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REVIEW

Research Progress in Structure Synthesis, Properties, and Applications of Small-Molecule Silicone Surfactants

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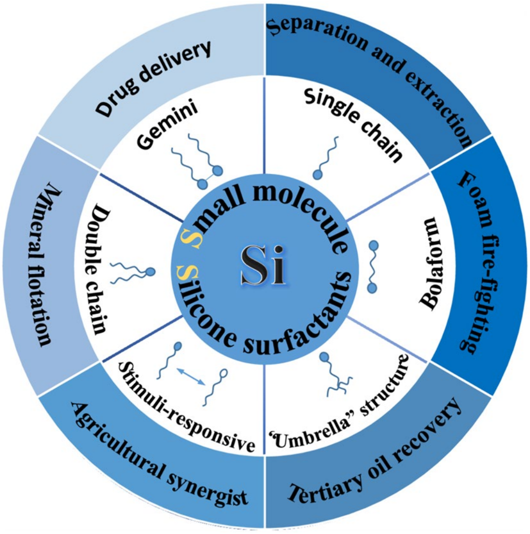
Abstract

Silicone surfactants have garnered significant research attention owing to their superior properties, such as wettability, ductility, and permeability. Small-molecular silicone surfactants with simple molecular structures outperform polymeric silicone surfactants in terms of surface activity, emulsification, wetting, foaming, and other areas. Moreover, silicone surfactants with small molecules exhibit a diverse and rich molecular structure. This review discusses various synthetic routes for the synthesis of different classes of surfactants, including single-chain, “umbrella” structure, double chain, bolaform, Gemini, and stimulus-responsive surfactants. The fundamental surface/interface properties of the synthesized surfactants are also highlighted. Additionally, these surfactants have demonstrated enormous potential in agricultural synergism, drug delivery, mineral flotation, enhanced oil recovery, separation, and extraction, and foam fire-fighting.

Extended author information available on the last page of the article

Graphical Abstract



Keywords Silicone surfactants · Trisiloxane surfactants · Gemini · Synthesis · Application · Aggregation

1 Introduction

Surfactants are amphiphilic substances composed of both lipophilic and hydrophilic groups. The charge of hydrophilic groups often influences the application of surfactants; For instance, cationic surfactants containing ammonium or imidazole as polar head groups find widespread use in antibacterial applications [1, 2]. Similarly, anionic surfactants featuring a polar head group of sulfonic acid are extensively employed in oilfield chemistry [3]. Within the same hydrophilic group, the structure of hydrophobic groups determines factors such as aggregation state, interfacial activity, and other physicochemical properties [4]. Amphiphiles are classified on the basis of the number and type of connections between the polar head and hydrophobic tail, encompassing single-chain, double-chain, bolaform, and Gemini surfactants.

Hydrophobic groups can be categorized into alkane surfactants, fluorinated surfactants, and silicone surfactants on the basis of the constituent atoms. Compared with hydrocarbon surfactants, fluorinated and organosilicon surfactants have garnered significant attention owing to the distinctive properties associated with fluorine and silicon atoms within their hydrophobic groups [5]. However, fluorosurfactants face challenges regarding their long-term nondegradability in soil and water environments [4]. Silicon, the second most abundant nonmetallic element in the Earth's crust, undergoes processing by marine life at a rate of approximately 6.7

billion tons per year, thereby reducing barriers to the application of silicone surfactants [5]. Moreover, silicone surfactants exhibit lower toxicity compared with fluorinated surfactants, further underscoring the advantages of employing silicon-based surfactants.

The primary hydrophobic chains of silicone surfactants consist of Si–O-Si, Si–C–Si, and Si–Si bonds [6, 7]. The Si–O bond, owing to its high polarity, 50% ionic property, and the presence of an empty 3*d* orbital in the silicon atom, readily dissociates under acid–base conditions. Introducing methylene groups between silicon atoms enhance the Lievesz–van der Waals force while mitigating torsional forces, consequently augmenting surface tension. In comparison with traditional long-chain alkyl surfactants, the covalent bond energy of Si–Si and Si–O bonds surpasses that of C–C and C–O bonds, rendering the hydrophobic groups more stable and bolstering their hydrophobic performance. The effectiveness of silicone surfactants in the interfacial adsorption layer predominantly hinges on the structure of the silicone backbone, particularly the concentration and arrangement of functional groups on the backbone [8].

Silicone surfactants can be categorized into polymer and small-molecule surfactants [9]. Polymer surfactants typically have relative molecular weight exceeding 10,000, while small-molecule surfactants have molecular weight of less than 1000. Polymer surfactants tend to exhibit weak directional arrangement and migration on surfaces, and their surface activity is generally low. Additionally, they may lack a distinct critical micelle concentration or require an extended period to reach equilibrium [10]. Conversely, small-molecule surfactants, widely utilized in various applications, demonstrate high surface activity and diffusion coefficients at the air–water interface. In recent years, there has been notable attention toward small-molecule surfactants derived from organosilicon compounds, owing to their unique molecular self-assembly and interface behavior [11]. Some of these compounds have already been commercialized, while ongoing research aims to further develop and exploit their novel functionalities.

This review examines the synthesis methodologies of various small-molecular silicon surfactants, with a focus on those containing one to eight siloxane units. The significance of this review lies in its coverage of diverse synthesis routes for single-chain, “umbrella” structure, double-chain, bolaform, Gemini, and responsive surfactants. By exploring the properties and applications associated with these structures, the review serves as a valuable guide for advancing research and development in the field of small-molecule silicone surfactants (Fig. 1).

2 Synthesis, Structural Design, and Properties

The synthesis of small-molecule silicone surfactants can be divided into two parts: hydrophobic precursors and hydrophilic groups. Hydrophobic precursors typically determine the molecular structure. Furthermore, the structure of small-molecule silicone surfactants is key to influencing their surface and interfacial activity [13, 14]. This section discusses various strategies for synthesizing and properties of

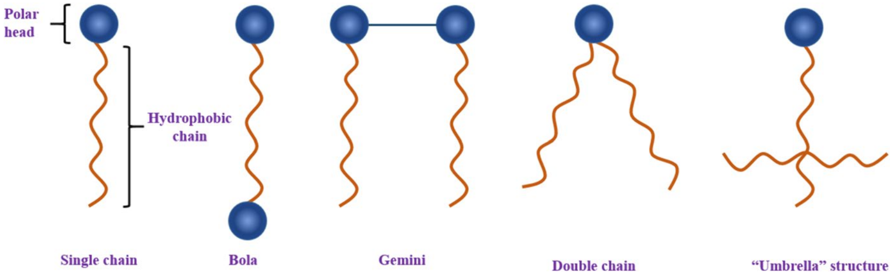


Fig. 1 Structure and classification of surfactants [12]

single-chain, umbrella-shaped, double-chain, bolaform, Gemini, and responsive surfactants based on small-molecule silicone.

2.1 Umbrella-Shaped Surfactants Based on Small-Molecule Silicone

Umbrella-shaped surfactants based on small-molecule silicone (also known as T-type structure) are highly efficient branched surfactants commonly referred to as trisiloxane and tetrasiloxane surfactants. Current mainstream research suggests that these surfactants are distributed at the interface in an "umbrella" structure [15]. There are numerous literature reports shedding light on the synthesis, structure, and properties of such umbrella-shaped silicone surfactants [16].

2.1.1 The Synthesis of Surfactants

The synthesis process for tri- and tetrasiloxane surfactants is essentially the same. However, the central Si atom of the raw material is connected to either two Si–O groups and one alkyl group or three Si–O groups. Depending on the different substituents, the hydrophobic group can be categorized into permethylated siloxane groups and non-permethylated siloxane groups. There are numerous reports on the synthesis of permethylated siloxane surfactants compared with non-permethylated siloxane surfactants. Representative chemical structures of classes of umbrella-shaped siloxane surfactants are also provided in Table 1.

Umbrella-shaped siloxane surfactants are obtained by introducing siloxane as a hydrophobic precursor into hydrophilic group. There are generally four synthetic strategies for obtaining hydrophobic precursor (Fig. 2).

In path 1, a siloxane precursor with functional groups (R_2) was prepared through the hydrolysis and polycondensation of hexamethyldisiloxane and siloxane compounds. The appropriate catalyst was selected based on the different R_2 substitutions. Acidic catalysts are typically employed for synthesizing nonamine siloxane precursors. The Fittrow bentonite acid clay, traditionally used, has gradually been replaced by sulfuric acid owing to its lower cost and wider availability [38, 39]. The basic catalyst utilized is tetramethylammonium hydroxide; however, the yield obtained with this catalyst is relatively low. As the most commonly employed hydrophobic group, the preparation process for heptamethyltrisiloxane precursor has

Table 1 Representative chemical structures of different classes of umbrella-shaped siloxane surfactants

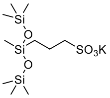
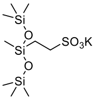
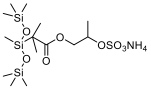
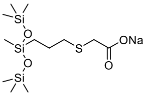
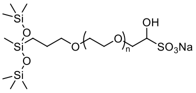
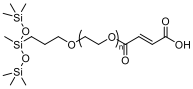
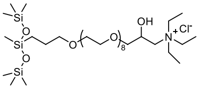
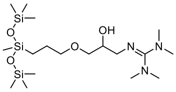
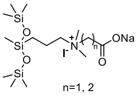
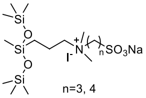
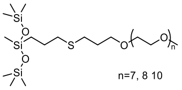
No.	Surfactant chemical structure	Class	CMC(mmol/L)	γ_{CMC}(mN/m)	Ref.
1		Anions	33.0 ^{a} 30.0 ^{b}	20.0	17
2		Anions	48.3 ^{a}	19.8	18
2		Anions	31.60 ^{a}	23.3	19
3		Anions	28.3 ^{a}	19.8	20
4		Amphoteric	1.60 ^{a}	23.68	21
5		Amphoteric	1.3 g/L ^{a}	24.50	22
6		Amphoteric	0.66 ^{a}	22.84	23
7		Amphoteric	-	-	24
8		Amphoteric	0.6wt% ^{a}	21.2(n=1) 21.0(n=2)	25
9		Amphoteric	0.3wt%(n=3) ^{a} 0.4wt%(n=4) ^{a}	-	25
10		Non-ionic	0.0425 (n=7)^a 0.0135 (n=8) ^{a} 0.0145 (n=10) ^{a}	22.9 23.1 21.5	26

Table 1 (continued)

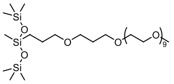
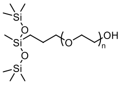
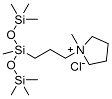
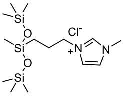
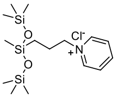
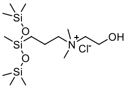
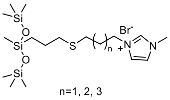
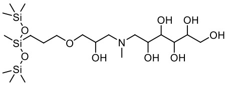
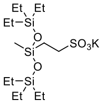
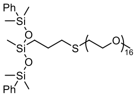
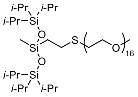
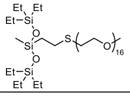
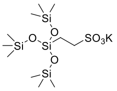
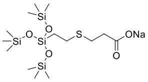
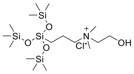
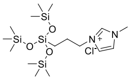
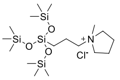
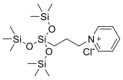
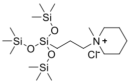
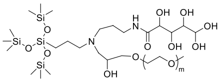
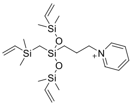
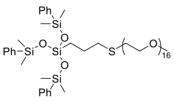
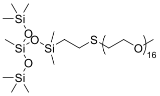
11		Non-ionic	67.5 mg/L^{a}	21.5	[27]
12		Non-ionic	0.62^{a}	18.52	[28]
13		Cations	23.9^{a} 24.5^{b}	24.5	[16]
14		Cations	2.4^{a} 2.4^{b}	27.5	[29]
15		Cations	25.4^{a} 25.0^{b}	22.6	[30]
16		Cations	122.1^{a}	24.2	[31]
17		Cations	2.2(n=1)^{a} 2.3(n=1)^{b}	28.2	[29]
18		Amphoteric	0.36^{a}	19.04	[32]
19		Anions	3.2^{a}	25.3	[18]
20		Non-ionic	2.41^{a}	40.4	[33]
21		Non-ionic	0.2^{a}	31.1	[34]
22		Non-ionic	0.9^{a}	28.2	[34]

Table 1 (continued)

23		Anions	4.3[a]	19.6	18
24		Anions	48.3 [a]	19.8	18
25		Cations	11.4[a] 11.6[b]	21.2	35
26		Cations	7.4[a] 7.5[b]	20.4	35
27		Cations	5.7 [a] 5.5 [b]	20.0	35
28		Cations	6.5 [a] 6.8 [b]	20.3	36
29		Cations	6.0 [a] 5.6 [b]	21.9	36
30		Amphoteric	0.03(m=1)[a] 0.06(m=2)[a] 0.08(m=3)[a]	20.18(m=1) 20.58(m=2) 20.64(m=3)	37
31		Cations	1.6 [a] 1.7[b]	21.7	30
32		Non-ionic	1.63 [a]	35.4	33
33		Non-ionic	1.2 [a]	25.8	34

*[a]Determined from surface tension

*[b]Determined from electrical conductivity

proven suitable for industrial production, yielding products with purity up to 99% [40, 41.

In path 2, the siloxane precursor can also be rapidly prepared through an alcoholysis–hydrolysis reaction. This method is commonly utilized for synthesizing siloxane precursors. Siloxane precursors are readily obtained by reacting

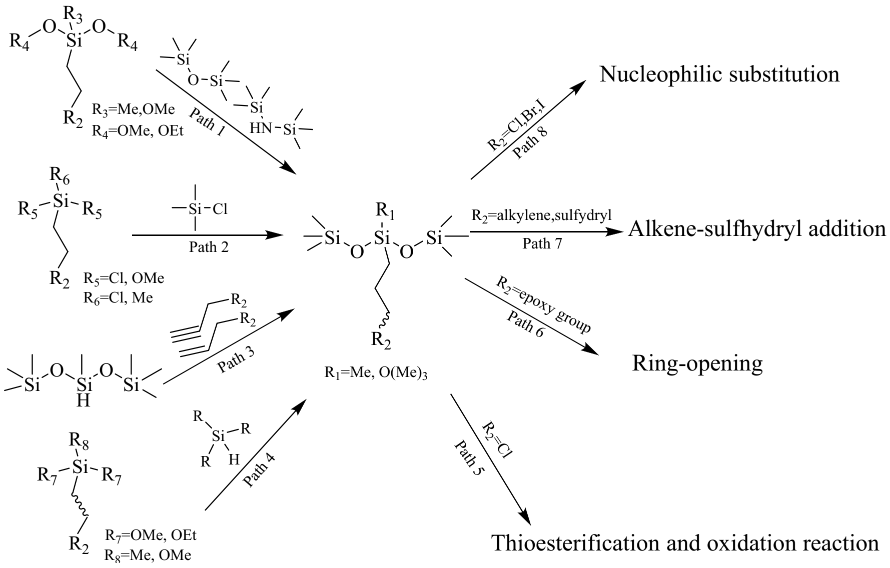


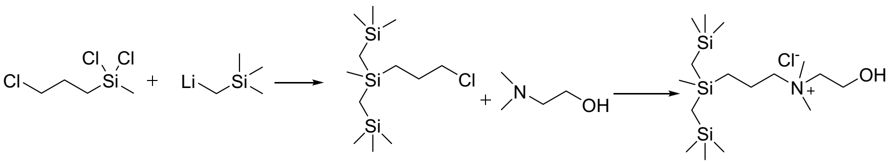
Fig. 2 Synthesis of umbrella-shaped siloxane surfactants

siloxanes with side chains containing chloropropyl and vinyl groups with chlorosilanes having methyl or nonmethyl substituents. Although this reaction does not necessitate a catalyst and is brief, it generates HCl gas as a byproduct [16].

In path 3, heptamethyltrisiloxane compounds are obtained by reacting a trisiloxane precursor containing a Si–H bond with unsaturated compounds under platinum-based catalysis [42, 43]. The hydrosilylation reaction can directly introduce polar groups such as polyether, yielding a nonionic heptamethyltrisiloxane surfactant 44.

In path 4, the Piers–Rubinsztajn reaction (P-R) can also be employed to prepare umbrella-shaped precursors [34, 45]. Moreover, non-permethylated siloxane surfactants can be efficiently synthesized via the P–R reaction [33, 46]. The functional group tolerance of P–R reactions enables the introduction of reactive groups such as allyl, chloropropyl, and azide. By utilizing P–R reactions, it is feasible to synthesize more siloxane structures with high yields, particularly those bearing steric hindrance substituents.

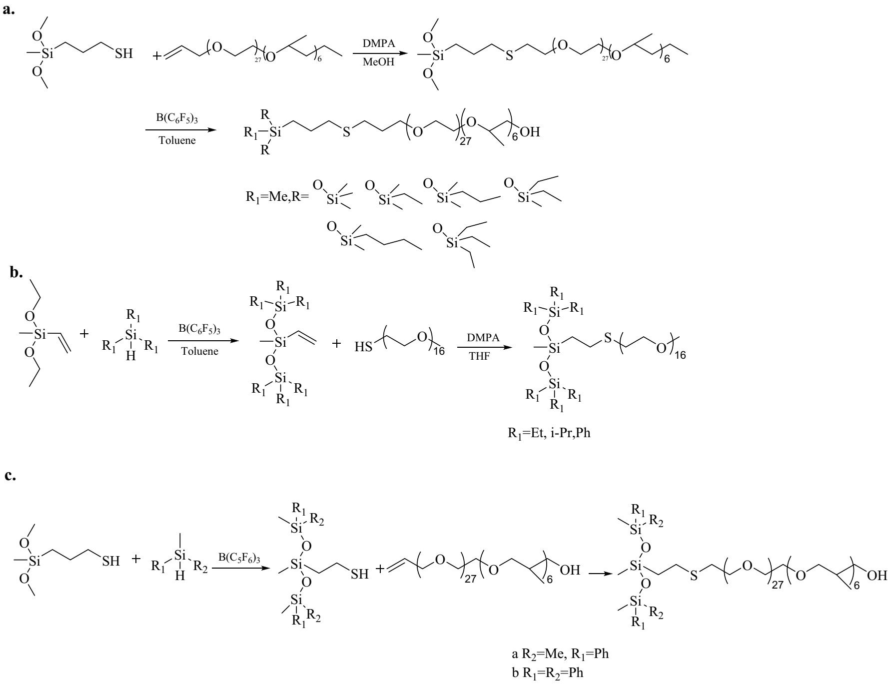
Compared with the Si–O–Si hydrophobic precursor, there are fewer preparation methods available for the Si–C–Si hydrophobic group, primarily relying on nucleophilic substitution reactions. Nucleophilic reagents commonly utilized include Grignard reagents and organolithium reagents for synthesizing tricarbonsilane. The Grignard reaction is characterized by intense heat release and intricate operational requirements [47]. Organolithium reagents, on the other hand, exhibit stronger nucleophilicity than Grignard reagents. Jinglin Tan et al. [48] reported the preparation of tricarbonsilane at room temperature using (trimethylsilyl) methyllithium as a nucleophile (Scheme 1). The reaction necessitates anhydrous and anaerobic conditions. However, this method is currently limited to the preparation of tricarbonsilane,



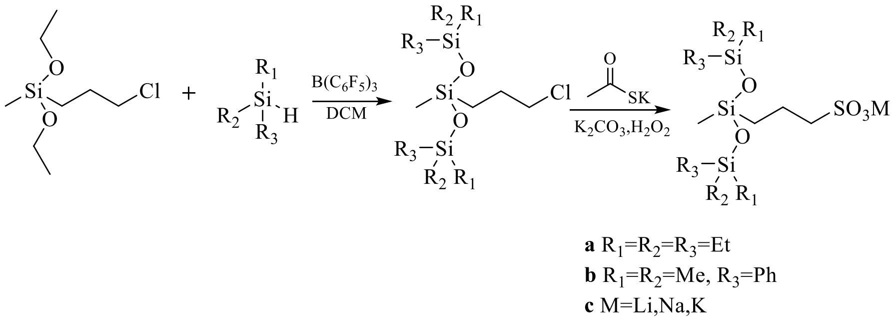
Scheme 1 Synthesis of cationic carbon–silicone surfactants

as the synthesis of tetracarbonsilane may be hindered significantly by steric effects [47].

The introduction of hydrophilic groups depends on the side chain (R_2) of the hydrophobic precursor. Typically, R_2 on siloxane precursors contains reactive groups such as halogen, amine, epoxy, and olefin. Hydrophilic groups can be introduced into siloxane precursors through thiolesterification and oxidation reactions (Fig. 2, path 5), epoxy ring-opening reactions (Fig. 2, path 6), thiol–ene click reactions (Fig. 2, path 7), and nucleophilic substitution reactions (Fig. 2, path 8) [15]. Amine compounds such as imidazole, pyridine, and pyrrole are commonly used as raw materials for producing cationic surfactants. Polyethers and carbohydrates can be converted into nonionic surfactants through thiol–ene reactions (Scheme 2) and esterification reactions. In recent years, the Shengyu Feng group has studied preparation methods for anionic surfactants and developed the preparation of sulfonic



Scheme 2 Synthesis of polyether trisiloxane surfactants



Scheme 3 Synthesis of sulfonated trisiloxane surfactants

acid surfactants by hydrogen peroxide oxidation using potassium thioacetate and ethanethioic acid as raw materials (Scheme 3) [17]. Additionally, carboxylic acid surfactants were prepared by thiol–ene reactions using mercapto carboxylic acid compounds [20, 49]. However, there are few reports on the research of phosphate-type surfactants based on small silicone.

In brief, synthesis methods for siloxane hydrophobic precursors encompass dehydration condensation reactions, alcoholysis–hydrolysis reactions, hydrosilylation reactions, and P–R reactions. The introduction of hydrophilic groups primarily involves nucleophilic substitution, thiol–ene reactions, thiolesterification, oxidation, and epoxy ring-opening reactions.

2.1.2 Physicochemical Properties of Umbrella-Shaped Surfactants

Branched siloxane surfactants have garnered significant attention over the years owing to their "superspreader" capabilities and low surface tension [50, 51]. This is attributed to the dense arrangement of methyl groups at the air–liquid interface and the flexible Si–O chain [52]. The aggregation structure of trisiloxane surfactants at the solid–liquid interface resembles that of hydrocarbon surfactants, albeit differing depending on the specific structures of trisiloxane surfactants [53]. The aggregation behavior and the impact of hydrophobic, electrolyte, and hydrophilic groups of umbrella-shaped surfactants in solution have been extensively investigated.

2.1.2.1 Hydrophobic Groups The hydrophobic group of umbrella-shaped surfactants can be divided into two parts: the siloxane group and the alkyl group. As the Si–O chains increase, the critical micelle concentration (CMC) and surface tension at CMC (γCMC) of these surfactants decrease owing to increased hydrophobicity [20, 31, 54]. This trend applies to both permethylated and non-permethylated siloxane surfactants [20, 33, 48]. The impact of hydrophobic tails on the physicochemical properties of sulfonate-based silicone surfactants was investigated by Yue Huang and colleagues [17]. They found that trisiloxane surfactants exhibit better surface activity and wettability compared with disiloxane surfactants, attributed to the umbrella structure of trisiloxane surfactants and the linear structure of disiloxane surfactants. Furthermore, dynamic light scattering (DLS) and transmission electron microscopy (TEM) studies revealed that the aggregation of silicone surfactants increases with the lengthening of Si–O chains in aqueous solutions. It is noteworthy that the γCMC of the Si–O chain is smaller for alkyl than for branched chains in siloxane surfactants, although the CMC value is larger [34]. Additionally, the surface activities and adsorption processes of silicone surfactants can be significantly influenced by the structure of the siloxane group [33, 34].

The physicochemical properties and aggregation behavior of silicone surfactants are significantly influenced by steric hindrance or π–π interaction resulting from silicon substituents [16]. These substituents can be categorized into alkyl and unsaturated groups. Polyether-based siloxane surfactants with different alkyl groups have been synthesized and characterized for their aggregation behavior [46]. The A_{min} and Γ_{max} decrease with the increase in the number of $–CH_2–$ groups in the siloxane groups. Results from TEM and freeze-fracture transmission electron microscopy (FF-TEM) indicate that these surfactants can form non-uniformly sized spheroidal aggregates in aqueous solution. In other studies, the CMC value and γCMC value of trisiloxane surfactants with alkyl groups were found to be much lower compared with trisiloxane surfactants with vinyl/phenyl groups, attributed to the steric hindrance of hydrophobic groups [16, 17]. Hao Chen et al. [55] found that imidazolium trisiloxane surfactants carrying phenyl groups in the hydrophobic siloxane part were more prone to micellization than corresponding surfactants with vinyl groups, owing to the increased hydrophobicity of the phenyl group in the siloxane group. However, the larger γCMC of surfactants with phenyl groups was due to the π–π stacking interaction among the phenyldimethylsiloxy groups. Additionally, permethylated siloxane surfactants have larger aggregate sizes and better wettability than non-permethylated siloxane surfactants [17, 18].

Jinlin Tan et al. [29] investigated the effect of the hydrocarbon chain length between the siloxane tail group and the polar head group on the micellization of trisiloxane surfactants. They found that, as the number of $–CH_2$- units increased, the A_{min} and the CMC value decreased, while the value of γCMC increased.

In comparison with the Si–O–Si hydrophobic tail, tricarbonsilane surfactants with a Si–C–Si hydrophobic tail exhibited greater hydrophobicity and demonstrated lower CMC values [48]. However, the excellent flexibility of Si–O-Si makes it more closely arranged at the air–liquid interface [47].

2.1.2.2 Hydrophilic Group The structure of the hydrophilic group is another factor that affects the surface activity and aggregation behavior of umbrella-shaped surfactants in aqueous solutions. Among all types of surfactants, umbrella-shaped surfactants with cationic head groups have received the most extensive research attention. These cations primarily consist of quaternary ammonium salts and heterocycles [48]. Heterocyclic head groups are constructed from imidazolium, pyridinium, pyrrolium, and piperidine [31, 36, 56]. Heterocyclic head groups exhibit higher interfacial activity than simple head groups owing to their greater hydrophobicity [57, 58].

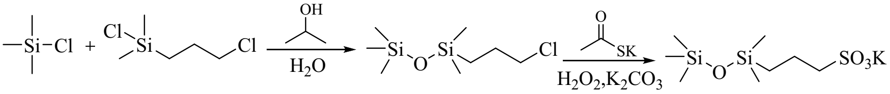
Zhiping Du et al. [58] investigated the effect of heterocyclic umbrella-shaped surfactants, including imidazolium and pyridinium, on aggregation behavior. Results demonstrated that pyridinium surfactants form larger-size aggregates and can generate bilayer vesicle-like aggregates in solution. Owing to the hydrophobicity of cationic head groups, imidazolium surfactants exhibit larger γCMC values [55]. Additionally, the π–π interaction between the head groups can effectively enhance the surface activity of the umbrella-shaped surfactants [31].

The introduction of a polyether group can enhance the wettability and hydrophilicity of surfactants [59]. Wenshan Qu et al. [60] conducted a study on the influence of polyether groups on physicochemical properties and spreading ability. The equilibrium surface tension of these surfactants is approximately 20 mN/m. Dynamic spreading behavior on parafilm demonstrated that the surfactant monolayer could completely wet the parafilm surface within 5 s, exhibiting high spreading ability. In another study, surfactants based on poly(ethylene glycol) and siloxane with varying lengths of the ethylene glycol (EO) chain were examined for their surface activity and aggregation behavior [54]. The CMC values increased with the lengthening of the EO chain, correlating with an increase in hydrophilicity. DLS and TEM results indicated that these surfactants can form nonuniform spheroidal aggregates of varying sizes in aqueous solutions.

Sugar-based surfactants belong to a class of renewable surfactants [61]. Umbrella-shaped sugar-based surfactants have demonstrated superior surface activity compared with conventional sugar-based surfactants with straight, long alkyl chains [62]. Aggregates of these surfactants have been characterized as spherical vesicles, as suggested by DLS and TEM analyses [37, 63]. Furthermore, the formation of these vesicles can be confirmed through the encapsulation of bromophenol blue.

The physicochemical properties of anionic umbrella-shaped surfactants, categorized into carboxylic and sulfonic types, are dependent on the hydrophobic structure and counterions [18, 20, 49]. Consequently, numerous studies have been conducted in these two areas. Regrettably, few studies have focused on the physicochemical properties of phosphate-based umbrella-shaped surfactants.

2.1.2.3 Counterions In addition to the hydrophobic group and the type of head group, counterions can influence the adsorption of umbrella-shaped surfactants and impact interfacial properties [64]. Research indicates that the ability of counterions to promote micellization of pyrrolidinium-based tetrasiloxane surfactants follows the order $NO_3^- > Cl^- > CH_3^-$, aligning well with the Hofmeister series [65]. This phenomenon is attributed to the weaker hydration of counterions, which are more readily adsorbed on the micellar surface, thereby screening the charge at the micellar surface and effectively reducing the surface potential. Studies on tetrasiloxane surfactants with various alkaline counterions (Li^+, Na^+, and K^+) suggest that the effect of counterions on adsorption increases in the order $K^+ > Na^+ > Li^+$, consistent with their hydrated ion radius and polarizability [66]. This effect ultimately enhances the size of spherical aggregates in aqueous solutions. The addition of inorganic and organic salts also influences the aggregation behavior and surface activity of umbrella-shaped surfactants. In comparison with inorganic salts, the majority of organic salts have additional hydrophobic interactions with ionic surfactants, in addition to electrostatic interactions, in aqueous solutions. Lina Meng et al. [49] found that longer alkyl chains of the tetraalkylammonium cation exhibit lower values of CMC and larger aggregate sizes due to greater hydrophobicity and weaker hydration. They reported



Scheme 4 Synthesis of sulfonated disiloxane surfactants

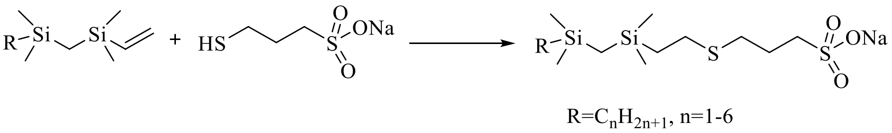
that tetraalkylammonium cations cause equilibrium surface tension reduction following the order $(C_3H_7)_4NBr > (C_2H_5)_4NBr > (CH_3)_4NBr$. The reason behind this is that the hydrophobic groups of organic salts make it easier for surfactant molecules to pack closely. Liying Fang et al. [56] systematically investigated the effects of organic salts on the aggregation behavior of pyridinium-based tetrasiloxane surfactants. The results revealed that the aggregation ability follows the order: sodium salicylate > sodium benzoate > sodium citrate > sodium oxalate > sodium acetate. Moreover, the micellization of the surfactant with and without organic salts in aqueous solution is spontaneous.

The effect of inorganic salts on umbrella-shaped surfactant aggregates follows the Hofmeister series [31, 67]. Liying Fang et al. [36] examined the impact of different negative halogen ions on cationic silicone surfactants and found that the CMC decreases in the order of $I^- > Br^- > SO_4^2 > Cl^-$. This trend was also observed in other investigations involving cationic tetrasiloxane surfactants [31]. Furthermore, Lina Meng et al. [49] demonstrated that the addition of inorganic salts can reduce both the CMC and the γCMC of carboxylate silicone surfactants, with the effect following the order $Na^+ > K^+$.

2.2 Single-Chain Surfactants with Single Hydrophobic Tail and Single Hydrophilic Headgroup

Single-chain surfactants based on small-molecule silicones have a linear structure comprising one head group and one hydrophobic tail. The hydrophobic group of these single-chain silicon-based surfactants primarily consists of disiloxane.

Sulfonate surfactants are a type of anionic surfactants extensively utilized in various industries and daily life. In 2019, Yue Huang et al. [17] obtained a chloropropyldisiloxane precursor through alcoholysis-hydrolysis reaction using chloropropyldimethylchlorosilane as raw material (Scheme 4). The sulfonated disiloxane surfactant was subsequently acquired through thioester functionalization and oxidation reaction. The CMC values and surface tension at CMC of this surfactant were observed to be higher than those of corresponding umbrella-shaped surfactants. This disparity arises owing to the increase in the hydrophobic effect with the rise in the number of Si–O bonds, thereby promoting the aggregation of sulfonate-based silicone surfactants. Results from DLS and TEM studies indicate the formation of spherical aggregates at concentrations higher than the CMC. More recently, a series of carbosilane sulfonate surfactants with short alkyl chains were prepared via thiol–ene reaction using sodium 3-mercapto-1-propanesulfonate as raw material (Scheme 5) [68]. Results from equilibrium surface tension studies revealed that the



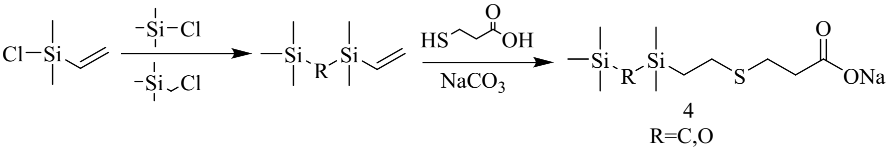
Scheme 5 Synthesis of carbosilane sulfonate surfactants having different alkyl chains

CMC of these carbosilane sulfonate surfactants decreases while the surface tension at CMC increases with the decrease in the length of the short alkyl chain. The aggregation behavior is driven by enthalpy at low temperatures and entropy at high temperatures. Additionally, it was observed through DLS and TEM that the diameter of the aggregates decreases with the increase in the length of the alkyl chain.

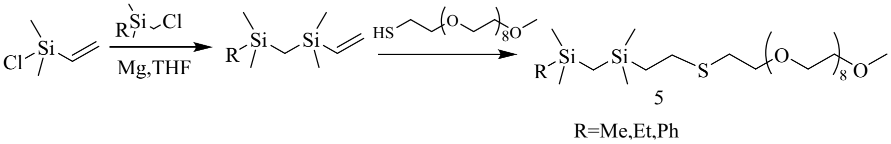
In another study, the hydrophobic groups of carboxylate-based silicone surfactants were synthesized through alcoholysis–hydrolysis reaction and Grignard reaction, respectively (Scheme 6) [69]. The hydrophilic group was introduced via thiol–ene reaction using mercaptoacetic acid as the raw material. Carboxylic-based dicarbonsilane surfactants exhibited smaller CMC values than carboxylic-based disiloxane surfactants. Mass spectrum analysis results indicated excellent stability for carboxylic-based dicarbonsilane surfactants, potentially owing to the lower ionization characteristic of the Si–C bond compared with the Si–O bond.

Polyether-based carbosilane surfactants with various hydrophobic groups were synthesized and examined for their surface activity and aggregation behavior (Scheme 7) [70]. The study revealed that the CMC of these nonionic surfactants decreased while surface tension at CMC increased with an increase in steric hindrance and hydrophobicity. Additionally, aggregate size increased with the increasing hydrophobicity of carbosilane (methyl < ethyl < phenyl).

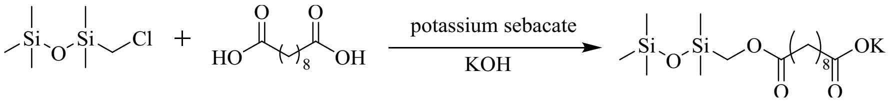
Carmen Racles et al. [71] reported that carboxylate-based silicone surfactants containing ester groups can be synthesized through the reaction of methylpentamethyldisiloxane and pentamethylchloromethyldisiloxane (Scheme 8). This reaction necessitates the use of polar solvents and high-temperature conditions. The



Scheme 6 Synthesis of carboxylate-based silicone surfactants



Scheme 7 Synthesis of nonionic disiloxane surfactants



Scheme 8 Synthesis of carboxylate-based silicone surfactants having ester group

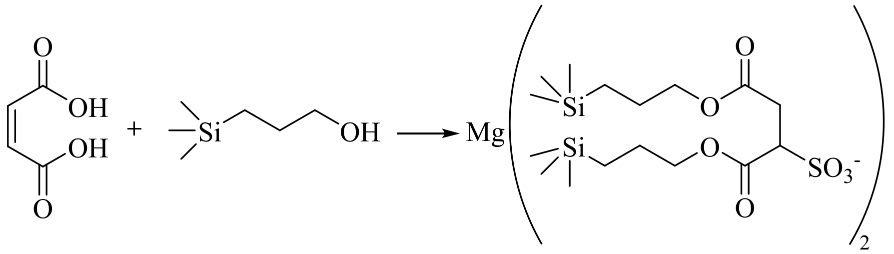
surfactant demonstrates the ability to form a uniform emulsion with polysulfone. However, results obtained from surface tension and DLS analyses indicated that the surfactant exhibited higher CMC values and larger sphericity micelles compared with corresponding bolaform silicone surfactants.

In summary, the synthesis methods for single-chain small-molecule silicone surfactant precursors primarily involve alcoholysis–hydrolysis and Grignard reactions. Hydrophilic groups are introduced through thioesterification reactions and thiol–ene reactions. Further research on cationic and amphoteric single-chain silicone surfactants is warranted.

2.3 Double-Chain Surfactant with Two Hydrophobic Tails and Single Head Group

Double-chain surfactants possess two hydrophobic groups and one hydrophilic group. The hydrophobic effect is more pronounced in double-chain surfactants, resulting in better distribution at the interface [72]. The diversity of double-chain silicone surfactants mainly arises from variations in their hydrophobic tails.

The surfactants with highly branched hydrocarbon chains have been referred to as “hedgehog surfactants” [73]. These surfactants exhibit low surface tension at the air–water interface. This low surface energy is attributed to the higher number density of CH_3 units in the surfactant chains, which helps mimic the density of a liquid alkane surface in the surfactant hydrophobic layer [74]. Kovalchuk et al. [75] reported a novel branched trimethylsilyl (TMS) hedgehog surfactant and investigated its superspreading performance on a hydrophobic polyvinylidenefluoride substrate (Scheme 9). The spreading performance and surface activity (γCMC = 21.8 mN/m) of the hedgehog surfactant with TMS tails were found to be similar to those of trisiloxane surfactants. Additionally, the hedgehog surfactant with TMS tails exhibited better hydrolysis resistance compared with trisiloxane surfactants. When compared with common hedgehog surfactants, it is evident that the surface activity of TMS



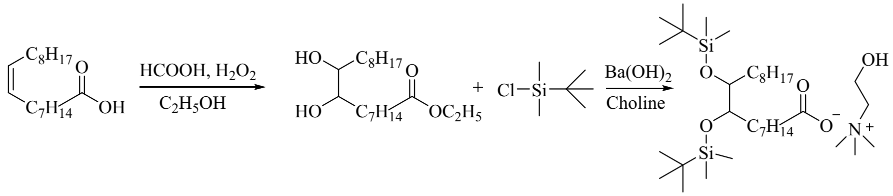
Scheme 9 Synthesis of trimethylsilyl hedgehog surfactants

tail-based surfactants is significantly higher than that of CH_3 tail-based surfactants [73].

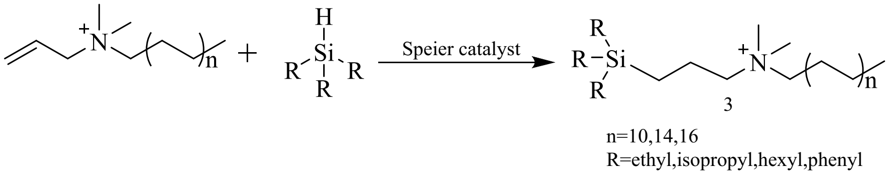
Zhihao Xu et al. [76] developed a dihydroxylation compound from natural oleic acid using hydrogen peroxide and formic acid, followed by the introduction of silyl groups through an alcoholysis reaction (Scheme 10). The presence of silicon branches leads to a decrease in the CMC and the γCMC of the corresponding surfactant, promoting thermodynamically favorable micellization and adsorption. Additionally, results from DLS and TEM indicated the formation of vesicles at low concentrations. However, foam measurements revealed no foaming property in the hybrid silicon-based surfactant.

In another study, carbosilane quaternary ammonium surfactants with different hydrophobic carbosilane structures and varying hydrocarbon chain lengths were synthesized via hydrosilylation reaction, and their surface activity was investigated (Scheme 11) [77]. These carbosilane surfactants exhibited lower CMC values compared with conventional quaternary ammonium hydrocarbon surfactants. The length of the hydrocarbon chain and the hydrophobic groups significantly influenced the CMC values.

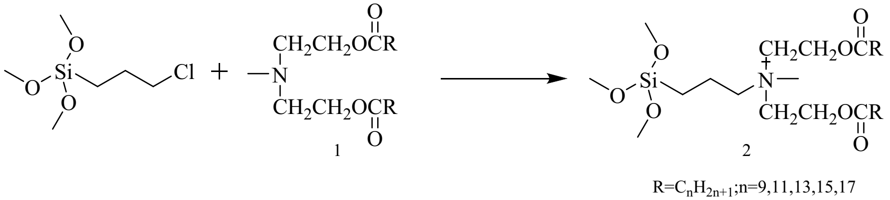
A series of cationic silicone surfactants containing esters with varying alkyl chain lengths has been synthesized via nucleophilic substitution reactions and characterized for both surface activity and antibacterial properties (Scheme 12) [78]. The



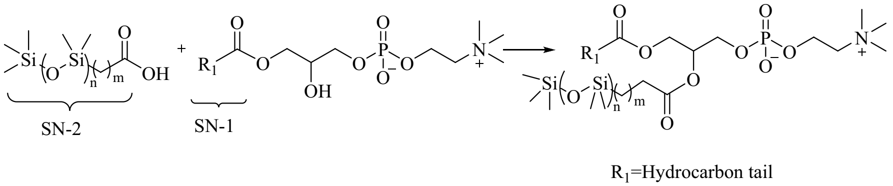
Scheme 10 Synthesis of hybrid silicon-based surfactant



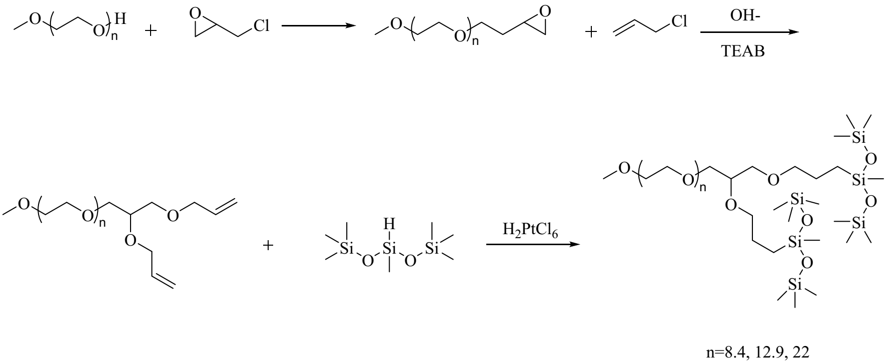
Scheme 11 Synthesis of carbosilane quaternary ammonium surfactants



Scheme 12 Synthesis of quaternary ammonium silicone surfactant with diester group



Scheme 13 Synthesis of hybrid siloxane phosphorylcholines

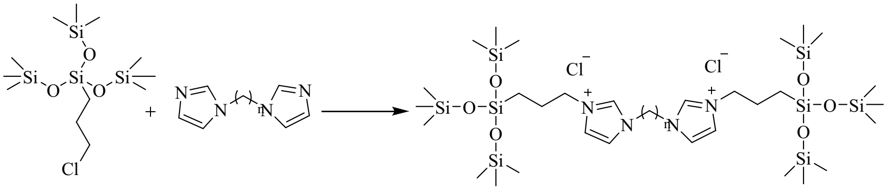


Scheme 14 Synthesis of double-tail trisiloxane surfactants

surface activity of these surfactants significantly increases with longer hydrophobic tail lengths. TEM revealed spherical or ellipsoidal aggregates with diameters ranging from 300 to 900 nm. Assessment of antibacterial activity demonstrated varying degrees of effectiveness against Gram-positive bacteria. However, the methoxy group attached to the silicon atom is prone to hydrolysis, forming hydroxyl-containing disiloxane compounds. Enhancing the stability of silicon atoms can be achieved by forming Si–N coordination bonds during the preparation of cage-type silatranes [79].

Hybrid siloxane surfactants, consisting of one hydrocarbon chain and one siloxane chain, have been synthesized and characterized using small-angle X-ray scattering (SAXS) and electron microscopy (Scheme 13) [80, 81]. The SN-1 fatty acid chain lengths ranged from C8 to C14, resulting in the formation of monolayer vesicles. Extending the chain length to C16 and C18 at the SN-1 position led to the formation of mixtures of unilamellar and multilamellar vesicles. The presence of mixtures in vesicle formation can be attributed to the dominance of the disiloxane fatty acid properties when the SN-1 chain length exceeds 16.

Double-chain trisiloxane surfactants with varying polyether hydrophilic groups have been synthesized, and double-chain trisiloxane hydrophobic groups have been introduced through hydrosilylation reaction (Scheme 14) [82]. The CMC values and the corresponding γCMC values of these double-chain trisiloxane surfactants increased with the degree of polymerization of polyoxyalkylene. Notably, the double-chain surfactant ($n = 8.4$) exhibits potential application as a wetting or



Scheme 15 Synthesis of Gemini imidazolium surfactants

spreading agent in extreme pH environments. Furthermore, double-chain trisiloxane surfactants, comprising one hydrocarbon chain and one siloxane chain, were synthesized through nucleophilic substitution reaction [83]. Their superior resistance to hydrolysis was observed compared with corresponding single-chain trisiloxane surfactants [72].

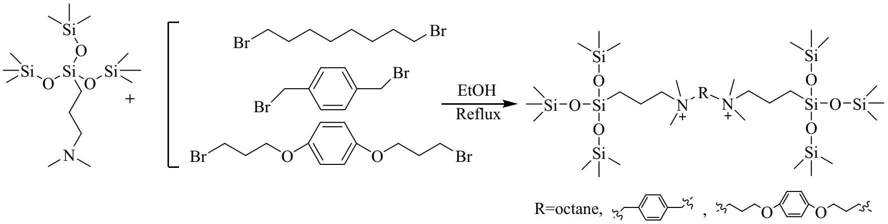
In summary, double-chain siloxane surfactants can be classified into two categories: those with two siloxane tails and those with a hybrid siloxane tail featuring one siloxane tail and one hydrocarbon tail. The incorporation of silicon effectively enhances the physicochemical properties of these surfactants.

2.4 Gemini Surfactants with Two Hydrophobic Tails and Two Hydrophilic Head Groups

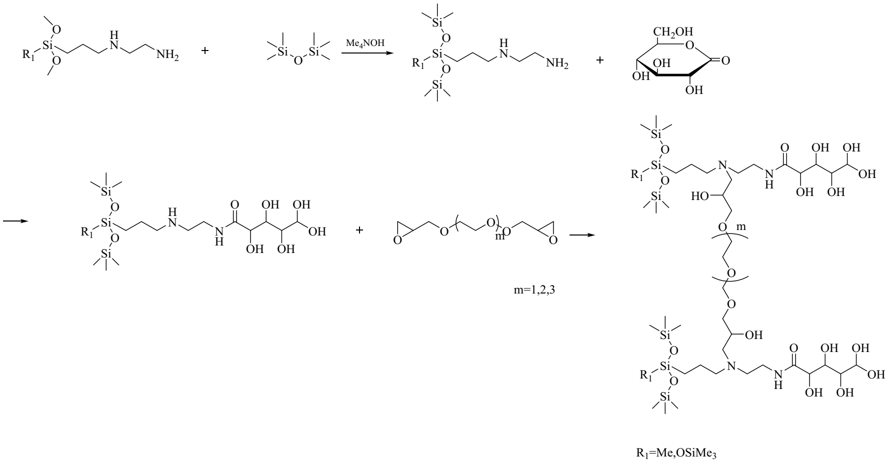
Gemini surfactants consist of two hydrophobic chains and two polar head groups covalently linked by a spacer [84]. These surfactants exhibit significantly low CMC values, enhanced solubilization power, and improved wetting and foaming properties compared with single-chain surfactants.

Nucleophilic substitution reactions are commonly employed for the preparation of Gemini surfactants. The extent of such reactions relies on the nucleophiles' activity and steric hindrance. Xiaohui Zhao et al. [85, 86] conducted a study where they synthesized a range of Gemini imidazolium surfactants with varying spacers and subsequently characterized their physicochemical properties (Scheme 15). They found that substituting chlorine atoms with iodine atoms using NaI enhanced the reaction activity. These surfactants exhibited superior surface properties compared with their corresponding single-chain counterparts. The results indicated that Gemini imidazolium surfactants with longer spacer groups had a higher capacity to form micelles but lower efficiency in reducing surface tension.

Tetrasiloxane Gemini surfactants, featuring three rigidity spacers, were synthesized and analyzed for their surface activity, aggregation behavior, and antibacterial activity (Scheme 16) [87]. The study revealed that the self-aggregation, wettability, and antibacterial activity of these surfactants depended on the rigidity of the spacer. Additionally, a Gemini-type structure, (1,6-bis(diethyl(3trimethoxysilylpropyl)ammonium) hexane bromide), was prepared via a simple synthesis route [88]. This Gemini surfactant, possessing double hydrolyzable $RSi(OMe)_3$ properties, was utilized as the mesoporogen for the synthesis of hierarchical porous ZSM-5 zeolite.



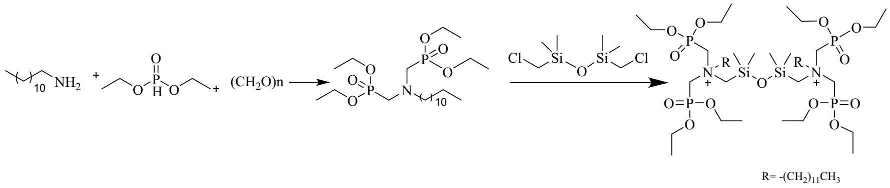
Scheme 16 Synthesis of tetrasiloxane Gemini surfactants with different spacers



Scheme 17 Synthesis of sugar-based Gemini siloxane surfactants

A series of sugar-based Gemini surfactants was synthesized through regioselective ring-opening of ethylene glycol epoxides by glycol diglycidyl ether (EO) and a twofold mole of sugar-based siloxane (Scheme 17) [89, 90]. Results from equilibrium surface tension studies revealed that these Gemini surfactants exhibit two CAC values. This behavior is attributed to the formation of premicellar aggregates preceding the formation of true micelles. TEM measurements demonstrated the ability of these Gemini surfactants to form vesicles in aqueous solutions [91]. Furthermore, the introduction of a $(EO)_m$ spacer chain at the head group induces a significant effect on the size of the aggregates.

Disilyl-tail Gemini surfactants are more common, but there are relatively few reports on the structure of siloxane-bridged groups. In 2004, Gemini surfactants with different siloxane moieties in the spacer were synthesized and utilized as organic templating agents to prepare highly stable mesoporous metal oxides [92]. However, their physicochemical properties were not thoroughly investigated. Recently, our group reported the synthesis of phosphate Gemini surfactants with disiloxane as the bridging group, characterized by tensiometry, DLS, and thermogravimetric analysis (TGA) (Scheme 18) [93]. The CMC of the Gemini



Scheme 18 Synthesis of phosphate Gemini surfactants

surfactant was found to be low compared with a double-chain surfactant with one hydrocarbon chain and one trisiloxane chain. Additionally, the Gemini surfactant exhibited good air–liquid interfacial activity at high temperatures and high concentrations of electrolytes (NaCl, $CaCl_2$, and $MgCl_2$). TGA results indicate that the compound is thermally stable up to 175°C, although slightly less so than the corresponding double-chain surfactant.

Currently, research on small-molecule silicone Gemini surfactants primarily focuses on methylated siloxane hydrophobic groups. Further exploration is needed to understand the influence of electrolytes on such surfactants and the performance of nonmethylated Gemini silicone surfactants.

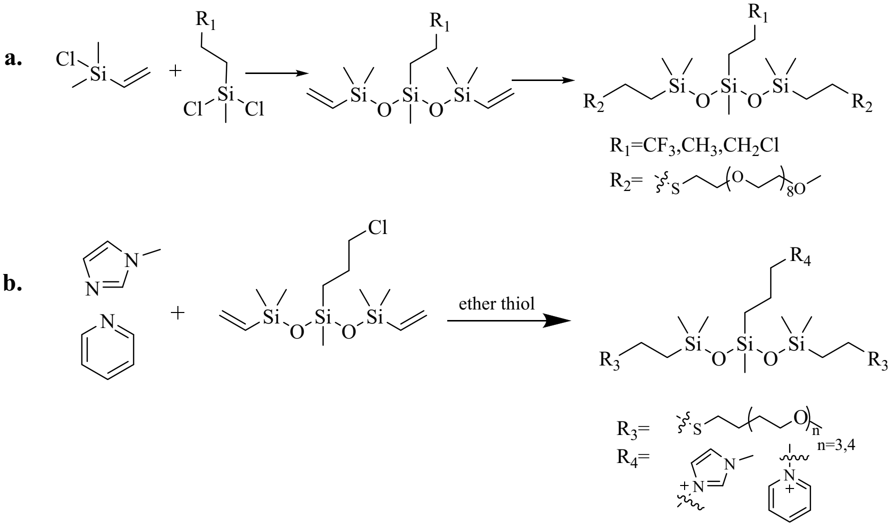
2.5 Bolaform Surfactants Contain Polar Head Groups at Both Ends of a Long Hydrophobic Chain

Bolaform surfactants constitute a series of surfactants characterized by two polar heads connected by one or two long hydrophobic spacers [94]. A single solution of a bolaform surfactant exhibits poor surface activity owing to the reverse U-shaped conformation of the bolas at the air–water interface, where both polar ends must attach to water while the hydrocarbon spacers protrude into the air.

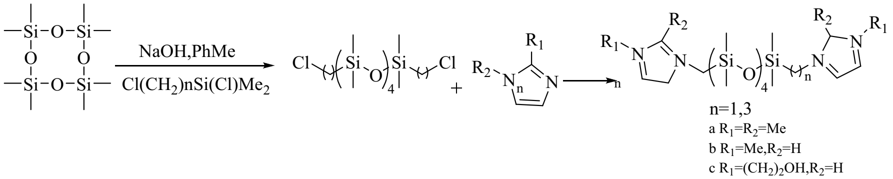
Jinlin Tan et al. [95] synthesized three nonionic bolaform surfactants with terminal groups (CH_3-, $ClCH_2$–, and CF_3–) positioned in the middle of trisiloxane (Scheme 19a). These surfactants underwent characterization via surface tension analysis, DLS, FF-TEM, and TEM. The γCMC values increased with the addition of terminal groups (intermolecular force and molecular volume of $CH_3– < ClCH_2– < CF_3–$). The TEM and FF-TEM results illustrated that nonionic bolaform surfactants could form spherical aggregates of nonuniform sizes.

Subsequently, imidazolium/pyridinium head groups were incorporated into nonionic bolaform surfactants with chlorine terminal groups (Scheme 19b) [96]. The CMC values of the resulting amphoteric surfactants, containing imidazolium head groups, decreased with decreasing EO segments, and their micellization process was enthalpy driven. The γCMC values of these surfactants exceeded 30 mNm^{-1}, surpassing those of permethyltrisiloxane surfactants (approximately 20 mNm^{-1}).

Krasovskiy et al. [97] reported the synthesis of bolaform imidazolium surfactants (Scheme 20). The main challenge in the synthetic route was the production of the dichlorosiloxane compound. Siloxane intermediates with varying Si–O chains could be obtained by hydrolyzing cyclic siloxane with NaOH and



Scheme 19 Synthesis of multipolar head-based bolaform silicone surfactants

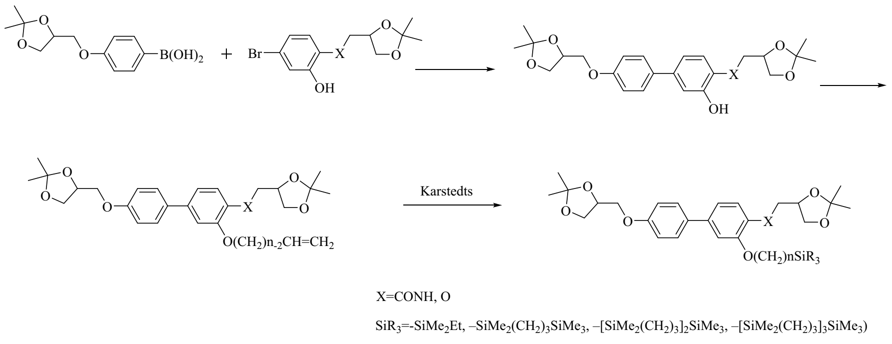


Scheme 20 Synthesis of bolaform imidazolium surfactants

subsequently reacting it with a capping agent [98]. These surfactants were characterized by low glass-transition temperature, low viscosity, and high thermal stability. Additionally, pentasiloxane imidazolium surfactants exhibited greater hydrolytic stability compared with analogous disiloxane surfactants owing to the lower influence of imidazolium cations on the polarity of siloxane bonds.

T-shaped bolaform surfactants with terminal diol groups and laterally attached oligo(siloxane) and carbosilane units were synthesized and investigated for their self-assembly into liquid-crystalline superstructures (Scheme 21) [99]. A hexagonal cylinder phase and three distinct types of lamellar phases were observed. The authors noted that the silyl units organized into distinct compartments either within columns or between layers. The silyl units in these surfactants were the primary reason for the lower transition temperature compared with analogous fluorinated compounds.

Owing to the complexity of the synthesis procedure, there are few literature reports regarding the physicochemical behavior of such surfactants.

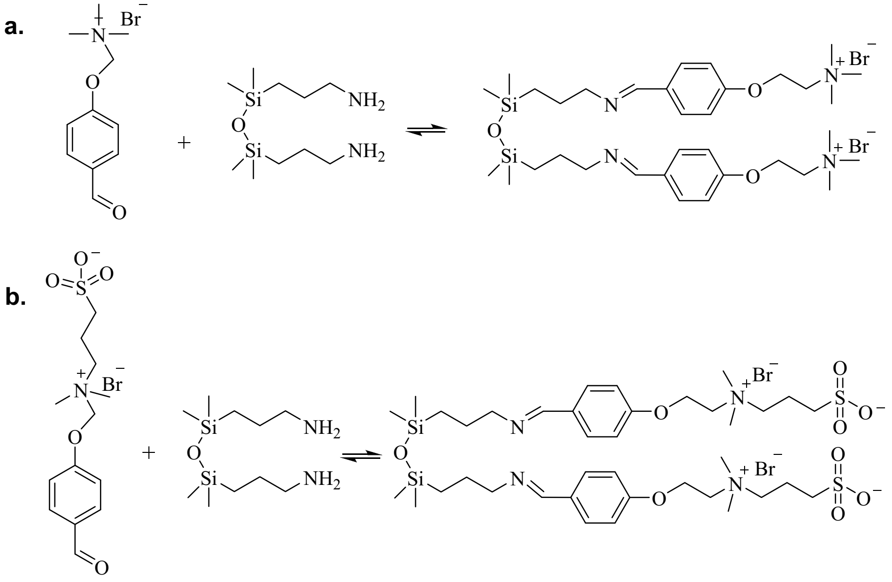


Scheme 21 Synthesis of T-shaped bolaform surfactants

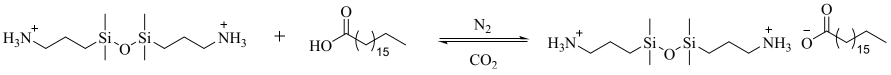
2.6 Stimulus-Responsive Silicone-Based Surfactants

A responsive surfactant is an amphiphilic molecule capable of realizing multifunctional self-assembly to achieve switchable behavior, as its interfacial activity can be modulated by external triggers such as pH, redox, and CO_2/N_2 [100].

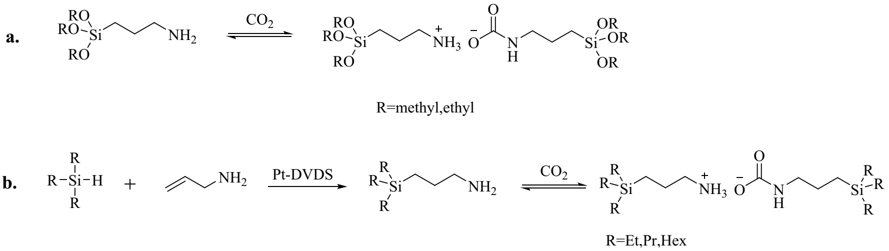
pH-responsive surfactants attract great interest owing to their potential applications in many fields. Meng Mu et al. [101] reported that pH-responsive surfactants are formed by pH-stimulated dynamic imine bonds (Scheme 22a). The results demonstrated that a traditional one-head one-tail silicone-containing surfactant is firstly formed at $pH > 7.0$ and then transforms into a bolaform surfactant at $pH > 9.0$. This type of bolaform surfactant, with two quaternary ammonium groups at $pH > 9.0$,



Scheme 22 Synthesis of pH-responsive silicone surfactant



Scheme 23 Synthesis of CO_2/N_2 response surfactants



Scheme 24 Synthesis of one-component CO_2 responsive ionic liquids

showed excellent foam performance. However, foam stability was found to be sensitive to different electrolytes (NaCl, $CaCl_2$, and $MgSO_4$). The foam exhibited greater stability at higher electrolyte concentrations ($t_{1/2}=0.5$–20 h) owing to a microstructure transition from low-viscosity spherical micelles to high-viscosity rod-like micelles.

Sulfobetaine surfactants are generally considered to have good salt resistance. To address concerns about salt tolerance with responsive surfactants, sulfonic acid groups were introduced into aromatic aldehydes to prepare responsive surfactants (Scheme 22b) [102]. The results showed that the interfacial tension and emulsion oil droplets of responsive surfactants with sulfonic acid groups were influenced by electrolytes (NaCl and $CaCl_2$).

CO_2-responsive surfactants exhibit selective surface activity, which can be activated or deactivated by either adding or removing CO_2 from the solution. A novel CO_2/N_2-responsive surfactant was synthesized using oleic acid and 1,3-Bis(aminopropyl)tetramethyldisiloxane, assembled based on electrostatic interactions (Scheme 23) [103]. This surfactant demonstrates superior interfacial activity compared with previous CO_2/N_2-responsive surfactants. The author observed that oil-in-water (O/W) emulsions stabilized by the responsive surfactant exhibited excellent stability, lasting for more than 60 days. Additionally, the CO_2/N_2-responsive surfactant demonstrated rapid and highly efficient switching behavior.

Compared with two-component response surfactants, one-component response surfactants offer a simpler and cleaner system [104]. One-component CO_2-responsive ionic liquids, derived from alkoxysilylamine and silylamine precursors, were synthesized and investigated for their separation and physicochemical properties (Scheme 24a) [104]. The incorporation of silicon into the surfactant structure introduces weak Lewis acid functionality, subsequently altering the solvent's physical properties. One potential application of CO_2-responsive ionic liquids derived from alkoxysilylamine precursors could be in the recovery of alkanes from heavy crude oil. However, owing to the presence of reactive alkoxy groups, these

CO_2-responsive ionic liquids may not perform well in environments with high water concentrations. To address this issue, Amy et al. [105] synthesized and evaluated the properties of silylamine reversible ionic liquids (Scheme 24b). The results showed that CO_2-responsive ionic liquids derived from silylamine precursors exhibit good stability [106]. The viscosity, density, and polarity of these surfactants can be effectively tuned by changing silane substituents [107].

In summary, the stimulation response mechanism primarily relies on pH and CO_2/N_2 stimulation responses. However, the Si–O bond is susceptible to breaking under extreme pH conditions, resulting in fewer response cycles. Therefore, it is necessary to develop other response methods to either reduce the interference of Si–O bonds or improve the stability of molecules.

3 Applications

Silicone surfactants exhibit favorable characteristics such as good wettability, surface activity, foaming, and emulsification properties [9]. The structural variability within silicone surfactants allows for customization to achieve specific physical and chemical properties tailored to particular applications. This section explores the diverse applications of silicone surfactants.

3.1 Agricultural Synergism

Trisiloxane surfactants have proven effective in agricultural practices, primarily owing to their exceptional wetting and superspreading capabilities. These properties make them valuable in various agricultural applications including the application of fungicides, insecticides, nutrients, growth regulators, and other applications related to plant leaves [9].

Pesticide efficacy plays a pivotal role in augmenting agricultural productivity and efficiency. However, the presence of a hydrophobic waxy layer on plant leaves can impede the diffusion of chemical agents [108]. Trisiloxane surfactants play a crucial role in enhancing the properties of pesticide formulations, facilitating improved adhesion, spreading, wetting, and penetration of pesticides onto plant surfaces. Furthermore, research indicates that polyether trisiloxane surfactants exhibit minimal mobility in soil [109], thereby exerting little impact on the environment. Nonetheless, it is observed that trisiloxane surfactants undergo degradation under acidic or alkaline conditions during application. Strategies to enhance the hydrolysis resistance of trisiloxane surfactants include the introduction of large substituents at the silicone tail, construction of double tails, and polyether capping [82]. Additionally, transitioning the hydrophobic tail group from a Si–O–Si chain to a Si–C–Si chain effectively improves stability but may lead to a decrease in surface activity [69].

Currently, researchers are primarily focused on developing sustainable preparation processes and response systems. One common method for preparing siloxane surfactants is through Pt-catalyzed hydrosilylation reactions. However, these homogeneous catalysts, particularly Speiers and Karsteds catalysts, pose challenges due to their difficulty in separation from the reaction mixture, making recycling and reuse arduous. Huilin Xie et al. [110] reported the utilization of chitosan-modified nanoporous silica supported platinum as catalysts for hydrosilylation reactions, resulting in a 94% yield of polyether trisiloxane surfactants. Furthermore, the catalysts were easily recyclable, retaining over 90% conversion after six reutilization experiments. The prepared trisiloxane surfactants significantly enhanced herbicide activity.

Avermectin exhibits broad insecticidal action but has low water solubility [111]. Xiyang Zhou et al. [112] prepared avermectin microemulsions using glucosamine tetrasiloxane surfactants. Performance test results demonstrated good wettability and low surface tension. The development of a highly efficient, low-toxicity, and environmentally friendly microemulsion for avermectin is crucial. In addressing the inefficient use of pesticides, Ming Zhao et al. [113] reported the synthesis of carboxymethyl chitosan grafted trisiloxane surfactant nanoparticles with pH sensitivity for sustained release of pesticides. The authors observed that the formation of nanoparticles through avermectin encapsulation effectively reduced avermectin decomposition under ultraviolet (UV) irradiation. While avermectin-encapsulated nanoparticles exhibited different sustained release rates under varying pH conditions, they did not significantly affect insecticidal activity. In conclusion, nanopesticide materials could effectively enhance pesticide performance.

3.2 Mineral Flotation

Flotation is an interfacial separation technology based on surface wettability differences of fine particles [114]. In the flotation process, the addition of surfactants could significantly improve separation efficiency by rendering the surface hydrophobic and affecting the bubble–mineral attaching kinetics. Siloxane-based materials are widely utilized as collectors and frothers [115, 116].

Typically, cationic surfactants are employed in mineral flotation due to electrostatic attraction [117]. Compared with hydrocarbon surfactants, cationic trisiloxane surfactants exhibit excellent performance in smithsonite flotation [118]. This can be attributed to the unique structure of trisiloxane, which features two coordination groups ($–NH_2$ and –NH–) and an “umbrella” shape of $–OSi(C_2H_5)_3$. Results obtained from zeta potential tests, X-ray photoelectron spectroscopy, and density function theory calculations indicate that the adsorption mechanism of trisiloxane surfactants on smithsonite surfaces primarily involves chemiadsorption and electrostatic adsorption.

In another study, heptamethyl trisiloxane surfactants were utilized as collectors to float wolframite and scheelite from calcite [119, 120]. These studies concluded that trisiloxane surfactants offer advantages such as low dosage, high selectivity, strong adaptability, and environmental friendliness compared with conventional surfactants. However, trisiloxane surfactant performance was found to be influenced by pH during the flotation process [118]. Therefore, Zhiqiang Huang et al. [120] synthesized Gemini trisiloxane surfactants and investigated their efficacy in the flotation of aluminosilicate minerals. Microflotation tests revealed that increasing pH had a minor influence on collecting performance, as the floatability of kaolinite, pyrophyllite, and illite varied only slightly even at pH > 10.

Further research is warranted to explore the potential of nonmethylated trisiloxane surfactants in flotation processes.

3.3 Drug Delivery

A drug delivery system serves as an excipient or carrier to minimize drug loss and enhance the therapeutic effects in pathological areas [121]. Surfactants are frequently utilized in drug delivery as they can self-assemble into various structures such as micelles and vesicles.

Siloxane materials have emerged as one of the most widely used biomaterials in the medical and healthcare industries [122]. This is due to their unique properties and excellent biocompatibility. Various structures of self-assembling siloxanes have been investigated for their potential applications in health and environmental contexts [122, 123]. Research results indicate their effectiveness in stabilizing polymer nanoparticles for drug delivery systems and encapsulating hydrophobic drugs through micellar solubilization. However, it should be noted that pyridyl siloxane surfactants exhibit low biocompatibility and may function as phase transfer agents. Considering that the polydimethylsiloxane component of the surfactant is readily permeable to drug diffusion, Nandhibatla et al. [124] reported that silicone surfactant micelles, in the presence of hydrocarbon surfactants as additives, act as effective drug carriers. The drug diffusion coefficient values were found to increase with the concentration of hydrocarbon surfactants. DLS studies revealed a decrease in the size of silicone surfactant micelles in the presence of hydrocarbon surfactants, attributed to the dissolution or destabilization effect on the micelles by the hydrocarbon surfactants. Furthermore, Lu Tong et al. [125] successfully developed supramolecular hydrogels using α-cyclodextrin and nonionic trisiloxane surfactants, which were characterized by their phase behavior and stability. The findings suggest that the hydrophilicity of the trisiloxane surfactant plays a crucial role in the formation and high stability of the hydrogels. In vitro studies demonstrated that these hydrogels could serve as injectable drug carriers with controlled release characteristics.

Liposomes have been demonstrated to be highly effective for the controlled release of therapeutic drugs. However, the small size required for preparing liposome formulations necessitates extrusion or ultrasonic treatment. Double-chain trisiloxane phosphocholine surfactants form nearly monodisperse vesicles without the need for secondary extrusion treatment [126]. According to SAXS measurements, trisiloxane phosphorylcholine surfactants exhibit similar bilayer structures to unsaturated phospholipids. Nevertheless, further optimization is needed to align their area per lipid and lipid volume values with those of phosphocholines. Additionally, a class of hybrid siloxane–phosphocholines has been prepared and investigated for their properties as drug delivery vehicles [80, 121]. Notably, nonextruded liposomes demonstrate significant entrapment efficiency and release rates, making these compounds valuable tools for delivering biologically active compounds.

3.4 Tertiary Oil Recovery

Enhanced oil recovery encompasses techniques such as CO_2 gas flooding and surfactant flooding. Siloxane surfactants can serve as thickeners, displacing agents, and foaming agents in enhanced oil recovery processes [127].

In CO_2 gas flooding, additives are utilized to increase the viscosity of CO_2 to prevent gas escape [128]. Siloxanes exhibit better compatibility with CO_2 compared with hydrocarbons. Mark et al. [129] synthesized a variety of siloxane thickeners from cycloamide and found that increasing the number of silicon atoms in linear siloxane segments improved solubility in dense CO_2. Branched siloxane segments were observed to have superior dissolution properties in dense CO_2 compared with linear siloxanes. Among these, propyl (trimethylsiloxane)-functionalized phenyltriurea and different proportions of propyl (trimethylsiloxane) silane and propyldimethylsiloxane butyl-functionalized triurea showed significant viscosity increase.

Surfactant flooding enhances the displacement of crude oil from pores through various techniques, such as reducing interfacial tension and altering wettability [130]. Jingjing Li [131] found that imidazolium surfactants containing silicomethyl exhibit greater surface activity compared with conventional imidazolium surfactants. The combination of sodium fatty alcohol polyoxyethylene ether sulfonate and silicon-containing ionic liquids at a mass ratio of 2:1 can reduce interfacial tension to 10^{-2} mN/m, with excellent stability of the combination system. Our group [93] reported on two phosphate siloxane surfactants with good interfacial activity and thermostability. Additionally, their surface activity remains largely unaffected by salt concentration (NaCl, $CaCl_2$, and $MgCl_2$) and high temperatures, suggesting suitability for high-temperature and high-salinity reservoir environments to enhance oil recovery.

Currently, there is limited research on small-molecular silicon surfactants in enhanced oil recovery. Thermal stability and high salinity pose challenges to the application of small-molecule silicone surfactants in oil fields.

3.5 Separation and Extraction

Extraction and separation are widely employed in industries. Given factors such as energy consumption and environmental pollution, there is significant value in developing new separation materials [132].

The unique structure and interfacial activity of "umbrella" structure silicone surfactants give them distinct extraction capabilities compared with ordinary hydrocarbon surfactants. The extraction behavior of two cationic tetrasiloxane surfactants was investigated in chloroform [36]. Results indicated their ability to extract Au(III) and Pd(II). In another study, an ionic liquid-type imidazolium tetrasiloxane surfactant formed a stable microemulsion when combined with *n*-heptane, *n*-hexanol, and NaCl [133]. The microemulsion functioned via an ionic-exchange mechanism, confirmed by the Job method and analyzed through Fourier-transform infrared spectra. This microemulsion efficiently extracted Pd(II), with an extraction percentage of up to 98%. The addition of NaCl successfully stripped Pd(II) from the microemulsion phase.

Polymer sponges, such as polyurethane, melamine, and silicone, have garnered significant attention as potential oil-absorbing materials. The surface properties of the sponge can be adjusted using hydrophobic materials to enhance adsorption selectivity. Trisiloxane-modified melamine sponges have been prepared via the formation of a polydopamine layer with nanoaggregates and the covalent grafting of 3-mercaptopropyltrisiloxane [134]. The hydrophobic groups of trisiloxane effectively improved the hydrophobicity of the sponge, with the water contact angle reaching 139.3°. Furthermore, the sponge exhibited a three-dimensional hierarchical structure with a high density of nanoaggregates on the interconnected skeleton of melamine sponges, which are crucial factors contributing to its excellent adsorption capacity and ease of reusability.

In another study, responsive silylated amine molecular liquids were designed for extracting hydrocarbons from tar sands/oil shale [106]. Crude oil and silylated amine precursors produced a product stream with less than 4 mol% contamination. Additionally, the silylated amine remained stable for 2 months in all atmospheric conditions measured. Scale-up simulations have demonstrated that the responsive ionic liquids can not only capture CO_2 but also recover hydrocarbons, offering significant profit potential and environmental benefits.

3.6 Foam Fire-Fighting

Aqueous film-forming foam is widely used as an effective method to extinguish liquid fires owing to its advantages of fast foam spread, dense foam layer, and strong self-sealing ability [135]. During the fire extinguishing process, the extinguishing agent is almost entirely absorbed by soil and surface water, necessitating consideration of the toxicity and biodegradability of the fire extinguishing agent.

The siloxane surfactant can effectively enhance the interfacial activity of water and stabilize foam when combined with hydrocarbon surfactants. It represents an ideal alternative to fluorocarbon surfactants, thereby indicating a promising research and development direction for the creation of green and environmentally friendly fire extinguishing agents.

Recent studies have revealed that nonionic heptamethyltrisiloxane surfactants demonstrate fire-extinguishing performance comparable to fluorocarbon surfactants in foam fire extinguishing. The thermal stability and mechanical durability of foam play pivotal roles in the effectiveness of fire extinguishing. Introducing silica nanoparticles has been identified as a method to effectively enhance the thermal stability and durability of foam [136]. Youjie Sheng et al. [137] conducted research where they prepared foam dispersions containing SiO_2, silicone, and hydrocarbon surfactants. They systematically investigated the impact of SiO_2 concentration on foam stability at various temperatures. The results indicated that the thermal stability of the foam is closely correlated with both SiO_2 concentration and temperature. Incorporating a high concentration of SiO_2 resulted in a slower drainage rate under thermal radiation and extended the coarsening time of the bubbles. Notably, when the concentration of SiO_2 reached 3 wt%, the coarsening time of the foam was significantly prolonged.

Considering the susceptibility of these compounds to high-temperature decomposition during fire extinguishing, evaluating the potential environmental impact of their thermal degradation products becomes essential. A study by Brian et al. [138] focused on the thermal degradation of polyether trisiloxane and revealed that all free radical intermediates originated from polyethylene glycol chains, irrespective of the pathway and temperature. These intermediates predominantly formed stable polydimethylsiloxane and minor organic compounds such as ethylene, formaldehyde, and acetaldehyde, among others. The environmental impact of these degradation products was found to be less severe compared with fluorine-containing surfactants.

Challenges persist for trisiloxane surfactants in replacing fluorinated surfactants as foam extinguishing agents, particularly regarding foam stability. Anirudha et al. [139] identified oleophobicity as a critical factor in stabilizing foam performance on hydrocarbon fuel oil for perfluoroalkyl surfactants. Therefore, enhancing the oleophobic properties of trisiloxane surfactants is a pressing issue that must be addressed to truly substitute fluorosurfactants. This could be accomplished by avoiding ethoxy as the head group of surfactants and instead employing glycoside, ion, or zwitterionic groups, which may contribute to achieving the desired overall oleophobicity of the surfactants and overcoming the ultimate challenge.

4 Conclusions and Prospects

This paper provides a review of the structural synthesis of small-molecular silicone surfactants and their applications in various fields including agricultural synergism, mineral flotation, drug delivery, separation, foam fire-fighting, and enhanced oil recovery. Active functional groups are incorporated through Si–H, Si–Cl, and Si–O bonds to create corresponding surface-active structures. Small-molecular silicone surfactants exhibit excellent interfacial activity and possess a unique aggregation state. The structural diversity of small-molecular silicone surfactants results in a variety of properties, making them valuable for numerous applications. However, despite the described potential, further in-depth studies are warranted to facilitate more practical applications in the future:

1. Presently, traditional applications of silicone surfactants are abundant, yet there is a scarcity of research on responsive surfactants. Introducing responsive groups such as ferrocene and azobenzene could enable intelligent regulation, thus expanding their utility in drug release, Pickering emulsion, and other fields [140].
2. While there is a considerable body of research on the properties of air–liquid and liquid–solid interfaces, investigations into liquid–liquid interfaces remain relatively scarce. Further exploration of interfacial activity using methods such as interfacial tension measurement could broaden their application scope.
3. Despite theoretical research on unsaturated small molecule siloxane surfactants, there is a dearth of empirical studies. Future endeavors should delve deeper into related research areas. While trisiloxane surfactants have garnered significant

attention in applications, research into other types of applications remains limited. Therefore, there is a need to intensify research efforts in this area.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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