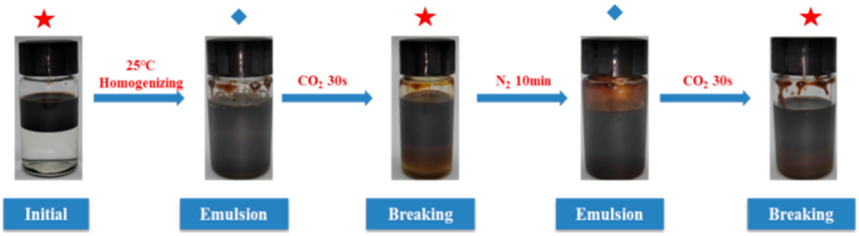


Figure 8. CNFS/*n*-butanol/water/simulated crude oil emulsion system CO_2/N_2 stimulation in response to emulsification/breaking processes.

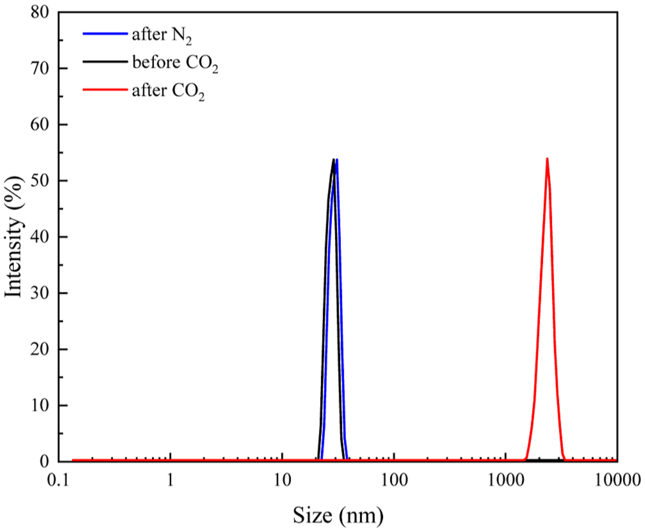


Figure 11. Changes in size of CNFS solution before and after the introduction of CO_2/N_2.

W/O microemulsion was formed again by bubbling with N_2 at 60 °C, the droplet size decreased to 30.93 nm, which is very close to its original value. Thus, the CO_2-responsive microemulsion system can be reversibly destroyed and reformed by alternating between bubbling and CO_2 removal.

3.5. Microemulsion Stability Measurement. The crude oil component is an important factor affecting the degree of emulsification, and the degree of emulsification of CNFS varies for oil phases with different carbon chain lengths.[41] In order to evaluate the effect of the carbon chain length of the oil phase on the stability of the CNFS microemulsion system, the microemulsion stability of three oil phases, $C_8/C_{16}/C_{12}$, was determined. While the TSI value can quantitatively characterize the advantages and disadvantages of the emulsion stability, the larger TSI value indicates that the fluctuation of the average value of the backscattered light intensity during each scan is larger and that the system is more unstable. As can be seen from Figure 12, the TSI values of the three systems are comparable at the beginning of the test, and the three TSI curves basically overlap, and the TSI values of the C_{16} and C_{24} systems start to increase after 700 s. The TSI value of the C_{24} system is 7.41, that of the C_{16} system is 5.95, and that of the C_8 system is 2.70, which proves that the CNFS has a certain emulsifying effect on the three types of crude oil. As the number of carbon chains increases, the TSI value gradually increases, which proves that CNFS has the best emulsifying effect on the light component crude oil.

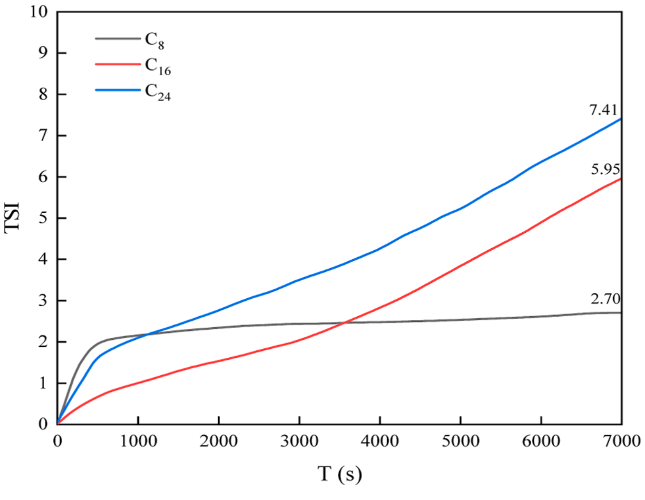


Figure 12. Changes in TSI values of microemulsion systems with different carbon chain lengths.

4. CONCLUSIONS

In summary, we have developed a CO_2-responsive superamphiphilic molecule CNFS assembled on the basis of protonation-driven electrostatic adsorption, which can form CO_2-responsive microemulsion systems with crude oil. It is found that the microemulsion can be reversibly switched between single phase and complete phase separation under the alternating action of CO_2 and N_2 and that the microemulsion can still maintain good stability, and the switching action can still be effectively maintained after multiple alternating passes. The designed superamphiphilic molecule has a lower CMC value, and the solubilizing ability is improved after the addition of the cosurfactant *n*-butanol, and the optimum quality fraction of *n*-butanol addition is derived from the experimental results. The CNFS is a liquid at room temperature, and the CNFS system can be switched to respond to CO_2 within a few seconds compared to other CO_2 switching systems. Emulsification and demulsification experiments with simulated oils showed that rapid phase separation of crude oil from emulsions can be achieved by CO_2 injection. The stability of the microemulsion system formed by different components of crude oil was determined by the TSI value, and the experimental results showed that the CNFS system has a certain emulsifying effect on crude oils within the range of C_8−C_{12} carbon fractions; however, the effect with light fraction crude oils is relatively better, and at the same time, the separation of products and the recycling of the components of the microemulsion were integrated. The fast response to CO_2 and complete emulsification of CNFS superamphiphiles make them potentially useful for separation of reaction products and recycling of microemulsions as well as for improving crude oil recovery.

■ AUTHOR INFORMATION

Corresponding Author

Liyuan Cai − *Key Laboratory for EOR Technology (Ministry of Education), Northeast Petroleum University, Daqing 163318, China;* orcid.org/0000-0002-7402-8458;
Email: sygc9212@163.com

Authors

Jingchun Wu − *Key Laboratory for EOR Technology (Ministry of Education), Northeast Petroleum University, Daqing 163318, China*
Miaoxin Zhang − *Key Laboratory for EOR Technology (Ministry of Education), Northeast Petroleum University, Daqing 163318, China*
Keliang Wang − *Key Laboratory for EOR Technology (Ministry of Education), Northeast Petroleum University, Daqing 163318, China*
Zhao Yang − *Key Laboratory for EOR Technology (Ministry of Education), Northeast Petroleum University, Daqing 163318, China;* orcid.org/0000-0003-0991-8689

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.4c04779

Author Contributions

[†]L.C. and J.W. contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

The Natural Science Foundation of Heilongjiang Province, LH2022E020: Research on Biomethanation Mechanism in Tight Oil Reservoirs and Postdoctoral Top-up Grants in Heilongjiang Province (LBH-Z23040) are the funding sources.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the Natural Science Foundation of Heilongjiang Province (LH2022E020) and Postdoctoral Top-up Grants in Heilongjiang Province (LBH-Z23040).

■ REFERENCES

(1) Kumar, N.; Pal, N.; Mandal, A. *Polymeric Surfactant Stabilized Nanoemulsion Characterization for Enhanced Oil Recovery*; European Association of Geoscientists & Engineers, 2020; Vol. *2020*, pp 1−5..

(2) Naik, N. S.; Padaki, M.; Déon, S.; Karunakaran, G.; Dizge, N.; Saxena, M. The Efficient Mixed Matrix Antifouling Membrane for Surfactant Stabilized Oil-in-Water Nanoemulsion Separation. *J. Water Process Eng.* **2019**, *32*, 100959.

(3) Wang, H.; Wang, W.; Zhu, G.; Cao, Y.; Zhang, L. A Perspective of Microemulsions in Critical Metal Separation and Recovery: Implications for Potential Application of CO2-Responsive Microemulsions. *Chemosphere* **2023**, *338*, 139494.

(4) Li, X.; Wang, B.; Dai, S.; Lu, H.; Huang, Z. Ionic Liquid-Based Microemulsions with Reversible Microstructures Regulated by CO $_2$. *Langmuir* **2020**, *36* (1), 264−272.

(5) Pei, X.; Li, Z.; Wang, H.; Zhou, Q.; Liu, Z.; Wang, J. CO $_2$ -Switchable Phase Separation of Nonaqueous Surfactant-Free Ionic Liquid-Based Microemulsions. *ACS Sustainable Chem. Eng.* **2022**, *10* (5), 1777−1785.

(6) Hoar, T. P.; Schulman, J. H. Transparent Water-in-Oil Dispersions: The Oleopathic Hydro-Micelle. *Nature* **1943**, *152* (3847), 102−103.

(7) Smith, G. D.; Donelan, C. E.; Barden, R. E. Oil-Continuous Microemulsions Composed of Hexane, Water, and 2-Propanol. *J. Colloid Interface Sci.* **1977**, *60* (3), 488−496.

(8) Schöttl, S.; Marcus, J.; Diat, O.; Touraud, D.; Kunz, W.; Zemb, T.; Horinek, D. Emergence of Surfactant-Free Micelles from Ternary Solutions. *Chem. Sci.* **2014**, *5* (8), 2949−2954.

(9) Hou, W.; Xu, J. Surfactant-Free Microemulsions. *Curr. Opin. Colloid Interface Sci.* **2016**, *25*, 67−74.

(10) Chen, X.; Ma, X.; Yan, C.; Sun, D.; Yeung, T.; Xu, Z. CO2-Responsive O/W Microemulsions Prepared Using a Switchable Superamphiphile Assembled by Electrostatic Interactions. *J. Colloid Interface Sci.* **2019**, *534*, 595−604.

(11) Lai, N.; Zhu, Q.; Qiao, D.; Chen, K.; Wang, D.; Tang, L.; Chen, G. CO2/N2-Responsive Nanoparticles for Enhanced Oil Recovery During CO2 Flooding. *Front. Chem.* **2020**, *8*, 393.

(12) Zhou, Y.; He, S.; Li, H.; Zhang, Y. CO $_2$ and Temperature Control over Nanoaggregates in Surfactant-Free Microemulsion. *Langmuir* **2021**, *37* (5), 1983−1990.

(13) Chen, X.; Ma, X.; Yeung, T.; Sun, D.; Xu, Z. Comprehensive treatment of oil-contaminated soils using CO2-Responsive O/W microemulsions. *J. Cleaner Prod.* **2022**, *341*, 130857.

(14) Xu, P.; Wang, Z.; Xu, Z.; Hao, J.; Sun, D. Highly Effective Emulsification/Demulsification with a CO 2 -Switchable Superamphiphile. *J. Colloid Interface Sci.* **2016**, *480*, 198−204.

(15) Wang, J.; Liu, W.; Luo, G.; Li, Z.; Zhao, C.; Zhang, H.; Zhu, M.; Xu, Q.; Wang, X.; Zhao, C.; Qu, Y.; Yang, Z.; Yao, T.; Li, Y.; Lin, Y.; Wu, Y.; Li, Y. Synergistic Effect of Well-Defined Dual Sites Boosting the Oxygen Reduction Reaction. *Energy Environ. Sci.* **2018**, *11* (12), 3375−3379.

(16) Pei, X.; Xiong, D.; Pei, Y.; Wang, H.; Wang, J. Switchable Oil−Water Phase Separation of Ionic Liquid-Based Microemulsions by CO2. *Green Chem.* **2018**, *20* (18), 4236−4244.

(17) Zhang, Y.; Liu, D.; Wang, B.; Lu, H.; Huang, Z. Reversible Temperature Regulation of CO2-Responsive Ionic Liquid Microemulsion. *Colloids Surf., A* **2020**, *601*, 125000.

(18) Du, W.; Lyu, L.; Zhang, X.; Xu, H. Form CO $_2$ -Responsive Microemulsion for Extracting Ethanol from Water by Triethylamine. *Iop Conf. Ser.: Earth Environ. Sci.* **2021**, *781* (5), 052001.

(19) Jessop, P. G.; Phan, L.; Carrier, A.; Robinson, S.; Dürr, C. J.; Harjani, J. R. A Solvent Having Switchable Hydrophilicity. *Green Chem.* **2010**, *12* (5), 809−814.

(20) Zhao, F. Y.; Cai, H.; Zhang, S. Y.; Song, Z.; Liu, Q. L. Octahedron-Dependent near-Infrared Luminescence in Cr3+-Activated Phosphors. *Mater. Today Chem.* **2022**, *23*, 100704.

(21) Chen, Z.; Chan, M. H.-Y.; Yam, V. W.-W. Stimuli-Responsive Two-Dimensional Supramolecular Polymers Based on Trinuclear Platinum(II) Scaffolds: Reversible Modulation of Photoluminescence, Cavity Size, and Water Permeability. *J. Am. Chem. Soc.* **2020**, *142* (38), 16471−16478.

(22) Mondal, A.; Mukhopadhyay, S.; Banerjee, S.; Ahmmed, E.; Hansda, S.; Chattopadhyay, P. Combined Experimental and Theoretical Studies on the Rubbing-Induced Fluorescence Behavior of a Luminophore in the Solid State. *ACS Omega* **2023**, *8* (1), 373−379.

(23) Ren, H.; Zhang, R.; Zheng, Y.; Liu, Y.; Zhang, Q.; Zhang, J.; Chen, C.; Duan, E. Fluorescence Visualization of CO2-Responsive Phase Transfer Materials Targeting at the Heterogeneous Interfacial Reactions in Advanced Oxidation of Naphthenic Acid in Wastewater. *Sci. Total Environ.* **2024**, *933*, 173235.

(24) Liang, Q.; Peng, N.; Xie, Y.; Kumar, N.; Gao, W.; Miao, Y. MolPhase, an Advanced Prediction Algorithm for Protein Phase Separation. *EMBO J.* **2024**, *43* (9), 1898−1918.

(25) Bazel, Y.; Reč1o, M.; Chubirka, Y. Switchable Hydrophilicity Solvents in Analytical Chemistry. Five Years of Achievements. *Microchem. J.* **2020**, *157*, 105115.

(26) Liu, D.; Zhao, Y.; Zhang, Y.; Wang, Z. The Key to Surfactant-Free Microemulsion Demulsification: CO2 Promotes the Transfer of Amphiphilic Solvent to Aqueous Phase. *J. Mol. Liq.* **2022**, *345*, 117000.

(27) Liu, D.; Lu, H.; Zhang, Y.; Zhu, P.; Huang, Z. Conversion of a Surfactant-Based Microemulsion to a Surfactant-Free Microemulsion by CO2. *Soft Matter* **2019**, *15* (3), 462−469.

(28) Eastoe, J.; Yan, C.; Mohamed, A. Microemulsions with CO2 as a Solvent. *Curr. Opin. Colloid Interface Sci.* **2012**, *17* (5), 266−273.

(29) Wang, B.; Zhu, Z.; Yin, J.; Lu, X. Microemulsion System Formed with New Piperazinium-Based Surface-Active Ionic Liquid. *J. Mol. Liq.* **2023**, *371*, 121103.

(30) Huang, Y.; Zhang, Z.; Cao, Y.; Han, G.; Peng, W.; Zhu, X.; Zhang, T.; Dou, Z. Overview of Cobalt Resources and Comprehensive Analysis of Cobalt Recovery from Zinc Plant Purification Residue- a Review. *Hydrometallurgy* **2020**, *193*, 105327.

(31) Shieh, Y.-T.; Chen, Y.-D.; Don, T.-M. Carboxymethyl Chitosan Has Sensitive Two-Way CO2-Responsive Hydrophilic/Hydrophobic Feature. *Carbohydr. Polym.* **2020**, *241*, 116408.

(32) Ding, Y.; Zhao, Y.; Wen, X.; Liu, Y.; Feng, M.; Rui, Z. Development and Applications of CO2-Responsive Gels in CO2 Flooding and Geological Storage. *Prog. Coll. Polym. Sci. S.* **2023**, *9* (12), 936.

(33) Saboorian-Jooybari, H.; Chen, Z. Critical Review of Microemulsion Phase Behavior Models: Benefits, Research Gaps, Industrial Challenges, and Roadmap. *J. Ind. Eng. Chem.* **2024**, *129*, 1−23.

(34) Li, Y.-B.; Jia, H.-F.; Pu, W.-F.; Wei, B.; Wang, S.-S.; Yuan, N. Investigation of Feasibility of Alkali−Cosolvent Flooding in Heavy Oil Reservoirs. *Pet. Sci.* **2023**, *20* (3), 1608−1619.

(35) Sharifi, N. Molecular Dynamics: Investigating the Self-Association of Stearic Acid and Heteroassociation of Stearic Acid−Water in Cyclohexane. *ACS Omega* **2023**, *8* (44), 41100−41106.

(36) Bartokova, B.; Laredo, T.; Marangoni, A. G.; Pensini, E. Mechanism of Tetrahydrofuran Separation from Water by Stearic Acid. *J. Mol. Liq.* **2023**, *391*, 123262.

(37) Zhang, W.; Zhu, D.; Qin, Y.; Ou, W.; Bao, Y.; Song, L.; Zhang, Q. Effects of Compositions on the Stability of Polyols-in-Oil-in-Water (P/O/W) Multiple Emulsions. *J. Dispersion Sci. Technol.* **2018**, *39*, 1344−1351.

(38) Kumar, N.; Mandal, A. Surfactant Stabilized Oil-in-Water Nanoemulsion: Stability, Interfacial Tension, and Rheology Study for Enhanced Oil Recovery Application. *Energy Fuels* **2018**, *32* (6), 6452−6466.

(39) Rufford, T. E.; Smart, S.; Watson, G. C. Y.; Graham, B. F.; Boxall, J.; Diniz da Costa, J. C.; May, E. F. The Removal of CO2 and N2 from Natural Gas: A Review of Conventional and Emerging Process Technologies. *J. Pet. Sci. Eng.* **2012**, *94*−*95*, 123−154.

(40) Xiao, M.; Liu, H.; Gao, H.; Liang, Z. CO2 Absorption with Aqueous Tertiary Amine Solutions: Equilibrium Solubility and Thermodynamic Modeling. *J. Chem. Thermodyn.* **2018**, *122*, 170−182.

(41) Al-Sakkaf, M. K.; Onaizi, S. A. Effects of Emulsification Factors on the Characteristics of Crude Oil Emulsions Stabilized by Chemical and Biosurfactants: A Review. *Fuel* **2024**, *361*, 130604.