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Review

Research of CO_2-Responsive Surfactants for Enhanced Oil Recovery: Review and Outlook

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Abstract: In enhanced oil recovery (EOR), various processes have specific requirements concerning surfactant surface activity. High surface activity is essential during the oil production, whereas low or even negligible surface activity is required during the oil separation process. CO_2-responsive surfactants can regulate their surface activity through the addition or removal of CO_2 in their aqueous solutions. This property makes them suitable for the formulation of CO_2-responsive displacement systems, including CO_2-responsive foam, emulsion, and hydrogel systems. These three systems hold significant application value within the realm of enhanced oil recovery. This paper reviews the structure, types, synthesis methods, applications in EOR technology, and the effects of EOR in both field and laboratory settings. This method is both environmentally friendly and efficient for enhancing oil recovery. Furthermore, the application of CO_2-responsive surfactants facilitates carbon capture, utilization, and storage, contributing to the achievement of carbon neutrality and the carbon peak.

Keywords: CO_2-responsive; surfactant; EOR; system

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1. Introduction

As global energy demand continues to grow, oil, as one of the key energy sources, holds a pivotal position in the world economy. Among various oil displacement technologies, CO_2 flooding is a mature secondary/tertiary oil recovery method. However, as oil production progresses, reservoir pressure decreases, leading to the occurrence of "gas channeling" during CO_2 flooding, which, in turn, results in a decline in the oil recovery rate [1–5]. To enhance oil recovery and extend the productive life of oilfields, it is essential to optimize and innovate oil displacement technologies.

Among the emerging oil displacement technologies, surfactant flooding, emulsion flooding, microemulsion flooding, foam flooding, and hydrogel flooding are also widely employed worldwide, these methods improve oil recovery by reducing water content, expanding the swept volume, and lowering interfacial tension. Surfactant flooding reduces interfacial tension by adsorbing to the oil–water interface, thereby reducing adhesion between oil droplets and water, promoting dispersion and flow of oil droplets, and facilitating oil recovery through water flooding. However, under conditions of complex pore structure and high residual oil saturation, the oil displacement effect is less effective than that of microemulsion flooding [6,7]. For instance, Neha Saxena's research team [8] synthesized alpha sulfonated ethyl ester (α-SEE), an anionic biodegradable surfactant, from palm oil and improved α-SEE by 25 to 27 percentage points following water flooding in a simulated oil displacement experiment. Emulsion flooding primarily utilizes its emulsifying properties, enabling oil droplets in the emulsion to fuse with the oil in the reservoir under specific conditions, thus facilitating oil movement through the rock pores. However, it is a thermodynamically unstable system, much less stable than microemulsion flooding [9,10]. Microemulsion flooding relies on its ultra-low interfacial tension and solubilization ability, allowing it to form a miscible phase with oil. The synergistic action of surfactants and co-surfactants enables the microemulsion to solubilize oil, acting as a "solvent" that effectively dissolves and transports oil through the reservoir pores and alters the wettability of the rock surface [11,12]. This alters the wettability, facilitating oil detachment from the rock surface and its displacement. CO_2 foam and hydrogel primarily function as plugging agents and profile control agents during oil displacement, selectively blocking high-permeability channels [13–15] to expel oil from low-permeability zones. Surfactants are involved in these systems, causing oil, water, and surfactants to form emulsions. Due to the presence of CO_2, these emulsions exhibit good stability, which increases separation difficulty and associated costs in subsequent oil separation processes. Meanwhile, formation pressure gradually increases with the sealing of CO_2 foam and gel; however, excessively high formation pressure may cause large cracks to form, potentially compromising the effectiveness of oil displacement.

The aforementioned challenges in enhanced oil recovery can be effectively addressed by responsive surfactants, a concept first proposed by Jessop [16]. The stimulus sources for this type of surfactant include various types, such as reoxidation stimulus [17], light stimulus, pH stimulus, temperature stimulus, electric stimulus, and CO_2 stimulus [18–20]. Among these, CO_2 has emerged as the most suitable stimulus due to its cost-effectiveness, environmental friendliness, non-toxicity, and abundant availability. CO_2-responsive surfactants function similarly to a lamp in a room: they "work" when activated and cease to function when deactivated. During oil production, following the occurrence of "gas channeling" in CO_2 flooding, a significant amount of CO_2 gas remains in the formation. This surfactant can respond to CO_2. Upon injection into the formation, it can function as a surfactant when stimulated by CO_2, enhancing emulsification performance, sealing properties, wettability, and more. The efficiency of oil removal from the formation is enhanced, and CO_2 gas escape or artificial separation renders the surfactant non-surface-active post-oil removal, thereby improving oil separation efficiency and ultimately enhancing oil recovery. Additionally, CO_2-responsive surfactants further improve CO_2 gas utilization, contributing to the achievement of carbon peak and carbon neutrality goals [21,22].

In summary, CO_2-responsive surfactants, as a novel class of surfactants, offer a distinct advantage in enhancing oil recovery. As research deepens and technological advancements progress, they are expected to play an increasingly pivotal role in the future of enhanced oil recovery. This review examines the types of CO_2-responsive surfactants, their research progress, and practical applications in various enhanced oil recovery technologies, while also discussing their future development directions to promote their broader application in the field.

2. Structure, Classification and Synthesis of CO_2-Responsive Surfactants

2.1. Structure of CO_2-Responsive Surfactant Molecules

The surfactant molecule consists of a head group and a tail group, and different head groups and tail groups have different effects on the performance of the surfactant.

The structure of the surfactant head group significantly influences its water solubility and CO_2 responsiveness, and therefore, the molecular structure should be carefully considered and designed according to the intended use prior to preparation. Scott [23] primarily investigated the effects of head groups, such as long-chain amide, cyclic imide, aromatic amide, and guanidine, on the performance of CO_2-responsive surfactants. The results demonstrated that the long-chain amide group exhibits strong alkalinity, rapidly converting into bicarbonate under CO_2 conditions, and displaying a high CO_2 response. In comparison to long-chain amides and cyclic imines, tertiary amines exhibited the slowest response to CO_2. Among these five head groups, the guanidine group exhibits the strongest alkalinity and water solubility, with the most rapid and thorough response and conversion rates. Song [24] also found that guanidinyl, in addition to its responsiveness, effectively reduced the surface tension of water. However, both studies lacked data on the stability of surfactants after long-term storage or continuous recycling, which is critical for industrial applications. Su [25] explored the influence of $C_{12}N$ and $C_{12}E_2N$ (where E represents the number of ethoxyl groups) structures on CO_2 responsiveness. The head group structures of both amine groups exhibit good CO_2 responsiveness, but the latter's head group contains ethoxyl groups, allowing it to maintain hydrophilicity and surface activity even in its neutral aprotonated form, which is the primary difference compared to the $C_{12}N$ head group structure. Fowler [26] found that amidinyl is the most alkaline among the various head groups studied, enabling it to form bicarbonate salts quickly and efficiently in the presence of CO_2. Additionally, amidinyl loses surface activity more rapidly after CO_2 removal compared to other head groups, such as amides and tertiary amines. The carboxylate head group structure is also responsive to CO_2, but, unlike the response process of amine, guanidine, amidine, and other head groups, the carboxylate surfactant loses surface activity after contact with CO_2 [27,28]. In general, four main head group structures have been identified that exhibit good CO_2 responsiveness: carboxyl, amine, amidine, and guanidine. However, carboxyl surfactants are unsuitable for reservoirs after CO_2 flooding, as residual CO_2 gas in the formation causes them to lose their surface activity, thereby failing to enhance oil recovery.

The tail groups of surfactants are typically hydrophobic, such as long-chain alkyl or fluoroalkyl groups. The structure and properties of the tail group regulate the surfactant's performance, with the length and type influencing the critical micelle concentration (CMC). In general, the longer the tail chain, the smaller the CMC, making it more likely for the surfactant to form micelles [29]. Butler [30] conducted a detailed study on the effect of tail base length on surfactants. Using betaine surfactants as an example, changes in tail base length directly affect the size and morphology of the aggregates, with surfactants having longer tail bases tending to form larger aggregates. This is because a longer hydrophobic tail provides a stronger hydrophobic effect, promoting greater intermolecular aggregation. Additionally, an increase in tail base length generally reduces surfactant solubility, but enhances its ability to reduce the surface tension of water. These results indicate that tail base length is a crucial consideration when designing surfactants. Silva [31] found that the presence of fluoroalkyl tail groups allows surfactants to exhibit lower surface tension and enhanced chemical stability. Li [32] also investigated fluorocarbon surfactants and further examined the influence of fluorination degree on their performance. The results showed that fluorine atoms have strong electronegativity, and when incorporated into the hydrophobic tail, they enhance its hydrophobicity. This increased hydrophobicity allows the surfactant to more efficiently reduce surface tension at the water–oil interface, resulting in a lower CMC and larger micelle size, meaning that fluorinated surfactants can form stable micelles at lower concentrations [33–35]. Additionally, in the emulsion system, the tail group can insert into the surface of the oil drop, allowing surfactant molecules to adsorb onto the oil–water interface and function as emulsifiers. Longer chains can more easily insert into the oil–water interface, more effectively reducing the surface tension between oil and water, thereby promoting the formation of smaller droplets and a more stable emulsion. This enhances the mechanical stability of the droplets and prevents their polymerization and rupture. While surfactants with longer carbon chains form more stable emulsions, excessively long chains may crystallize at low temperatures, weakening emulsification performance in cold environments [36,37]. Therefore, when designing the structure of a surfactant molecule, it is essential to consider not only whether the head group structure meets the functional requirements, but also the structure, length, and type of the tail group.

When designing the structure of surfactant molecules, the design of the head and tail groups is crucial because they directly affect the surfactant◎s performance and range of applications. The choice of head group determines the surfactant◎s solubility in water or other solvents, as well as its hydrophilic or lipophilic properties. It typically involves considering the type of charge (cationic, anionic, non-ionic, or zwitterionic) to suit the specific application environment. For example, in CO_2 flooding processes, where a large amount of CO_2 is present in the formation, it is essential that the surfactant remains surface-active in the CO_2 environment. Therefore, the head group should avoid carboxyl groups and instead include amine, amidine, or guanidine groups. The length and saturation of the tail base influence its hydrophobicity and aggregation tendency. Long, unsaturated chains tend to enhance the hydrophobic effect and contribute to the formation and stability of micelles [30,38]. The branching of the tail base should also be considered in the design, as a branched structure affects stacking density and fluidity. In conclusion, the optimal design of the head and tail groups should be based on required surface activity, environmental adaptability, and biocompatibility to achieve the best application performance.

The CO_2-responsive surfactants discussed in this paper, including amidine-based, guanidine-based, and amine-based types, are non-toxic, harmless, and environmentally friendly. Consequently, their application in oilfields poses no significant environmental risks [16,18].

2.2. Response Mechanism of CO_2-Eesponsive Surfactants

The mechanism of response of CO_2-responsive surfactants primarily involves the protonation and deprotonation of the responsive group. For surfactants with amine (-NH_2) head groups, such as R-NH_2, when they come into contact with CO_2, the amine group, being basic, reacts with the acidic CO_2 to form an ammonium carbonate salt. During this process, the charge state of the head group changes from the neutral amine form to a positively charged ammonium ion (R-NH_3^+), thereby increasing its hydrophilicity. This enhanced hydrophilicity alters the behavior of the surfactant molecules in solution, making them more easily dispersible in water, and potentially changing their ability to adsorb at the oil–water interface, thus exhibiting surface activity [16,39]. The response mechanism of the amidine group is illustrated in Figure 1.

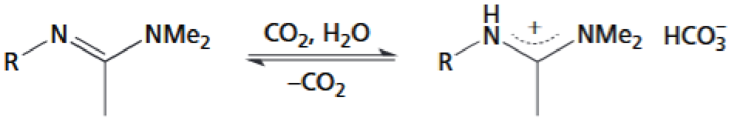


Figure 1. Schematic of the response mechanism of amidine-based surfactants.

2.3. Classification of CO_2-Responsive Surfactants

CO_2-responsive surfactants can be mainly classified into amidine-based responsive surfactants, guanidine-based surfactants, and amine-based surfactants.

2.3.1. Amidinoyl Responsive Surfactants

The advantage of amidine-based surfactants lies in their exceptional CO_2 responsiveness, characterized by the fastest response rate and the highest conversion efficiency. Numerous research teams have already designed and synthesized amidine-based surfactants.

Jessop [40] synthesized a bicyclic amidine-based surfactant, named DBU, and discussed in detail how this surfactant transitions from a non-ionic liquid state to an ionic liquid state under CO_2 conditions, as well as how it returns to its original state under the influence of nitrogen or argon.

Yang [41] synthesized a series of amidine-based surfactants with varying carbon chain lengths, including *N*,*N*-dimethyl-*N*′-dodecyl amidine, *N*,*N*-dimethyl-*N*′-tetradecyl amidine, and *N*,*N*-dimethyl-*N*′-hexadecyl amidine. The surface activity and CO_2 responsiveness of these surfactants were evaluated. The results demonstrated that these amidine-based surfactants exhibited good surface activity and effectively reduced the surface tension of water. In the absence of carbon dioxide, the surfactants existed in a non-ionic form, whereas in the presence of CO_2, they transformed into an ionic form, displaying enhanced surface activity. Additionally, the concentration of CO_2 influenced their surface activity, allowing for control of the strength of the surface activity by adjusting the CO_2 concentration in practical applications.

Ma [42] prepared C_{12}-DMAA by introducing a dodecyl chain into *N*,*N*-dimethylacetamide and conducted a detailed study on the protonation behavior of amidine-based surfactants in saline environments. The results demonstrated that, after the addition of C_{12}-DMAA, significant changes occurred in the solution's conductivity and pH, reflecting an increase in the degree of protonation.

Wang [43] synthesized a series of double-chain, single-head amidine-based surfactants, such as *N*,*N*′-tetracosyl amidine. Surface tension tests revealed that the critical micelle concentration (CMC) of these double-chain surfactants was significantly lower than that of their single-chain counterparts, indicating that the double-chain structure is more effective in reducing surface tension and enhancing surface activity. Furthermore, when CO_2 was introduced into the surfactant solution, the conductivity of the solution increased significantly, suggesting the formation of bicarbonate, which also indicates that the surfactants are responsive to CO_2.

Fowler [26] synthesized *N*′-(4-decylphenyl)-*N*,*N*-dimethylacetamidine surfactant and found that aromatic amidine surfactants exhibited excellent surface activity, significantly reducing the surface tension of water. This made them particularly effective in stabilizing emulsion polymerization systems, where they could produce fine and uniformly distributed polymer particles. Additionally, aromatic amidine surfactants also exhibited responsiveness, and because their alkalinity is weaker than that of long-chain alkyl amidine, they lost their surface activity more quickly after CO_2 was removed from their aqueous solution.

Qiao [44] synthesized 2-alkyl-1-hydroxyethyl imidazoline through a condensation reaction, and then further reacted it with dry ice to transform it into the corresponding imidazoline-based bicarbonate cationic surfactant. This surfactant exhibited excellent surface activity and low critical micelle concentration (CMC), and significantly reduced the surface tension of water.

Hou [45] successfully synthesized C_{12}-DMAA, C_{14}-DMAA, C_{16}-DMAA, and C_{18}-DMAA, and investigated the effect of chain length on the surfactant properties. The results showed that as the carbon chain length increased, the critical micelle concentration (CMC) of the surfactant decreased. Surfactants with longer carbon chains (e.g., C_{18}-DMAA) were more effective in reducing the surface tension of water at lower concentrations compared to those with shorter chains (e.g., C_{12}-DMAA). Furthermore, surfactants with longer carbon chains exhibited stronger surface tension reduction and enhanced emulsifying ability. This made long-chain surfactants more effective in stabilizing emulsions or emulsifying oil–water mixtures. Finally, surfactants with longer carbon chains had poorer solubility at low temperatures but exhibited better stability at high temperatures. This suggested that long-chain surfactants are more suitable for applications in high-temperature environments, such as oilfield extraction.

Harjani [46] synthesized a series of amidine-based surfactants, including various long-chain amidine surfactants and aromatic amidine surfactants, and summarized their synthesis methods. Performance analysis of the synthesized surfactants showed that these amidine-based surfactants possessed good water solubility and interfacial activity.

Scott [23] synthesized cyclic imidazoline-based surfactants (a type of amidine surfactant) and aromatic amidine surfactants, and conducted performance studies. The results showed that the imidazoline ring structure generally exhibits better chemical and thermal stability, making it suitable for more demanding application environments. However, its stability is still lower than that of aromatic amidine surfactants. On the other hand, the aromatic structure may lead to lower water solubility, which limits their application in aqueous systems.

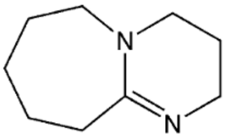
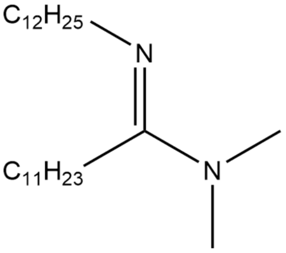
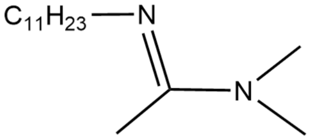
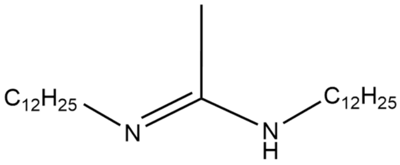
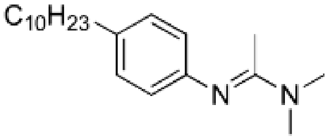
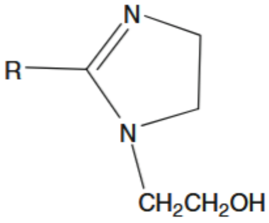
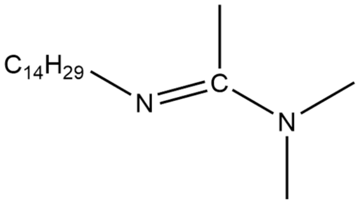
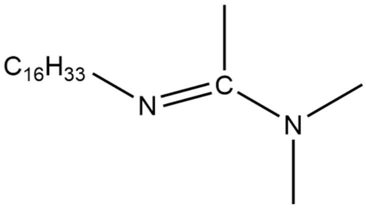
Hegh [47] studied the CO_2-triggered release performance of tetradecyl amidine chloride. The research found that by introducing CO_2 into the system, the rapid release of fluorescein could be effectively triggered, with the release dynamics being most significant in the first 75 s, after which it leveled off. Additionally, the experiment showed that changes in pH significantly affected the amount of fluorescein released, with higher pH values reducing both the release rate and the total amount of release.

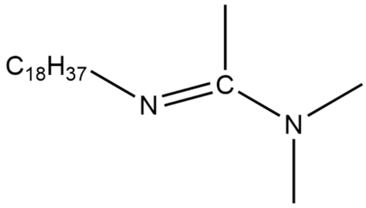
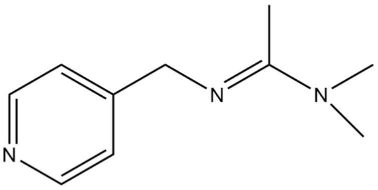
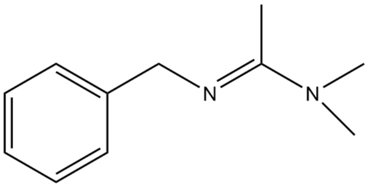
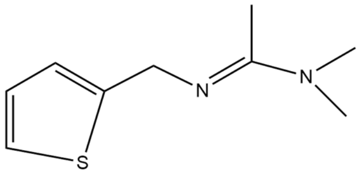
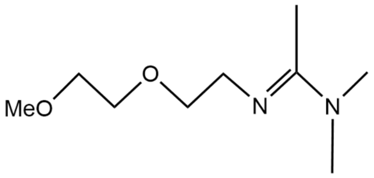
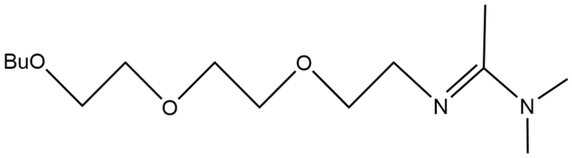
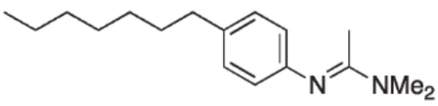
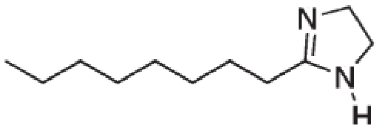
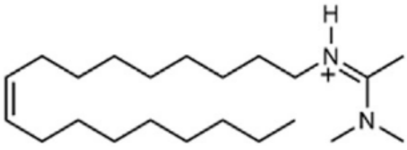
Debas [48] synthesized oil-based amidine (OAm) surfactants and combined them with glyceryl monooleate (GMO) to form CO_2-responsive nanomaterials. Under the influence of CO_2, the lipid nanoparticles formed by OAm and GMO underwent significant structural and morphological changes.

Pauer [49] synthesized long-chain alkyl amidine surfactants and studied the effects of tail group length and temperature on their responsiveness. The results showed that for amidine surfactants with longer tail groups, higher temperatures favored protonation in CO_2. Additionally, during the deprotonation process, higher temperatures facilitated the recovery of the amidine group. For the emulsification process, amidine surfactants with shorter tail groups (less than $C_{18}H_{33}$) were less sensitive to temperature, whereas temperature had a more significant impact on those with longer tail groups (e.g., C_{18}-DMAA). Overall, higher temperatures enhanced emulsification performance because the solubility of the amidine group increased, promoting the formation of amidine bicarbonate and thus reducing surface tension.

The most research has been conducted on long-chain amidine-based surfactants. These surfactants exhibit strong responsiveness, high surface activity, good chemical stability, and solubility in water. However, their production cost is relatively high, primarily due to the complex and tedious synthesis steps involved in producing amidine-based surfactants. Therefore, challenges still exist in large-scale industrial production. Some of the surfactants mentioned in this section can be found in Table 1.

Table 1. The names and structures of the amidine surfactants mentioned in part.

Name	Structure	CMC (mol/L)	Ref.
DBU		-	[40]
N,*N*-dimethyl-*N*′-dodecylamidine		$5.62 \times 10^{-4} \pm 1.27 \times 10^{-6}$	[41]
C_{12}-DMAA		-	[42]
N,*N*′-tetracylamidine		8.97×10^{-5}	[43]
N′-(4-decylphenyl)-*N*,*N*-dimethylacetamidine		-	[26]
2-alkyl-1-hydroxyethylimidazolines	 , R=$C_{17}H_{35}$	1.35×10^{-4}	[44]
C_{14}-DMAA		2.0×10^{-3}	[45]
C_{16}-DMAA		1.0×10^{-3}	[45]

C_{18}-DMAA		7.0×10^{-4}	[45]
N,*N*-Dimethyl-*N*-(pyridin-4-ylmethyl)acetimidamide		-	[46]
N-Benzyl-*N*,*N*-dimethylacetimidamide		-	[46]
N,*N*-Dimethyl-*N*-(thiophen-2-ylmethyl)acetimidamide		-	[46]
N-(2-(2-Methoxyethoxy)ethyl)-*N*,*N*-dimethylacetimidamide		-	[46]
N-(2-(2-(2-Butoxyethoxy)ethoxy)ethyl)-*N*,*N*-dimethylacetimidamide		-	[46]
Aryl acetamidine		-	[23]
Imidazolines		-	[23]
OAm		-	[48]

2.3.2. Guanidine-Based Responsive Surfactants

Compared to amine-based and amidine-based surfactants, guanidine-based surfactants exhibit the strongest alkalinity, resulting in the highest responsiveness and surface activity. Likewise, numerous research groups have synthesized a series of guanidine-based surfactants.

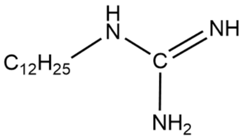
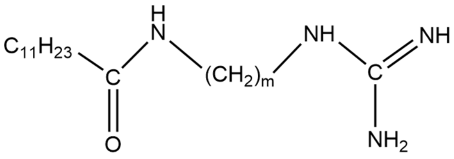
Miyake and Fukui [50–52] synthesized dodecylguanidine hydrochloride ($C_{12}G$) and dodecanoyl amidoalkylguanidine hydrochlorides [$C_{12}AmG$ (Am represents an amide alkyl group, and m denotes the number of methylene groups)]. The research found that guanidine-based surfactants exhibited low critical micelle concentration (CMC) and high aggregation numbers. Additionally, it was observed that $C_{12}G$ showed a stronger self-aggregation tendency compared to dodecyltrimethylammonium chloride (DTAC) [53–55] and sodium dodecyl sulfate (SDS) [56–58], which have the same alkyl chain length. Furthermore, Am, as a spacer group, significantly affected the surface activity of guanidine-based surfactants. As the length of the spacer group increased, both the surface tension and adsorption amount increased, indicating that these surfactants are more effective in reducing the surface tension of water.

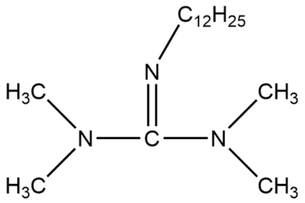
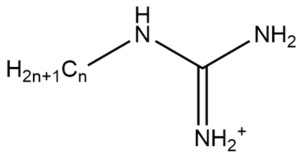
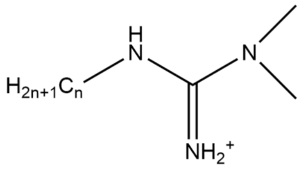
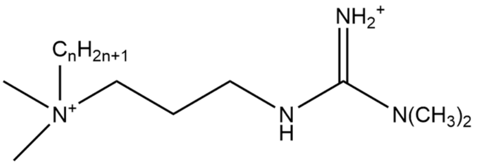
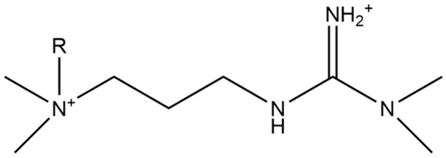
Chen and Tian [59,60] synthesized and characterized dodecyltrimethylguanidine (DTMG), which, upon sufficient contact with CO_2, transforms from a non-ionic surfactant to the cationic surfactant DTMG·CO_2, demonstrating excellent responsiveness. Qin [61] also synthesized dodecyltrimethylguanidine and performed structural identification, surface activity measurement, and responsiveness testing. They confirmed that, like amidine-based surfactants, DTMG can form ionic complexes with CO_2 and water, and that guanidine exhibits more stable performance than amidine [40,62].

Song [63–65] synthesized a series of guanidine-based surfactants, including mono-alkylguanidine (CnG), *N*,*N*,*N′*-dimethyl alkylguanidine (CnMG), dicephalic guanidine surfactant (CnGQ), and heterogemini guanidine surfactant (diCnGQ), and performed physicochemical characterization and biological performance evaluations. The results indicated that alkylguanidine cationic surfactants exhibited a strong tendency for self-aggregation and demonstrated excellent biological performance. He also synthesized a novel bifunctional surfactant containing both quaternary ammonium and guanidine groups (DMAPA) [24], which significantly reduced the surface tension of water. He plans to continue investigating the influence of its structure on the formation of micelles in this novel bifunctional surfactant.

Overall, guanidine-based surfactants exhibit strong alkalinity and high surface activity, which provides them with significant potential for enhancing oil recovery. However, these surfactants may present certain toxicity risks. Therefore, if they are to be injected into reservoirs for oil displacement, careful consideration of their molecular structure is necessary, with environmental protection as a fundamental priority. Some of the surfactants mentioned in this section can be found in Table 2.

Table 2. The names and structures of guanidin-based surfactants mentioned in part.

Name	Structure	CMC (mol/L)	Ref.
$C_{12}G$		6.0×10^{-3}	[51]
$C_{12}AmG$	 m = 2, 3, 4, 6	m = 2: 8.6×10^{-3} m = 3: 7.2×10^{-3} m = 4: 6.2×10^{-3} m = 6: 3.8×10^{-3}	[50]

DTMG		2.8×10^{-4}	[60,61]
CnG		-	[65]
CnMG		-	[65]
CnGQ		-	[65]
DMAPA		1.45×10^{-2}	[24]

2.3.3. Amine-Based Responsive Surfactants

Amine-based surfactants can exhibit different properties depending on the substituents and chemical environment. For example, primary, secondary, and tertiary amines have varying levels of alkalinity and reactivity, and the performance of the surfactant can be adjusted by changing the type and structure of the amine group. Compared to guanidine-based surfactants, amine-based surfactants are relatively less alkaline and have a smaller environmental impact. Additionally, the synthesis of amine-based surfactants is relatively simple, with multiple synthetic routes available. Moreover, the amine group can be easily modified through simple chemical reactions, such as the introduction of different alkyl chains or oxidation or reduction reactions, to obtain surfactants with varying properties [66–68]. This enables customized production according to specific application needs.

Diz [69] synthesized two amine-based surfactants in 1994: *N*,*N*-*bis*(N-dodecyl-*N*,*N*-dimethylglycine)cystamine dihydrochloride (DABK) and *N*,*N*-*bis*(*N*-dodecyl-*N*,*N*-dimethylglycine), 4-diaminobutane dihydrochloride (DABB). These novel *bis*-quaternary ammonium salt surfactants, which feature amide groups and disulfide bonds connected by an olefin spacer chain, exhibit good water solubility and extremely low critical micelle concentration (CMC), showing potential in reducing the surface tension of water.

Ghumare [70] synthesized a series of quaternary ammonium salt-based surfactants (QACs, where Q represents an alkyl chain with a spacer group containing $(CH_2)_3$ and $(CH_2)_6$ groups) using amide compounds as raw materials. QACs are widely used in various fields, especially in surfactant and biomedical applications [71–74]. The team measured the critical micelle concentration (CMC) and the ability to reduce surface tension, and the results showed that these surfactants have good water solubility and relatively low CMC values.

Hou [75] primarily studied three novel surfactants containing polyoxyethylene amide groups: polyoxyethylene amide oxide ($C_{12}EO_3AO$), the corresponding betaine ($C_{12}EO_3Be$), and sulfobetaine ($C_{12}EO_3SBe$). These surfactants exhibited low critical micelle concentrations (CMCs) and high surface activity, with $C_{12}EO_3AO$ distinguishing itself due to its significantly lower CMC compared to traditional surfactants of the same type, as well as its high adsorption efficiency and low interfacial tension.

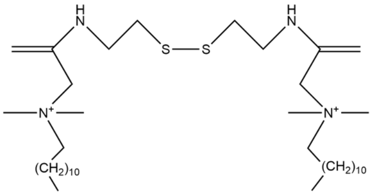
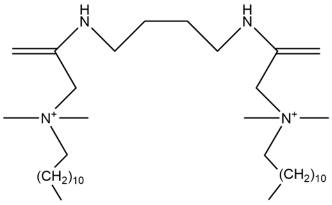
Cho [68] successfully synthesized cationic surfactants based on three different amines (triethylamine, tripropylamine, and tributylamine). The results showed that these surfactants effectively reduced surface tension and had relatively low CMC values.

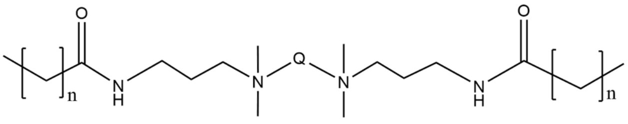
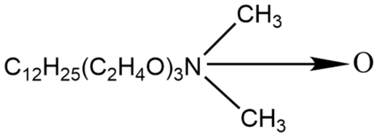
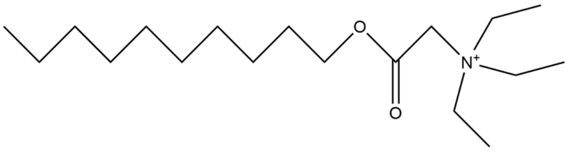
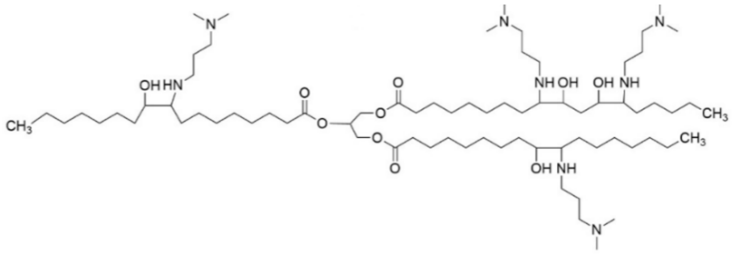
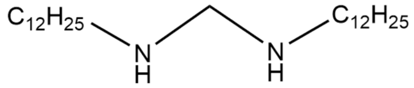
Huang [76] synthesized a series of novel oligomeric surfactants using epoxy soybean oil as the primary raw material, reacting it with dimethylamine and CO_2. Traditional surfactants tend to exhibit low surface activity due to separation caused by electrostatic repulsion between ionic headgroups or hydration of ionic groups [77,78], which hinders their ability to arrange closely at the interface. Consequently, their surface activity is reduced [79]. While polymeric surfactants possess favorable solubility-enhancing properties, thickening behavior, dispersibility, and flocculability [79], their surface tension is lower than that of traditional surfactants [80,81]. However, the oligomeric surfactants synthesized by Huang bridged the gap between these two types, exhibiting high efficiency, multifunctionality, and environmental friendliness [34,82–84]. Additionally, because the synthesized surfactants contain multiple amine groups, the team confirmed that these surfactants exhibit excellent CO_2 responsiveness, with their viscosity significantly increasing under the influence of CO_2.

Zhou [85] successfully synthesized *N*,*N*′-dimethyl *N*,*N*′-didodecyl ethylenediamine, *N*,*N*′-dimethyl *N*,*N*′-bistetradecyl ethylenediamine, and *N*,*N*′-dimethyl *N*,*N*′-bishexadecyl ethylenediamine, and confirmed that these compounds exhibited high surface activity and CO_2 responsiveness.

Overall, amine-based surfactants offer numerous advantages; however, their drawbacks should not be overlooked. Under extreme conditions, such as high salinity or strongly acidic/basic environments, the surface activity of amine-based surfactants may decrease significantly. Additionally, some amine-based surfactants exhibit relatively poor chemical stability, particularly in environments prone to oxidation or hydrolysis reactions. The research teams mentioned previously did not conduct long-term thermal stability evaluations of the synthesized surfactants. For the use of amine-based surfactants in oil displacement, it is essential to evaluate their long-term thermal stability to determine their suitability for application in target reservoirs. Some of the surfactants mentioned in this section can be found in Table 3.

Table 3. The names and structures of the amine-based surfactants mentioned in part.

Name	Structure	CMC	Ref.
DABK		4.1×10^{-5}	[69]
DABB		3.9×10^{-5}	[69]

QACs	 n = 18, Q = 6	0.46×10^{-3}	[70]
$C_{12}EO_3AO$	 $C_{12}H_{25}(C_2H_4O)_3N(CH_3)_2 \rightarrow O$	1.32×10^{-4}	[75]
TEA-12		1.48×10^{-3}	[68]
Oligomeric surfactants		0.2×10^{-3}	[76]
N,*N*′-dimethyl *N*,*N*′-bis-dodecyl ethylenediamine		1.0×10^{-4}	[85]

2.4. Synthesis of CO_2-Responsive Surfactants

2.4.1. Synthesis of Amidine Surfactant

Research on amide-based surfactants is the most extensive, and the synthesis technology is well established. A key aspect in the synthesis of these surfactants is the preparation of the amide group. Traditional methods for synthesizing amides include the nitrile ammonolysis method, formic acid ester method, and amide condensation method [86]. Recently, new methods for synthesizing amides have been proposed by various research teams [87–89]. These methods can generally be categorized into direct and indirect methods. Compared to indirect methods, the products synthesized using direct methods have lower purity, but offer higher yields and simpler synthesis steps, making them more suitable for industrial production.

Direct Synthesis

The carbonyl amine condensation reaction synthesizes amide compounds by forming carbon–nitrogen double bonds, a classic synthetic method. This reaction typically involves aldehydes, ketones, and other carbonyl compounds reacting with primary amines or hydrazines, following an addition–elimination reaction mechanism. The reaction process is shown in Figure 2. The carbonyl and amine groups undergo condensation to form the intermediate product α-hydroxyamine. Due to its instability, it undergoes a dehydration reaction. The hydroxyl group eliminates a hydrogen atom from the adjacent carbon, resulting in the formation of a carbon–nitrogen double bond. In this process, the formation of the intermediate α-hydroxyamine is the key step determining the reaction rate, which is directly related to the nucleophilicity of the amine and the electrophilicity of the carbonyl carbon atom, both of which are proportional. These reactions are generally carried out under acidic conditions; however, excessive acidity may reduce the nucleophilicity of the amine. Therefore, maintaining a pH of 4 typically optimizes the reaction. Mei [90] suggested that the reaction rate is fastest when the pH value is 4. Qiao [91] synthesized a series of amidoamine surfactants by reacting octylamine, decylamine, dodecylamine, tetradecylamine, and hexadecylamine as raw materials with *N*,*N*-dimethylacetamide in chloroform as a solvent at 70 °C for 12 h. The synthesis procedure is shown in Figure 3.

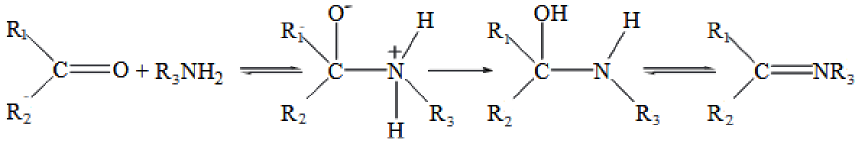
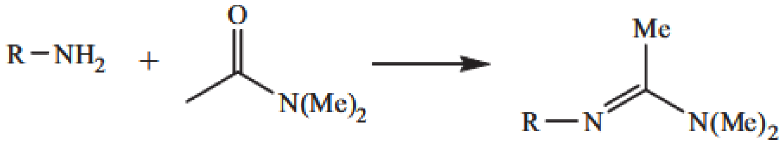


Figure 2. Addition-elimination process diagram.



R=C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$

Figure 3. Direct synthesis of long-chain alkyl amidine compounds.

Indirect Synthesis

The indirect method first converts carbonyl compounds into intermediates, such as hemiacetals, which then react with amines under milder conditions to prepare amidines. For example, in the reaction of amides with carbonyl compounds, the carbonyl group of the amide reduces the nucleophilicity of the amine, leading to a slower reaction rate. Additionally, the imine C=N double bond formed has high polarity, which increases the electrophilicity of the carbon atom, making it more susceptible to nucleophilic attack. Direct use of this method is not economically efficient; the process is complex and difficult to control. However, if the carbonyl group is modified into more reactive forms, such as hemiacetals, geminal halides, or enol esters, before the reaction, the reactivity can be enhanced. This allows the reaction with amides to proceed under milder conditions, while also increasing the yield. Liu [92] first converted 4-vinylbenzyl chloride into 4-vinylbenzylamine via the Gabriel reaction, then synthesized 4-vinylbenzyl amidine by reacting it with *N*,*N*-dimethylacetamide dimethyl ether under nitrogen protection. The synthesis route is shown in Figure 4.

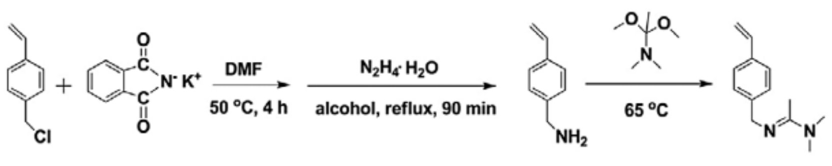


Figure 4. Indirect method for the synthesis of 4-vinylbenzyl amidine.

2.4.2. Preparation of Guanidine Surfactants

The preparation of alkyl guanidines in industry typically involves the reaction of cyanamide with amines [93]. This preparation method has a straightforward process, and its synthesis route is illustrated in Figure 5. The reaction of thiourea with amines is a classic method for preparing guanidine compounds, utilizing *S*-methyl isothiourea. The synthesis route is shown in Figure 6. However, this reaction produces toxic methyl mercaptan. To prevent the formation of toxic alkyl mercaptans, hydrogen peroxide and other oxidants can be employed to oxidize thiourea to thioperoxide prior to reacting with amines [90]. Additionally, the direct use of urea, instead of thiourea, can effectively prevent the formation of toxic alkyl mercaptans. Urea and thiourea can also react with phosgene, oxalyl chloride, or phosphorus trichloride at low temperatures to form "Vilsmeier salts", which then react with amines to produce guanidines [94]. These methods not only avoid harmful by-products but also expand the synthetic strategies for guanidine compounds.

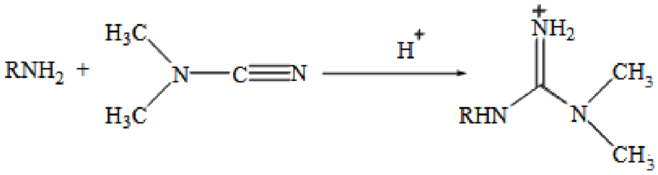
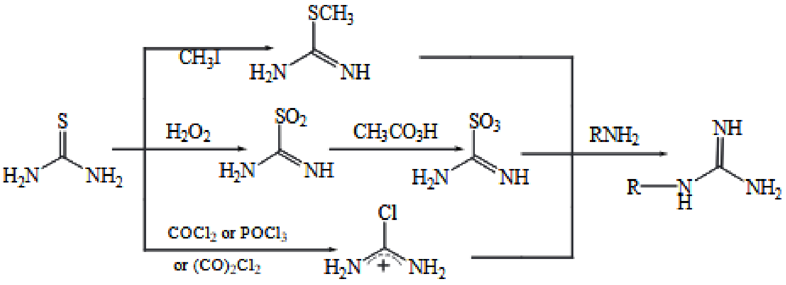


Figure 5. Reaction of cyanamide with amine to synthesize guanidine.



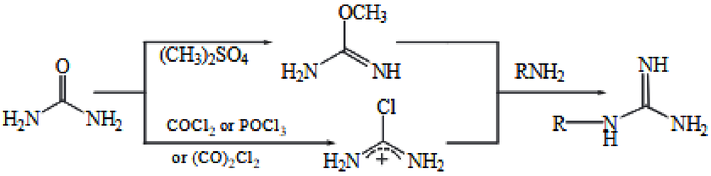
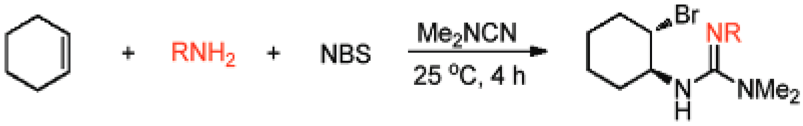


Figure 6. Reaction of thiourea, urea with amine to synthesize guanidine.

In recent years, Zhou [95] reported a novel electrophilic Br-initiated cascade reaction, applicable to the synthesis of aminoalkoxylation and imidazolines. Additionally, the team found that this method is also applicable to the synthesis of guanidine [96]. By reacting a mixture of *N*-bromosuccinimide (NBS), *p*-toluenesulfonamide ($TsNH_2$), cyclohexene, and *N*,*N*-dimethylcyanimide at 25 °C for 4 h, guanidine is synthesized with a yield of 72%. If p-nitrobenzenesulfonamide ($NsNH_2$) is used in place of *p*-toluenesulfonamide ($TsNH_2$), the yield increases to 85%. This method is straightforward and involves mild reaction conditions, making it suitable for industrial production. The synthesis route is illustrated in Figure 7.



1a R = Ts, 72%
R = Ns, 85%

Figure 7. One-pot guanidine synthesis.

2.4.3. Preparation of Amine-Based Surfactants

In the synthesis of amine-based surfactants, the methods for synthesizing alkyl tertiary amines are the most well-established. Traditional methods include fatty alcohol, Liucate, chlorinated alkylamine, sodium dodecyl sulfate, and α-olefin bromination methods. Recently, Kumar [97] reported a method that promotes carbonyl alkylation and amination reactions via visible light catalysis and silane reducing agents, facilitating the efficient synthesis of alkyl tertiary amines. The synthesis route is shown in Figure 8. In this method, secondary amines, aldehydes, and alkyl halides serve as raw materials, with tertiary amines synthesized by adding alkyl radicals to fully alkylated iminium ions in the absence of metals. The process is highly efficient and broadly applicable, capable of directly utilizing alkyl halides without activation while achieving high yields and selectivity by optimizing reaction conditions. A crucial step in the process is the use of visible light to promote unique free-radical initiation and efficiently obtain the target amine compounds through rapid hydrogen atom transfer reactions. The key advantages of this synthesis method lie in its ability to efficiently synthesize tertiary amines in a metal-free environment, with mild reaction conditions and broad applicability, offering an effective strategy for the synthesis of complex amine structures. This method is also suitable for industrial-scale synthesis.

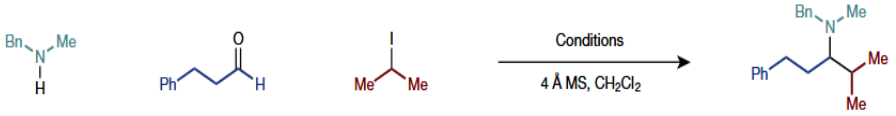


Figure 8. Photocatalytic synthesis of tertiary amine route map.

The synthesis routes for polyamines are not yet well established due to the unclear positioning and structure of functional groups in the products. Further research and exploration are needed.

3. CO_2-Responsive Surfactants in Enhanced Oil Recovery Technology

3.1. Application in CO_2 Foam Flooding for Oil Recovery

The application of foam is extensive, with one of its primary uses being in oil production. Since the first research on foam was published in 1958, it has become a critical technology for enhancing oil recovery [98]. CO_2 foam, in particular, has been widely applied in oil production due to its characteristics, such as small volume, large surface area, and good fluidity [99]. However, when oil contacts CO_2 foam, it is easily emulsified, complicating subsequent separation [100]. Furthermore, CO_2 foam primarily functions to block high-permeability channels in the reservoir, thereby increasing reservoir pressure during subsequent water and gas injection processes. This is especially useful for reservoirs with low formation pressure that cannot reach the CO_2 miscibility pressure. However, higher formation pressure is not always advantageous; excessive pressure can lead to the formation of large fractures, which may hinder oil displacement. Adding defoamers to resolve these issues may inhibit foam regeneration, which would be detrimental to surfactant recovery and reuse. Therefore, researching methods to form stable foam while being able to defoam as needed, without altering the system composition, is of significant importance. Several research teams have explored this issue and made notable progress.

In 2014, Chen [101] synthesized a series of ethoxylated amines, which undergo protonation of the amine group under CO_2 conditions, transforming into a cationic form that exhibits surface activity. This allows the formation of foam, and the surfactant can generate stable foam even under conditions of 182,000 mg/L salinity and 120 °C temperature. Overall, this surfactant shows great potential for applications in high-temperature, high-salinity oil reservoirs. In the same year, Lu [102] synthesized 2-alkyl-1-hydroxyethylimidazolinium bicarbonate cationic surfactants (HEAIBs). Under CO_2 conditions, HEAIBs displayed good foam-forming ability and moderate stability. Importantly, these foams quickly dissipated when exposed to air, demonstrating excellent controllability and responsiveness. This surfactant is able to effectively achieve on-demand foam generation or defoaming.

In 2018, Wang [103] successfully synthesized *N*-oleoylpropyl-*N*,*N*-dimethylammonium bicarbonate ($UC_{22}AMPM \cdot H^+$), which acts as a foam stabilizer and foaming agent, forming worm-like micelles (WLMs) under CO_2 conditions. This increases the system's viscosity and slows the liquid film drainage rate, thereby stabilizing the foam. When ammonia water ($NH_3 \cdot H_2O$) is introduced, the worm-like micelles are destroyed, the system's viscosity decreases, and the foam quickly collapses. The advantage of this system is its ability to form stable foam without the need for additional stabilizers, with foam stability being switchable between stable and unstable states by controlling the presence or absence of CO_2 gas. In the same year, Tang [104] synthesized N-dimethyl-oilamine propylamine (DOAPA), which demonstrates surface activity under CO_2 conditions. It can form worm-like micelles in the presence of sodium salicylate (Na-Sal), significantly increasing the apparent viscosity of the solution and greatly enhancing foam stability. Notably, even under high-temperature conditions, the foam's liquid drainage half-life does not significantly decrease. Additionally, by adjusting the pH value, DOAPA can be recovered, with the recovery rate exceeding 90% in laboratory experiments.

In 2020, Zhang [105] studied the foam performance of three tertiary amine surfactants with different alkyl chain lengths ($UC_{11}AMPM$, $UC_{17}AMPM$, and $UC_{22}AMPM$) under CO_2 conditions, with particular focus on foam stability and flow control under high-temperature and high-salinity conditions. The study found that as the carbon chain length increased, the critical micelle concentration (CMC) of the surfactants decreased, and the surfactant molecules densely covered the liquid film surface. This led to an increase in system viscosity, which slowed the foam collapse rate and enhanced foam stability. Moreover, these surfactants generated stable foam under CO_2 conditions, and when nitrogen (N_2) was introduced, the foam rapidly dissipated, demonstrating their excellent CO_2 responsiveness.

In 2022, Poole [106] conducted a detailed study on the foaming and defoaming properties of *N*,*N*-dimethyl tetradecylamine ($C_{14}DMA$) and compared it with its non-switchable counterpart, tetradecyltrimethylammonium bromide ($C_{14}TAB$). The results showed that, in the absence of CO_2, $C_{14}DMA$ is an organic molecule that is insoluble in water and lacks surface activity, thus making it unable to stabilize foam. However, in the presence of CO_2, the amine group becomes protonated, converting it into a cationic surfactant. As a result, this surfactant can rapidly eliminate foam when needed, and the foaming solution can be recovered and reused, which holds significant value in enhanced oil recovery.

Amine-based surfactants have significant application value in CO_2 foam systems. In reservoirs, they can generate foam to block high-permeability channels, thereby increasing the pressure within the formation to reach the CO_2 miscibility pressure. This assists CO_2 flooding to improve oil recovery. Subsequently, the surfactants can lose their surface activity as needed for separation, facilitating the separation process. Ultimately, this approach helps achieve the goal of enhancing oil recovery.

3.2. Application in Emulsion and Microemulsion forOil Recovery

Emulsions and microemulsions used in enhanced oil recovery (EOR) often encounter issues with oil emulsification, leading to separation difficulties. CO_2-responsive surfactants also hold significant potential in emulsion/microemulsion-based EOR, as they can control surfactant activity to regulate emulsification or demulsification during the oil recovery process [107,108]. This regulation improves both oil recovery and oil separation efficiency, ultimately contributing to an enhanced oil recovery factor.

In 2014, Ceschia [109] synthesized sodium nitrophenolate, sodium benzoate, and sodium laurate. These anionic surfactants rapidly lose their surface activity and demulsify under CO_2 conditions.

In 2016, Zhang [110] studied a CO_2-responsive microemulsion composed of *N*,*N*-dimethyl-*N*-dodecylamine and sodium dodecyl sulfate. In the absence of CO_2, the mixture exhibited a transparent, homogeneous single-phase microemulsion system. When CO_2 was introduced into the microemulsion, it rapidly became opaque and transitioned into two distinct opaque phases within one minute. After approximately 30 min of continued CO_2 injection, nearly complete phase separation of oil and water was observed. This process was reversible, and even after 10 cycles, a transparent and homogeneous microemulsion could still be easily obtained.

In 2018, Xu [111] synthesized 11-dimethylamino-undecyl sulfate sodium salt (DUSNa). Studies showed that this surfactant exhibited excellent emulsifying properties and a rapid demulsification rate. Under CO_2 conditions, DUSNa transitioned into its inactive form, DUS, which precipitated in the aqueous phase, leaving the oil phase almost free of surfactant, thereby enabling oil recovery.

Dai [112,113] studied the CO_2 responsiveness of alkyl tertiary amine and sodium dodecylbenzenesulfonate (SDBS) emulsion systems, as well as the influence of alkyl chain length and the number of amine groups on their responsiveness. The results showed that upon exposure to CO_2, these tertiary amines transformed into bicarbonates and formed ion pairs with SDBS through electrostatic interactions, destabilizing the emulsion. After CO_2 removal, the emulsion returned to a stable state. Furthermore, alkyl tertiary amines with longer carbon chains were more likely to mix with the oil phase, thereby accelerating the oil droplet rupture rate. An increase in the number of amine groups enhanced emulsion stability and accelerated the demulsification process.

In 2020, Chen [114] studied a novel CO_2-responsive surfactant that can regulate emulsion formation and breaking by controlling the presence of CO_2. This surfactant was assembled through electrostatic interactions between a cationic amine (1,3-*bis*(aminopropyl)tetramethyldisiloxane) and an anionic fatty acid (oleic acid) in a 1:1 molar ratio. The results of the study demonstrated that the surfactant exhibited excellent interfacial activity, significantly reducing the required amount of surfactant. At a concentration of 0.2 mM, it was able to reduce the interfacial tension between n-decane and water from 45 mN/m to 5 mN/m within 100 s. Furthermore, this surfactant enabled efficient emulsification and demulsification of oil-in-water emulsions at low concentrations (e.g., 20.0 mM), offering significant economic benefits and application potential compared to previous studies, which required concentrations as high as approximately 150 mM. The emulsion remained stable for over 60 days at room temperature, and upon treatment with CO_2 for 30 s, the emulsion quickly broke. Afterward, it could be re-emulsified by treatment with nitrogen gas, and the entire process could be repeated multiple times, demonstrating excellent cyclic emulsification performance.

In 2022, Pei [107] reported that tertiary amine surfactants would transform into Bola-type structures with strong hydrophilicity under CO_2 conditions due to protonation, resulting in demulsification. These Bola-type surfactants dissolve in the water phase after demulsification and can be recycled from the oil phase.

These CO_2-responsive emulsion systems are not suitable for reservoirs after CO_2 flooding, because CO_2 in the formation will affect their surface activity. They are more suitable for reservoirs after water flooding, and ultimately for oil separation under CO_2 conditions.

Despite the significant advantages of this responsive emulsion system, further research and technological breakthroughs are needed to precisely control the concentration and contact time of CO_2 in practical applications, and to maintain the stability and efficiency of the emulsion under a wider range of temperature and pressure conditions. In summary, CO_2-responsive surfactants offer new possibilities for innovative applications and environmentally friendly operations of emulsions [108], showing great potential for optimizing resource and energy use in modern industrial processes.

3.3. Application in Hydrogel Flooding for Oil Recovery

Gels have been widely used to suppress gas channeling during oil displacement, but the high viscosity of traditional gels may make it difficult to control the plugging performance during the process of controlling formation pressure. Therefore, it is of great significance to study CO_2-responsive hydrogels, which can significantly increase the viscosity of the system through self-assembly to form worm-like micelles, thus sealing large fractures in the reservoir and inhibiting gas channeling [115]. The conversion process between spherical micelles and worm-like micelles is shown in Figure 9. The spherical micelles formed by surfactant molecules and small molecular amines undergo self-assembly behavior under CO_2 conditions, generating worm-like micelles. These micelles entangle with each other, significantly enhancing the viscosity of the system. Currently, there have been some reports on CO_2-responsive hydrogels, most of which are hydrogels formed by mixing tertiary amine compounds with anionic surfactants [116–118].

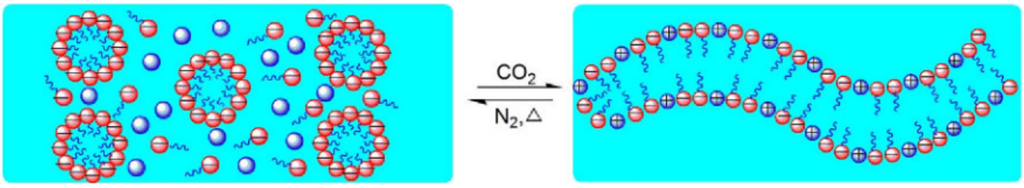


Figure 9. Schematic diagram of conversion between spherical micelles and worm-like micelles (red represents surfactant molecules, blue represents small molecule amines).

In 2013, Su [119] reported a responsive hydrogel system based on sodium octadecyl sulfate ($C_{18}SNa$) and 2-(dimethylamino) ethanol (DMAE). The viscosity of the system increased from 1.2 mPa·s to about 26,000 mPa·s under CO_2 conditions. After removing CO_2 50 min, the viscosity of the system recovered to its original value.

In 2015, Lu [120] reported a responsive hydrogel system based on a mixture of *N*,*N*-dimethyloleamine (DOAPA) and sodium p-toluenesulfonate (SPTS). Under CO_2 conditions, DOAPA is protonated to form quaternary ammonium salts, and the electrostatic attraction between DOAPA and SPTS forms worm-like micelles. After CO_2 is removed, the quaternary ammonium salts are deprotonated back to the tertiary amine state, and the system returns to a water-like state of low viscosity. This conversion between high and low viscosity can be achieved through the introduction and removal of CO_2. In the same year, Zhang [121] reported a responsive gel system mixed with triethylamine (TEA) and the natural anionic surfactant sodium erucate (NaOEr), which could transform spherical micelles into worm-like micelles by injecting or removing CO_2, thus affecting the viscosity of the system. The following year, Lu [122] reported a responsive gel system based on sodium octadecanoate and *N*-(3-(dimethylamino)propyl)-octanamide. Under CO_2 conditions, the system can change from spherical micelles to worm-like micelles, and then return to the original spherical micelles after CO_2 removal.

The advantage of this hybrid system lies in its ability to exhibit CO_2 responsiveness without the need for complex organic synthesis. However, the use of tertiary amines is relatively high, with the molar ratio of tertiary amine to surfactant generally being 4:1. This increases the cost when used in oil displacement processes. In contrast, during organic synthesis, the molar ratio of tertiary amine to surfactant is approximately 1.5:1, significantly reducing the amount of tertiary amine used, thus lowering the cost slightly compared to the hybrid system. However, when compared to the traditional method using only commercial surfactants, both of these systems incur higher costs due to the addition of tertiary amines. In recent years, some research teams have reported the application of single amine-based surfactants in responsive hydrogels.

In 2013, Zhang [123] synthesized octadecyl dipropylene triamine (ODPTA), a long-chain polyamine surfactant. Under CO_2 conditions, the aqueous solution of ODPTA can quickly change from a low-viscosity state to a transparent "gel" with high viscosity. The principle is the same as the above mixed system, relying on the mutual transformation of spherical micelles and worm-like micelles to regulate the system's viscosity, allowing it to switch between the solution and gel states.

Tertiary amine surfactants $UC_{11}AMPM$, $UC_{17}AMPM$ and $UC_{22}AMPM$ [103,105] can be applied not only to CO_2-responsive foam, but also to the CO_2-responsive hydrogel system by using their characteristics of mutual transformation between spherical micelles and vermicelles.

In 2024, Fang [124] synthesized a long-chain tertiary amine surfactant (HXB-2), which contains both tertiary amine and carboxyl groups and can increase viscosity, forming a gel in situ when interacting with CO_2 in aqueous solution. However, once this hydrogel is formed, it cannot completely revert to the previous solution state, and the viscosity remains 4 to 5 times higher than the initial viscosity, making it difficult to use this hydrogel to control formation pressure.

In general, whether the hydrogel system is mixed with amine and anionic surfactants or contains a single surfactant, it has great application potential in the field of enhanced oil recovery. Specifically, the viscosity of the system is similar to that of water during injection into the formation, but it increases sharply after injection, forming a gel in situ, which leads to excellent plugging performance.

4. Effect of CO_2-Responsive Surfactants on Enhancing Oil Recovery

There are few reports on the application of CO_2-responsive surfactants in oilfields and on the evaluation of simulated oil displacement performance in laboratories. Since 2016, the "pseudo-Gemini" surfactant D-OA has been used in numerous tests in oil wells in Sinopec Shengli Oilfield, with more than 90% of the test results showing that it can significantly enhance oil recovery [125]. In 2024, PetroChina produced 10 tons of alkylamidine surfactant for the first time in China and conducted field tests in Dagang Oilfield [126]. The surfactant has on-demand defoamer and demulsification functions, as previously hoped, and its main technical indicators have reached international advanced levels. This is of great significance in the construction of the carbon capture, utilization, and storage (CCUS)-EOR project, preventing gas flooding in low-permeability reservoirs, and enabling efficient development of heavy oil reservoirs. These two field tests provide empirical support for the large-scale field application of CO_2-responsive surfactants in the future. In addition, Du [127] used a CO_2-responsive emulsion system to conduct indoor simulation flooding experiments, with the oil recovery rate ranging between 20.7% and 31.9%, demonstrating good field application value. Fang [124] conducted high-temperature and high-pressure long-core displacement experiments using a CO_2-responsive hydrogel system. The results showed that the total recovery rate increased by 23.53 percentage points compared to primary (water flooding) and secondary (CO_2 flooding). These experimental results indicate that CO_2-responsive surfactants have great potential in the field of enhanced oil recovery.

5. Conclusions and Outlook

Compared with other response systems, CO_2-responsive surfactants do not produce salt accumulation during the CO_2 cycle and can be recycled many times, making it an environmentally friendly process that helps achieve the goals of carbon neutrality and carbon peak.

CO_2-responsive surfactants have been successfully applied in CO_2-responsive foam systems, CO_2-responsive emulsion systems, and CO_2-responsive hydrogel systems. They have great application potential in the field of enhanced oil recovery. In practical applications, they can improve oil–water interfacial tension, regulate the ability to seal large fractures, and reduce the difficulty of oil separation by controlling the activity of surfactants. Moreover, the injectability of these surfactants is excellent, and there is no issue of excessive viscosity causing wellbore blockage.

Amines are the most promising molecules for CO_2-responsive surfactants. They can be used in combination with common anionic surfactants available on the market or used alone by preparing amine surfactants through a series of synthetic steps. The advantage of the former is that the system can be responsive without the need for complicated synthesis steps. The advantage of the latter is that it requires a small amount, there is no need to worry about the ratio, and it is easy to operate.

To date, almost all studies have explored the response performance of CO_2-responsive surfactants and their application potential in the field of enhanced oil recovery from a microscopic perspective, with few reporting results from laboratory simulation flooding and field applications. Of course, one of the main reasons is that the synthesis steps for this type of surfactant are complex, making it difficult for large-scale industrial production. Therefore, in the future, it will also be necessary to optimize the synthesis steps and explore more convenient and high-yield synthesis methods to reduce costs. In addition, small-scale field tests can be conducted first to determine its effect in practical applications. These two points could be the subject of further research in the future.

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