

Dual CO₂ Responsiveness of an Oil-In-Water Emulsion by Using Sodium Oleate and Water-Soluble Tertiary Amines

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Cite This: *Langmuir* 2021, 37, 750–758



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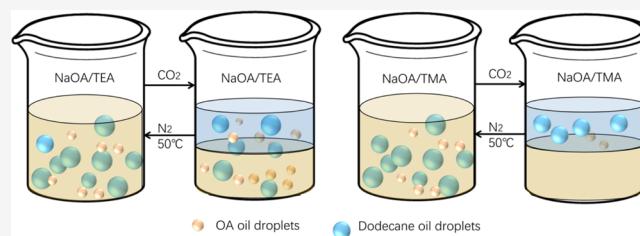
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ABSTRACT: Two kinds of water-soluble tertiary amines (TAs), triethylamine (TEA, monoamine), and tetramethyltrimethylenediamine (TMA, diamine) were introduced into a NaOA stable oil–water (O/W) emulsion, respectively, and their dual reactivity to carbon dioxide was studied. TA was converted into bicarbonate after bubbling of CO₂, which induced the increase of ionic strength of the aqueous phase, and formed ion pair with NaOA through electrostatic interaction. NaOA itself can also be protonated into oleic acid, which can be reversibly deprotonated by alternating bubbles of CO₂ at 25 °C and N₂ at 50 °C, thus affecting the stability and demulsification process of the emulsion. In order to demonstrate TA's and NaOA's synergistic effect on CO₂ responsiveness, gas chromatography–mass spectrometry, ζ potential, electrical conductivity, pH value, ¹H nuclear magnetic resonance, morphological evolution, and interfacial tension were used to study the contributions of the single component and two components of NaOA, TEA, and TMA to emulsion stability and CO₂ responsiveness, respectively. Combined with the composition distribution under different pH conditions, it was further proved that TAs had an effect on the stability and CO₂ responsiveness of the NaOA emulsion.



INTRODUCTION

CO₂ as a recycled and safe material has been widely reported in its application of stimuli trigger of emulsions.^{1–4} A number of traditional surfactants together with additives have been used to formulate the stimuli-responsive emulsion, which can reversibly switch their properties whenever CO₂ is bubbled or removed.^{5–9} The most typical additive is the tertiary amine (TA), which can react with CO₂ and water, becoming cationically charged and then forming ion pairs with anionic surfactants. Oil-soluble TA^{10–12} is usually chosen because of the bad water solubility of the corresponding ion pairs, which could be easily separated from the water after demulsification.^{13–15} The result of Jessop's study shows that the demulsification is imperfect when the TAs are water soluble, but less water-soluble TAs will remain in the oil phase.¹⁶ However, few efforts to date have been devoted to study the CO₂-responsive behavior and this imperfect demulsification of the system accompanying water-soluble TA.

As shown in the previous research,^{17–19} the mixture of surfactants exhibits remarkable synergistic effect with a better performance than the single component, which might contribute to the demulsification of the system of water-soluble TA. As a traditional surfactant, sodium oleate (NaOA) can respond to CO₂ by itself. The water-soluble TA may further enhance the CO₂ responsiveness. Therefore, NaOA, with CO₂-responsiveness itself, triethylamine (TEA) as a monoamine, and tetramethyltrimethylenediamine (TMA) as a diamine with water solubility, were chosen in this work to form the dual CO₂-responsive O/W emulsion. ζ potential (ZP),

conductivity, ¹H nuclear magnetic resonance (¹H NMR), morphology evolution, and interfacial tension^{20–25} are applied to figure out the difference and relationship of CO₂ responsiveness between NaOA and TA. Combined with the species distribution under different pH, the respective contribution of NaOA and TA to the stability of the emulsion, emulsion behavior, and the demulsification process shows up, so did the synergistic effects between NaOA and TA.

EXPERIMENTAL SECTION

Materials. TEA, TMA, *N,N*-dimethylcyclohexylamine (DMCHA), and NaOA were bought from Aladdin Reagent (Shanghai, China) and used without further purification. Dodecane was purchased from Kelong Chemical Reagent Factory (Chengdu, China) and used as the oil phase. The deionized water was used as the water phase in all the experiments. The octanol–water partition coefficient log $K_{o/w}$ ²⁶ and the corresponding molecular structure of TAs are shown in the Table 1.

Preparation of the CO₂-Responsive O/W Emulsion. NaOA and TEA with a molar ratio of 1:1, 1:2, and 1:4 were also dissolved in deionized water as the water phase. NaOA and TMA with a molar ratio of 2:1, 1:1, and 1:2 were also dissolved in deionized water as the

Received: October 18, 2020

Revised: December 23, 2020

Published: January 5, 2021

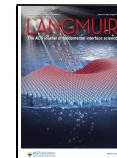
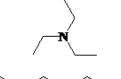
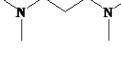


Table 1. $\log K_{o/w}$ and Molecular Structure of TAs

TA	$\log K_{o/w}$	Molecular structure
TEA	1.51	
TMA	0.27	

water phase. Dodecane as the oil phase was mixed with the abovementioned water phases to form a series of CO_2 -responsive O/W emulsions with magnetic stirring at 200 rpm for 12 h. Our previous work²⁷ proved that the applied concentration of NaOA (0.5 wt %) is much higher than its critical micelle concentration. The corresponding emulsion was instilled into water, and it dispersed immediately, meaning that the prepared emulsion is the O/W emulsion. All the emulsions were stored at room temperature for further testing.

To investigate the switching behavior, the prepared emulsion was bubbled of CO_2 at a rate of 40 mL/min for 30 min accompanying by a magnetic stirring of 200 rpm at 25 °C. N_2 was bubbled at 50 °C for 5 h with a magnetic stirring of 200 rpm. CO_2 was repeatedly bubbled or removed for 3 times in the multicycling test.

Conductivity Measurement. The conductivity of TEA, TMA, and NaOA aqueous solution was measured by a conductometer of DDS-307A from Shanghai Precision and Scientific Instrument (China). Continuous bubbling of 40 mL/min CO_2 into the NaOA aqueous caused clear emulsification, while there was no noticeable appearance in the TEA and TMA aqueous. Then, CO_2 was removed by the subsequent bubbling of N_2 with the same speed at 50 °C. The average values were calculated from three cycles. Similarly, the conductivity of each emulsion was measured. Continuous bubbling of 40 mL/min CO_2 and N_2 was performed as a cycle.

pH Measurement. A PHS-3E benchtop pH meter, produced by Rex Shanghai INESA Scientific Instrument, was used to measure the pH of TEA, TMA, and NaOA aqueous solution and each emulsion during the process of CO_2 bubbling until the corresponding pH became stable at 25 °C.

ζ potential Measurement. The ζ potential of prepared emulsions was measured by ZetaPALS 190 Plus of Brookhaven Instruments (USA). The average values were reported from three measurements at 25 °C.

Morphology Evolution of Emulsions. The morphology evolution of emulsions before or with bubbling of CO_2 was recorded by taking the micrographs of the droplets using a digital fluorescence microscope of EVOS FL produced by Thermo Fisher Scientific (China). The samples of the emulsion with a certain time of standing or bubbling of CO_2 were placed on the slide, and then, a cover glass was gently placed on the top. The program Image-Pro Plus 6.0 was used to calculate the diameter of droplets of emulsion.

Tension Measurement. The surface tension of aqueous solution and oil–water interfacial tension (IFT) between the aqueous solution and oil phase (dodecane) was determined at 25 °C every 10 min by spinning drop technology on DSA30S analyzer of KRUSS GmbH (Germany). The density of dodecane and water ($\rho_{\text{dodecane}} = 0.87487 \text{ g/cm}^3$; $\rho_{\text{water}} = 0.99705 \text{ g/cm}^3$) was the input for computer calculation using the Laplace equation. All the values are the average of three measurements.

$^1\text{H NMR}$ Measurement. NaOA was dissolved in D_2O , TEA and TMA were dissolved in CDCl_3 , the mixtures of NaOA and TEA, and NaOA and TMA were also dissolved in D_2O and then measured by Bruker AVANCE III HD 400 (Bruker Instruments, Ltd. CHE.) at 25.0 ± 0.1 °C. All of them were dissolved in D_2O and bubbled with CO_2 for 5 min for the preparation of $^1\text{H NMR}$ measurement.

Gas Chromatography–Mass Spectrometry Measurement. After bubbling of CO_2 , the NaOA aqueous solution was placed in a volumetric flask, and anhydrous NaCl was added. After fully dissolving and oscillating, a mixture of *n*-hexane and dichloromethane (1:1) was added. After full oscillation, the solution was divided into

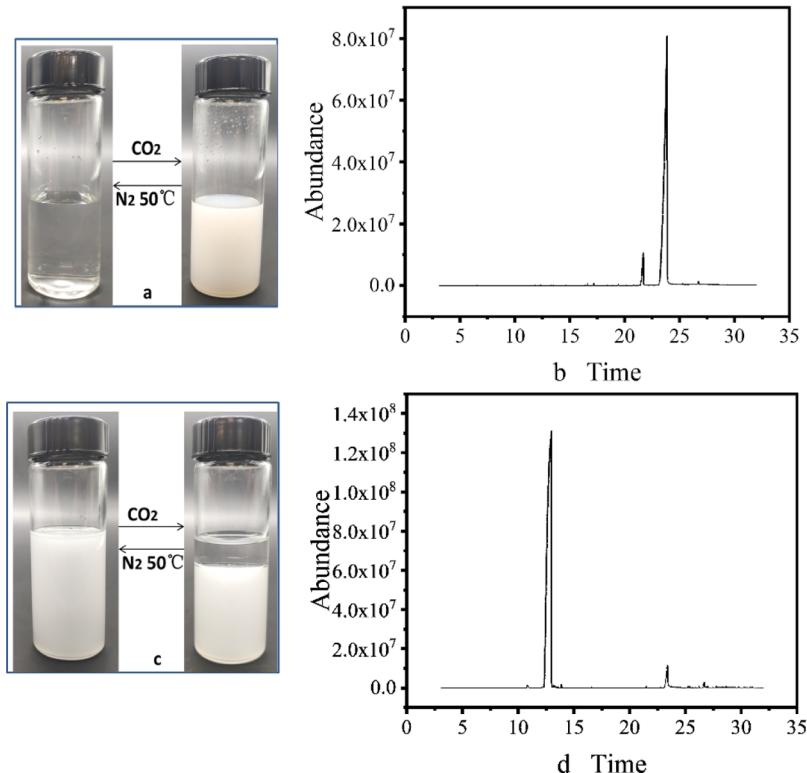
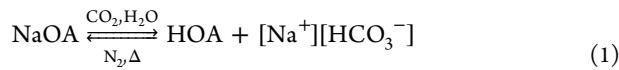


Figure 1. (a,c) Appearance photo of NaOA aqueous solution and its emulsion of alternating bubbling of CO_2 at 25 °C and N_2 at 50 °C; (b) the oil-phase composition of the NaOA solution after bubbling of CO_2 ; (d) oil-phase composition of the lower liquid after emulsion demulsification.

two phases for standing, and the oil phase was passed through anhydrous Na_2SO_4 to obtain the organic phase and then tested by gas chromatography–mass spectrometry (GC–MS) (7890A 5975C, Agilent Technologies) at 25.0 °C. When the NaOA emulsion was demulsified after bubbling of CO_2 , the lower solution was taken for the above treatment and tested by GC–MS. When the NaOA/TEA and NaOA/DMCHA emulsions were demulsified after bubbling of CO_2 , the upper phases were taken for the above treatment and tested by GC–MS.

RESULTS AND DISCUSSION

CO_2 Responsiveness of Single Component. CO_2 Responsiveness of NaOA. NaOA is in its anionic form (OA^-) in water in the absence of CO_2 , and it partly converts into the neutral form [oleic acid (OA)] by addition of CO_2 . As shown in Figure 1a, the transparent aqueous solution gradually became the emulsion, while the OA was obtained from the protonation of NaOA^{28,29} as the oil phase, and the residual unprotonated NaOA as an emulsifier. By testing the conductivity, as shown in Figure S1, the system can be cycled at least 3 times during the process of repeated CO_2 bubbling or removal. The conductivity rises sharply with bubbling of CO_2 and then drops obviously with bubbling of N_2 .



As shown in eq 1, sodium hydrogen carbonate (NaHCO_3) is one of the products of the reaction among NaOA, water, and CO_2 . Although the other product, OA, is in a nonionic state, the ionic concentration is still enhanced because the ionization of NaHCO_3 is much easier than NaOA. This reaction is easily reversed if N_2 is bubbled at a higher temperature, accompanied with the decrease of conductivity. The conductivity changes similarly in the subsequent cycles, and partial recovery of the conductivity indicates the incomplete deprotonation of the system.

Because NaOA aqueous solution can form an emulsion when CO_2 is bubbled as shown in Figure 1a, we also investigated the CO_2 response of NaOA-based emulsion. In the absence of CO_2 , NaOA, water, and oil (dodecane) can form the NaOA-based emulsion. By continuous bubbling of CO_2 , we found that the emulsion was rapidly demulsified, forming a two-phase mixture of the upper oil phase and the lower emulsion, and the lower emulsion was very stable, as shown in Figure 1c. We used GC–MS to test the oil-phase composition of the NaOA aqueous solution after bubbling of CO_2 and the oil-phase composition of the lower liquid after the demulsification of the NaOA-based emulsion.

The oil phase in NaOA aqueous solution peaked at 23.856 min, as shown in Figure 1b, proving the existence of OA.^{30,31} The oil phase of the lower phase of the NaOA-based emulsion peaked at 12.977 and 23.385 min, as shown in Figure 1d, indicating the oil is not only the OA but also the dodecane of the lower phase. It also proves the incomplete protonation of NaOA during bubbling of CO_2 . According to the above results, the demulsification mechanism of NaOA aqueous solution and emulsion are shown in Figure 2.

CO_2 Responsiveness of TAs. It is known that TEA, TMA, and their bicarbonates are all water-soluble, and there is no noticeable change in appearance. The reaction among TEA, water, and CO_2 is shown in eq 2, and the reaction among TMA, water, and CO_2 is shown in eq 3.

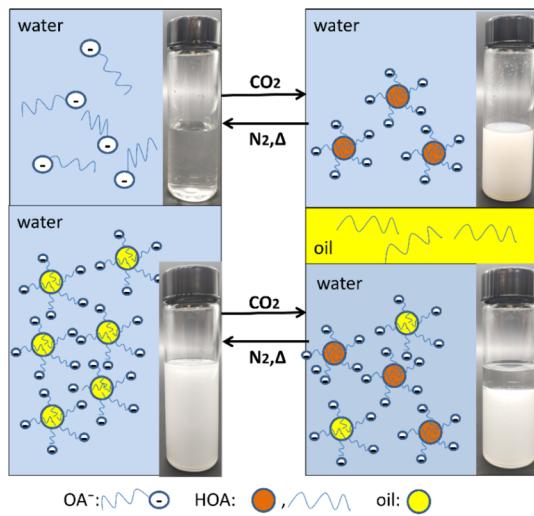
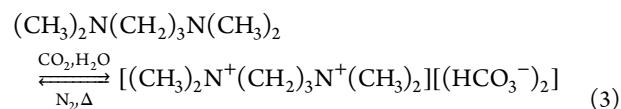


Figure 2. Demulsification mechanism diagram of NaOA aqueous solution and emulsion.



The conductivity of TEA aqueous solution increased with the addition of CO_2 and decreased with the removal of CO_2 , as shown in Table 2. The change in conductivity of TMA

Table 2. Conductivity of TEA and TMA during three Cycles of Alternating Bubbling of CO_2 at 25 °C and N_2 at 50 °C

TAs	cycle						
	0	0.5	1	1.5	2	2.5	3
TEA (mS/cm)	0.47	0.71	0.51	0.69	0.51	0.69	0.51
TMA (mS/cm)	0.20	2.4	0.21	2.39	0.20	2.40	0.20

aqueous solution is similar to that of TEA, as shown in Table 2, indicating the corresponding protonated and deprotonated process. The imperfectly recovered conductivity during the three cycles indicates incomplete deprotonation. After bubbling of CO_2 , the conductivity of TMA increased to 2.4 mS/cm, while that of TEA only increased to 0.7 mS/cm. This indicates that TMA has a higher degree of protonation and better electrostatic combination with NaOA, which may have a more prominent effect on emulsion formation and demulsification.

Some would expect this change to be possible, provided that the CO_2 combines with water and lowers the pH of the aqueous solution. The conductivity of the pure water only increases to 38 $\mu\text{S}/\text{cm}$ from 10 $\mu\text{S}/\text{cm}$ after bubbling of CO_2 and decreases to 17 $\mu\text{S}/\text{cm}$ with bubbling of N_2 . This blank measurement further proves the CO_2 responsiveness of TAs.

Because we wanted to compare the effects of different ratios of NaOA and TAs on emulsification and demulsification, we bubbled CO_2 into TA aqueous solution with different concentrations and tested the conductivity and pH, and the results are shown in Figure 3. We found that the conductivity and pH of the solution increased with the increase of TA concentration. After bubbling of CO_2 , the conductivity

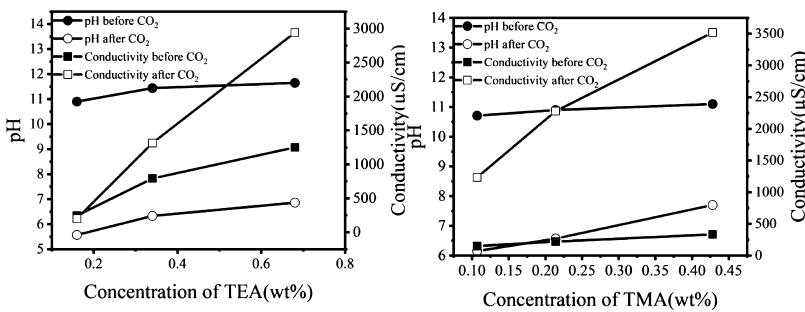


Figure 3. Conductivity and pH of 0.16, 0.34, and 0.68 wt % TEA aqueous solutions before and after bubbling of CO₂ at 25 °C (left) and the conductivity and pH of 0.107, 0.214, and 0.428 wt % TMA aqueous solutions before and after bubbling of CO₂ at 25 °C (right).

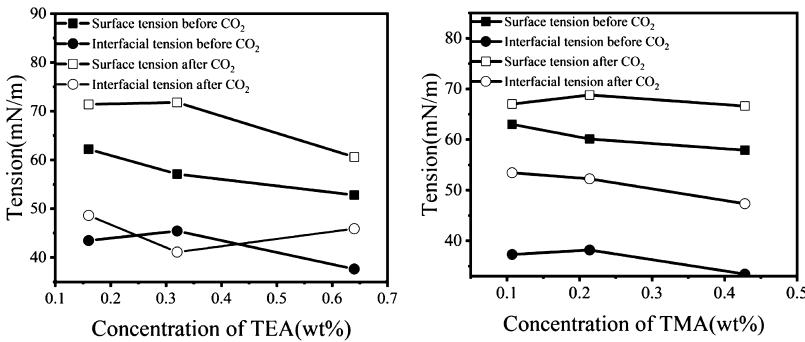


Figure 4. Surface tension and interfacial tension of 0.16, 0.34, and 0.68 wt % TEA aqueous solutions before and after bubbling of CO₂ at 25 °C (left) and the surface tension and interfacial tension of 0.107, 0.214, and 0.428 wt % TMA aqueous solutions before and after bubbling of CO₂ at 25 °C (right).

increased greatly and pH greatly decreased. The decrease in pH indicated that TA is protonated because of the bubbling of CO₂, and the increase in electrical conductivity also proved this conclusion. At the same time, we also found that the conductivity increased with the increase of TA concentration. Although pH is lower than that before bubbling of CO₂, it also increased with the increase in concentration. This also indicates that TA aqueous solution with high concentration has a higher degree of protonation after bubbling of CO₂.

In order to verify the effects of TAs on the surface tension of water, we tested the surface tension of aqueous solutions with different concentrations of TAs, and the results are shown in Figure 4. From the results, we found that TAs can reduce the surface tension of water, but the effect is not significant. We also discussed the effect of TAs on interfacial tension of water and oil. Bubbling of CO₂, and removal of CO₂, and testing water and oil interfacial tension is shown in Figure 4 too. After bubbling of CO₂, the surface tension of TAs aqueous solution increased, but the interfacial tension of water and oil decreased. Before bubbling of CO₂, TA is not protonated and exists as a TA molecule in water, which can reduce the surface tension of water. TA is present as an ion in water after bubbling of CO₂, which can reduce the interfacial tension between water and oil.

CO₂ Responsiveness of NaOA/TAs. There is one TA responsive group in the TEA molecule and two TA responsive groups in the TMA molecule, which could be protonated to be the cationic state under acidic conditions. Interestingly, NaOA itself also can be protonated into OA with bubbling of CO₂. Switching of TAs or NaOA between the ionic and neutral form requires usage of CO₂ to adjust the pH up and down. With bubbling of CO₂, the composition of the system can be analyzed according to the pH-molecular compositional distribution curve. Therefore, it is important to identify the

molecular compositions of TAs and NaOA at different pH. pK_a (TEA) = 10.75 and pK_a (NaOA) = 9.89^{32,33} are needed for the calculation of compositional distribution at different pH values by using the following equation³⁴

$$x_i = \frac{[\text{H}^+]^i \prod_{i=0}^{n-i} K_{ai}}{\sum_{i=0}^n [\text{H}^+]^i \prod_{i=0}^{n-i} K_{ai}} \quad (K_{a0} = 1; i = 0, 1, \dots, n)$$

The molecular compositional distribution of the corresponding TEA and NaOA aqueous solution in different acidity environments is shown in Figure S2. It is shown that at different pH, there are mainly two states of TEA, namely, cationic state (solid blue line, TEAH⁺) and neutral state (dashed blue line, TEA). When pH > 13, TEA exists in the neutral state; when 8 < pH < 13, TEA and TEAH⁺ are mixed together, and when pH < 8, all the CO₂-sensitive TA groups in TEA will be protonated into the cationic TEAH⁺. NaOA also appears in two states. When pH > 12, NaOA exists in the anionic state OA⁻ (red dash line); when 8 < pH < 12, OA⁻ is partly protonated into OA (red solid line); when pH < 8, all OA⁻ will be protonated into OA.

The molecular compositional distribution of TMA is much more complicated than TEA, as shown in Figure S3, TMA mainly exists in three states, divalent cations (blue solid line, TMAH²⁺), monovalent cations (blue dot and dash line, TMAH⁺), and neutral state (blue dash line, TMA) under different pH. When pH > 12, TMA exists in the neutral state; when 8 < pH < 12, TMA, TMAH⁺, and TMAH²⁺ are mixed together. When 6 < pH < 8, TMAH⁺ and TMAH²⁺ are mixed together. When pH < 6, two of the CO₂-sensitive TA groups in

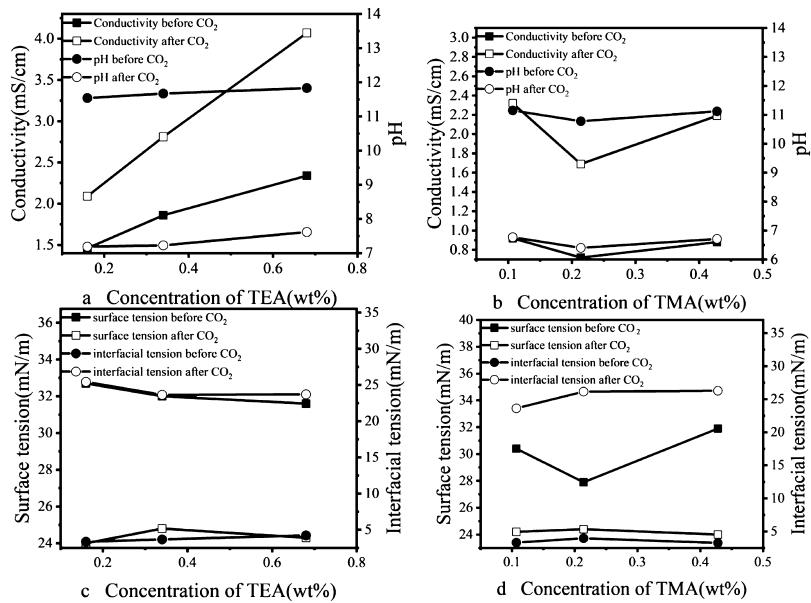


Figure 5. Conductivity and pH (a) and the surface tension and interfacial tension (c) of 0.16, 0.34, and 0.68 wt % TEA-based aqueous solution before and after bubbling of CO_2 at 25 °C; the conductivity and pH (b) and the surface tension and interfacial tension (d) of 0.107, 0.214, and 0.428 wt % TMA-based aqueous solution before and after bubbling of CO_2 at 25 °C (b).

TMA is all protonated into the divalent cationic state, TMAH^{2+} .

CO_2 Responsiveness of Aqueous Solution of NaOA/TAs. In the previous experiments, it was found that the conductivity, pH, surface tension, and water–oil interfacial tension of a single-component aqueous solution changed before and after bubbling of CO_2 . In order to study the response behavior of the NaOA and TA mixture, CO_2 is continuously bubbled into NaOA/TAs aqueous solution, and the process lasted for 30 min. NaOA aqueous solution is also tested as a reference. The following is a brief discussion of the case in which both components exist. First, the conductivity, pH, surface tension, and interfacial tension of NaOA/TA aqueous solutions with three different molar ratios were tested before and after bubbling of CO_2 , as shown in Figure 5. When the concentration of NaOA was fixed at 0.5 wt %, TA concentrations were changed, so that the molar ratios of NaOA/TEA were 1:1, 1:2, and 1:4, TEA concentrations were 0.16, 0.34, and 0.68 wt %, while the molar ratios of NaOA/TMA were 2:1, 1:1, and 1:2, and TMA concentrations were 0.107, 0.214, and 0.428 wt %.

Comparing Figures 3 and 4, it was found that when the two components were simultaneous, various properties of the aqueous solution changed more greatly, and the reduction of interfacial tension showed that the two components indeed have synergistic emulsification effect.

CO_2 Responsiveness of Emulsion of NaOA/TAs. Stability of the Emulsion. Before bubbling of CO_2 , the effective ζ potential increases to 49.90 mV by addition of TEA and the effective ζ potential increases to 51.2 mV by addition of TMA, as shown in Figure 6, while the effective ζ potential is 38.38 mV with only NaOA. The increase indicates the obviously improved stability of the emulsion^{35,36} by addition of TEA or TMA compared with the only NaOA-based emulsion.

The photos of the appearance of the emulsion, the micrographs of droplets, and the corresponding diameter were further applied to certify the conclusion mentioned above. As shown in Figure 7, the system was separated into

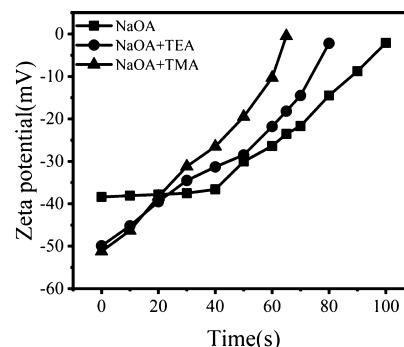


Figure 6. ζ potential of emulsions with 0.5 wt % concentration of NaOA and equimolar TEA, TMA during the process of bubbling of CO_2 at 25 °C.

two distinct phases from a single phase of the prepared emulsion. Water appears in the lower phase, while the upper phase is still the emulsion in 24 h standing. The droplet size of the NaOA-based emulsion was larger than that of the emulsions with TAs, indicating that the addition of TAs could make the emulsion more stable.

CO_2 Responsiveness of the Emulsion. With bubbling of CO_2 , the effective ζ potential of the emulsion only with NaOA at first stands for 40 s and then decreases close to zero in 100 s, as shown in Figure 6. However, the effective value of ζ potential of the emulsion with TEA reduces sharply from the beginning and close to zero in 80 s; the effective value of ζ potential of the emulsion with TMA reduces sharply from the beginning and close to zero in 65 s, which brings the easier aggregation of the droplets of the emulsion because of the decreased electrostatic repulsion between the droplets.

The micrographs of morphology revolution of the emulsion during the process of bubbling of CO_2 are taken every 10 s, as shown in Figure 8. The diameter of droplets of the emulsion increases quickly with bubbling of CO_2 , and the phase separation of the emulsion with both NaOA and TAs takes place faster than the emulsion with only NaOA. As mentioned

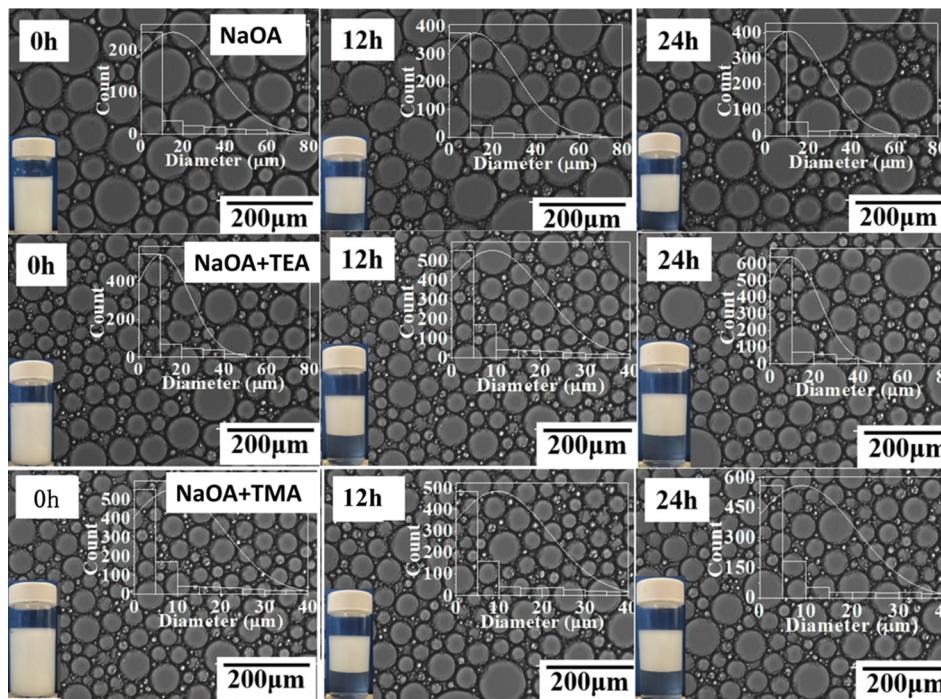


Figure 7. Photographs, micrographs, and diameter distribution of 0.5 wt % NaOA-based CO₂-responsive emulsion with or without equimolar TEA and TMA during 24 h standing.

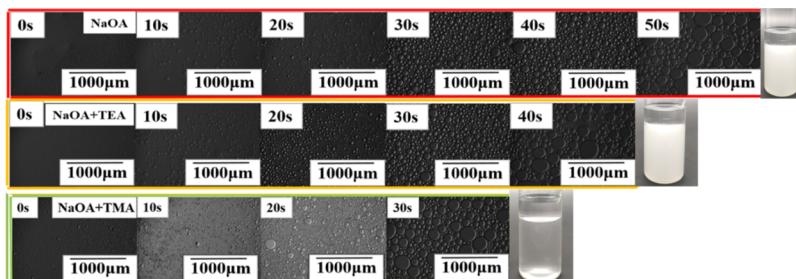


Figure 8. Micrographs of 0.5 wt % NaOA-based CO₂-responsive emulsion with or without equimolar TEA and TMA during the process of bubbling of CO₂ and the photos after bubbling of CO₂.

in the results of CO₂ responsiveness of NaOA/TAs, NaOA itself can be protonated into OA, which leads to further protonation of NaOA in the emulsion. The protonated TEA or TMA combines with NaOA through the electrostatic interaction, which could accelerate the demulsification.

We also tested the pH and conductivity of the emulsions prepared NaOA and TAs with different ratios with bubbling of CO₂ every 10 min, as shown in Figure S4. The decrease of pH and the increase of conductivity indicate the reduction of NaOA in the water phase, which will lead the demulsification of emulsion. The increase of interfacial tension, as shown in Figure S5, between NaOA based aqueous solution and oil phase indicate the demulsification with bubbling of CO₂. The IFT of the system with both NaOA and TEA is close to the system with only NaOA, while the IFT of the system with both NaOA and TMA is far from the system with only NaOA, which will lead the more complete demulsification. Although the increase of interfacial tension is beneficial to the demulsification, the strength of the interfacial film³⁷ also plays a role in the stability of the emulsion.

Mechanism of Demulsification of NaOA/TA-Based Emulsion. Mechanism of Demulsification of NaOA/TEA-

Based Emulsion. Combined with the results mentioned above, the mechanism of demulsification of NaOA/TEA-based emulsion is proposed in this paper. As shown in Figure 9, without TEA, the demulsification simply results from the protonation of NaOA. With TEA, actually, a small number of TEA is already protonated before bubbling of CO₂, which becomes an organic salt, and a single layer of NaOA molecules is inserted between the oil–water interface to reduce the electrostatic repulsion at the head of NaOA, making the single layer more compact and further stabilizing the emulsion as an auxiliary surfactant.³⁸ With bubbling of CO₂, a part of NaOA is protonated into OA, and it loses its function as an emulsifier. More and more NaOA combines with protonated TEA by electronic interaction, which further leads to the reduction of the residual ratio of NaOA. Therefore, the diameter of the droplet of emulsion increases with bubbling of CO₂, and phase separation happens more quickly compared with using only NaOA. However, as shown in the appearance photo, the dual CO₂ responsiveness of NaOA and TEA still leads to an imperfect demulsification. However, as shown in the Figure S6, adding water-soluble TEA can make the upper phase after demulsification free of amine, and upon adding oil-soluble

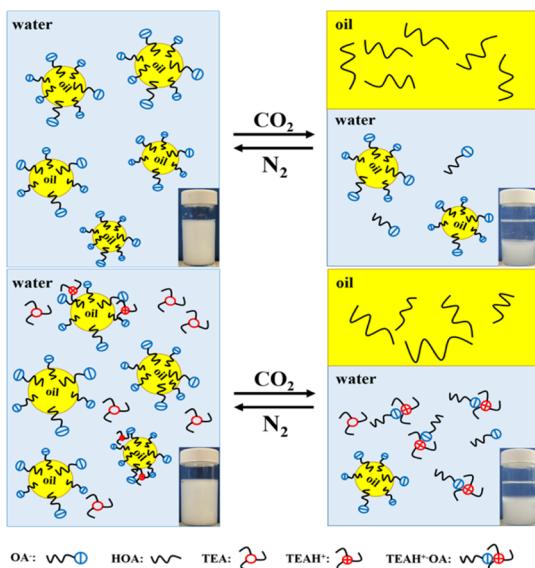


Figure 9. Demulsification mechanism of the NaOA emulsion and NaOA/TEA emulsion with bubbling of CO_2 .

DMCHA, the upper phase after demulsification contains amine. This also proves that the use of water-soluble TA can make the upper oil phase more pure.

To further confirm the formation of ion pairs between protonated TEA and protonated NaOA, the ^1H NMR characterization was applied to detect the possible electrostatic interaction between TEAH^+ and OA^- , as shown in Figure 10. Compared with the ^1H NMR spectra of NaOA (Figure S7c) and TEA (Figure S7a), while the signal of D_2O remains at 4.69 ppm, the chemical signals of hydrogen of the blend of TEA and NaOA (Figure 10a) shift from 1.23 to 1.18 (marked a), 0.81 to 0.76 (marked b), 1.47 to 1.43 (marked c), 1.96 to 1.91 (marked d), 2.11 to 2.02 (marked e), 5.28 to 5.25 (marked f), 2.51 to 2.66 (marked g), and 1.03 to 0.98 (marked h), which might have resulted from the partly protonated TEA according to the results of molecular state distribution before bubbling of CO_2 . Compared with the ^1H NMR spectra of TEA after bubbling of CO_2 (Figure S7b), the chemical signals of hydrogen of the blend of TEA and NaOA after bubbling of CO_2 (Figure 10b) shift from 1.15 to 1.06 (marked h), while the signal of D_2O remains at 4.69 ppm. The possible interaction between TEAH^+ and OA^- is indirectly demon-

strated by changes in chemical signals. The inductive effect is contributed to the formation of stable ion pairs.

Mechanism of Demulsification of the NaOA/TMA-Based Emulsion. Combined with the results mentioned above, the mechanism of demulsification of NaOA/TMA-based emulsion is proposed in this paper. As shown in Figure 11, with TMA,

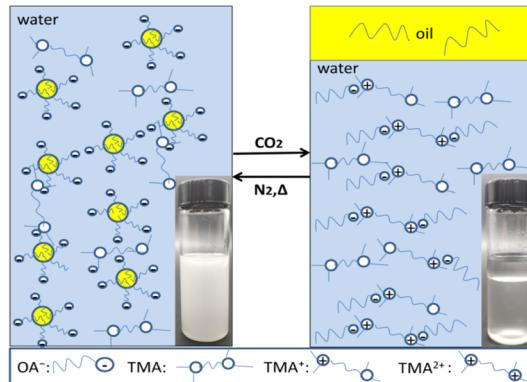


Figure 11. Demulsification mechanism of the NaOA/TMA emulsion with bubbling of CO_2 .

actually, just like TEA, a small amount of TMA has already been protonated and become organic salt before bubbling of CO_2 , which is inserted into the single molecular layer formed by the NaOA molecule at the oil–water interface, reducing the electrostatic repulsion between the NaOA head and the end, forming a more compact monolayer and further stabilizing the emulsion as a support. With bubbling of CO_2 , NaOA is protonated into OA, and it loses its function as an emulsifier. More and more NaOA combines with protonated TMA by electronic interaction, which further leads to more complete protonation of NaOA. Therefore, the diameter of the droplet of emulsion grows up with bubbling of CO_2 , and phase separation happens more quickly compared with using only NaOA. And as shown in the appearance photo, the dual CO_2 -responsiveness of NaOA and TMA leads to perfect demulsification. ^1H NMR characterization was applied to detect the possible electrostatic interaction between TMA and NaOA, as shown in Figures S7 and S8.

A possibility analysis was carried out for the difference of demulsification results between two TAs and NaOA. In the presence of TEA, NaOA is protonated after bubbling of CO_2 , and the final stable pH is around 6, as shown in Figure S4. In

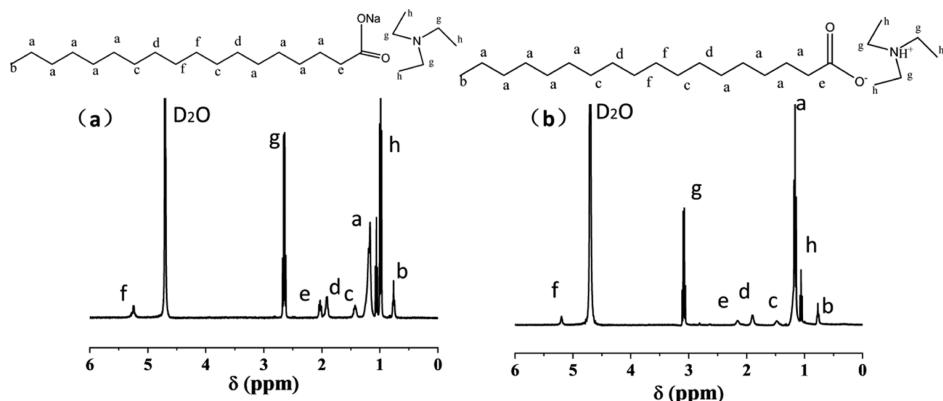


Figure 10. ^1H NMR spectra of (a) mixture of NaOA and TEA and (b) NaOA/TEA D_2O solution after bubbling of CO_2 .

this pH environment, TEA exists in the state of TEA, with a low degree of association with OA^- , and OA^- exists in the system as the emulsifier, so that emulsion is not completely demulsified. When TMA is present, NaOA is protonated after bubbling of CO_2 , and the final stable pH value is around 7.5, as shown in Figure S4. Under this pH environment, TMA exists in three states, TMA, HTMA^+ , and HTMA^{2+} , which can combine well with OA^- . Without OA^- in the system, there is no emulsifier, so that the emulsion can be completely demulsified.

CONCLUSIONS

The results of conductivity, pH, ^1H NMR, ZP, morphology evolution, surface and interfacial tension, GC-MS, combined with the compositional distribution prove that the addition of TEA and TMA strengthens the stability of the O/W emulsion that stabilized by NaOA before bubbling of CO_2 . NaOA can be protonated into OA with bubbling of CO_2 , leading to the reduction of the emulsifier in the system and the demulsification. TEA converts to bicarbonate salt in the process of bubbling of CO_2 , bringing the increase of ionic concentration of the aqueous phase, forming ion pairs with NaOA by electrostatic interaction, further reducing the residual NaOA, and finally accelerating the demulsification. As a diamine, TMA can be converted into a divalent cation by being protonated and be combined with OA through electrostatic interaction. Perfect demulsification can be achieved by adjusting the ratio of TMA with NaOA to 2:1, and the water-soluble TA makes the upper oil phase after demulsification free of amines and more pure. This allows the oil phase to be better recovered.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.0c03038>.

Conductivity and appearance; molecular state; pH and conductivity; interfacial tension; GC-MS; and ^1H NMR of TEA, NaOA, TMA, and the mixture of NaOA and TMA ([PDF](#))

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Sichuan Science and Technology Project (no. 2020YJ0343).

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