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Synthesis, Surface Properties, and Antibacterial Activity of Novel Ester-Containing Cationic Silicone Surfactants and Their Utilization as Fabric-Finishing Agents

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Abstract In this study, a series of cationic silicone surfactants SiQC_nCl containing ester groups and double longchain alkyls (n = 9, 11, 13, 15, and 17) were synthesized by microwave irradiation and characterized using infrared Fourier transform (FTIR), ¹H nuclear magnetic resonance (¹H NMR), and thermogravimetric analysis (TGA). Surface activity and adsorption of these surfactants were investigated by measuring the equilibrium surface tension. The critical micelle concentration (CMC) decreased with increasing alkyl length of SiQC_nCl at 25 °C and so did the corresponding surface tension at the CMC (γ_{CMC}). The aggregation behavior in aqueous solutions was also investigated systemically through transmission electron microscopy (TEM) and dynamic light scattering (DLS). Spherical or ellipsoidal-like aggregates with diameters ranging from 300 to 900 nm were observed. It is also shown that the cationic silicone surfactants exhibit certain antibacterial properties against Staphylococcus aureus but slightly poor to Escherichia coli. The morphological structure of SiQC15Cl-treated cotton fabrics was observed using scanning electron microscopy (SEM), which showed that the surface became neat and smooth. What is more, the finished cotton fabrics maintained some antibacterial

Supporting information Additional supporting information may be found online in the Supporting Information section at the end of the article.

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² Guangzhou Vocational College of Science and Technology, Guangzhou, Guangdong 510550, China properties with improved softness, which may provide a more comfortable and healthy lifestyle. This work may also be helpful to the design and application of functional cationic silicone surfactants.

Keywords Cationic silicone surfactants · Ester bonds · Aggregation behavior · Performance test · Fabric finishing

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Introduction

In aqueous solution, surfactants can assemble into various kinds of aggregates, such as spherical micelles, ellipsoidal-like micelles, worm-like micelles, and vesicles, and so on (Das et al., 2012; Fang et al., 2017; Yu et al., 2012). The conformations of these highly ordered aggregates are closely related to their wide-ranging applications in many fields. Meanwhile, silicone surfactants are composed of hydrophobic silicon groups that are attached to one or more polar groups. Owing to the low glass transition temperature, flexibility, and low cohesive energy, these novel efficient surfactants have wide industrial applications, such as textile finishing, agricultural adjuvants, paint additives, and emulsifiers in cosmetics (Chen and Mullin, 2015; Lin and Alexandridis, 2002; Peleshchuk et al., 1991).

Over the past few decades, the aggregation behavior in aqueous solutions of silicone surfactants with various chemical structures has received much research attention. Wang et al. have prepared four kinds of novel carbohydrate-modified siloxane surfactants and studied their adsorption and aggregation behavior. The siloxane

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surfactants in aqueous solutions self-assembled into spherical vesicles, indicating that they may have potential application as a microsphere drug-delivery system (Wang et al., 2010, 2011).

Numerous experimental results have showed that common cationic surfactants are not readily biodegradable and create environmental pollution. Since the 1990s, the use of N, N-dimethyl-N, N-dioctadecylammonium chloride (D1821), and Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammoniumchloride (DC-5700) was limited due to pollution in rivers and will gradually be eliminated. The wellknown environmental issues have driven researchers to develop more biodegradable products (Han et al., 2014; Miao et al., 2008). To solve the problem, Sadeghi-Kiakhani and Tehrani-Bagha (2015) and Tehranibagha and Holmberg (2010) have followed the method of adding an easily cleavable bond in the structural design of cationic surfactants. The physical and chemical properties of cationic surfactants containing ester bonds have also been systemically studied.

Consumers' attitude toward hygiene and active lifestyle in recent years has created a rapidly increasing market for antimicrobial textiles. The cross infection of bacteria between people in public areas can be reduced or eliminated by using antimicrobial textiles. The production of antimicrobial textiles is becoming a new important industry (Gao and Cranston, 2008). Lua et al. (2007) synthesized a series of polymeric quaternary ammonium salts with different carbon chain lengths and investigated their bactericidal activities against Gram-positive bacteria (Staphylococcus aureus) and Gram-negative bacteria (Escherichia coli) by minimal bactericidal concentration (MBC) and minimal inhibitory concentration (MIC) tests. The results showed that the cationic surfactants exhibited better antimicrobial activity against E. coli, whereas poorer activity against S. aureus. Feng et al. (2016) reported a water-soluble quaternary ammonium chitosan derivative and was used for durable antibacterial finish of cotton textiles. Gram-positive bacterium (S. aureus and B. cereus) and Gram-negative (E. coli and MRSA) were used to evaluate the antibacterial activity of the treated cotton textiles, which showed that the cotton textiles exhibited a broad spectrum of effectiveness and good durability against the bacterium.

In the present work, we synthesized a series of estercontaining cationic silicone surfactants $SiQC_nCl$ (n = 9, 11, 13, 15, 17) by using microwave irradiation technology. This work will help to understand how the chemical structure (alkyl chain and functional groups) affects the aggregation behavior and application of cationic silicone surfactants. The aggregation behavior and adsorption properties of $SiQC_nCl$ in the aqueous solutions were investigated through static surface tension, transmission electron microscopy (TEM), and dynamic light scattering (DLS). The bactericidal activities of $SiQC_nCl$ were evaluated by MIC and MBC tests against *S. aureus* and *E. coli*. In this study, we also evaluated the cationic silicone surfactants as softeners in fabric finishing. In addition, the solubilization and wettability of cationic silicone surfactants were also investigated, which may have potential application in the other fields related to the colloid and interface science.

Experimental

Materials

3-Chloropropyltrimethoxysilane (CPTMO, 98%), methyldiethanolamine (MDEA, 99%), fatty acid (97%), hypophosphorous acid (H₃PO₂, 50%), and potassium iodide (KI, 99%) were obtained from Shanghai Macklin Biochemical Co., Ltd., Shanghai, China. Isopropanol (≥99%), methanol $(\geq 99\%)$, alcohol polyoxyethylene ether (AEO-3, 98%), phosphate polyoxyethylene nonyl phenol (NP-10P, 98%), polyoxyethylene nonylphenol ether (TX-10, 98%), polyoxyethylene sorbitol monolaurate (Tween-20, Tween-80, 98%), and isomeric alcohol ethoxylates (nonionic surfactants 1310, 98%) were obtained from Tianjin Damao Chemical Reagent Co., Ltd., Tianjin, China. Biochemical reagents, nutritious broth (NB) and nutritious agar (NA), were supplied by Guangdong Huankai microbial Sci. & Tech, Co., Ltd., Guangzhou, China. All reaction solvents were analytical reagents and used without further purification. The water used in the experiments was all doubledistilled water.

Methods

Surface Tension

Static surface tension was measured using a BZY-1 surface tensiometer (Shanghai Hengping Instruments Ltd., accuracy = ± 0.1 mN m⁻¹) by the platinum ring method at 25 °C.

DLS Measurements

DLS was performed using a Zetasizer Nano S90 Particle Analyzer (Malvern Instruments Ltd., Malvern, UK) at a scattering angle of 90°.

TEM Measurements

The morphologies of the aggregates for $SiQC_nCl$ in aqueous solutions (10 mmol L⁻¹) were examined via a JSM-7001F TEM (JEOL, Japan) at 20 kV. The samples were

prepared by placing the solutions on a copper grid. After the pretest, we found that the samples need not to be negative stained and the grids should be dried at room temperature directly.

Wettability Measurements

The wettability of silicone quaternary ammonium salt solutions on the surface of different substrates (including glass, iron, and sweet potato leaves) was characterized by measuring static contact angles. Contact angles were measured at 25 °C using a JC2000D1 optical contact angle goniometer (Shanghai Zhongchen Digital Technology Instruments Ltd.) via the sessile drop method. A solution of quaternary ammonium salt with the same concentration (10 mmol L^{-1}) was first prepared. The pre-prepared substrates were placed on the testing platform and 4 µL of the solutions were dropped on the surface of the substrates and the drop images were recorded using a video camera. The static contact angles were obtained using a software-controlled fitting system.

Measurement of Antimicrobial Activities

MIC test (Li et al., 2016): Aqueous solutions with different concentrations were prepared by dissolving SiQC_nCl into deionized water, respectively. All the glassware and plastic equipment used in the experiments were sterilized in an autoclave at 121 °C for 30 min and all the operations were carried out in a sterile environment. *Escherichia coli* (*E. coli* ATCC25922) and *S. aureus* (ATCC6538) were used as the test organisms. The amount of bacterial colonies in the bacterial suspensions was diluted to 10^5 cfu mL⁻¹ with NA solution [dilution multiple can be calculated by the fitting formulas shown in Fig. S3, Supporting information, according to the absorbance of bacterial suspensions cultured after 24 h]. The aqueous solutions of SiQC_nCl after gradient dilution were added to the tubes and incubated under shaking cultivation (250 r min⁻¹) at 37 °C for 24 h. The lowest concentration with no turbidity was taken as the MIC value.

MBC test (Cui et al., 2015): The mixed solutions of bacterial suspensions and SiQC_nCl aqueous solutions after the MIC test were also used in the MBC test. Ten microliters of the mixed solutions were coated onto the solid agar medium and the minimum concentration of no colony cultivated after 24 h was the MBC value.

Inhibitory zone method: The sterilized agar medium liquid (15 mL) was poured onto the culture dishes and allowed to solidify at room temperature. The suspension of bacteria with a bacterial content of 10^5 cfu mL⁻¹ (10 µL) was uniformly coated on the surface of the agar plate. The treated aseptic fabric samples (diameter = 1 cm) were gently attached to the sterilized medium. All agar culture dishes were incubated at 37 °C for 48 h and the inhibition zone diameters were measured.

Synthesis and Characterization

The silicone quaternary ammonium salts were synthesized by esterification (Step. 1) and quaternization (Step. 2). The synthesis procedure for SiQC_nCl is shown in Fig. 1.

Synthesis of Double-Chain Ester Amine (DCEAC₁₇)

Fatty acids (45.5 g) and the catalyst H_3PO_2 (0.38 g) were added successively to a four-neck flask (250 mL) equipped with a stirring apparatus, thermometer, and condenser at



Fig. 1 Synthetic routes of silicone quaternary ammonium salts

110 °C. Then, MDEA (9.5 g) was dropped slowly over 30 min and the mixture was heated to 190–200 °C for 9–10 h under a nitrogen atmosphere until the acid value was reduced to 5 mg KOH g^{-1} .

Synthesis of Silicone Quaternary Ammonium Salts (SiQC₁₇Cl)

Based on long-term experimental exploration and experience, we found that microwave irradiation has an excellent effect on the quaternization reaction, which can greatly accelerate the reaction rate and increase the yield of the reaction (Cheng et al., 2011; Zheng et al., 2009a, 2009b). Therefore, microwave was also introduced into this study and the method has achieved excellent application effectiveness. A mixture of DCEAC₁₇ (65.2 g), CPTMO (23.8 g), and mixed polar solvent [70 mL, isopropanol/methanol (1:1, by vol)] was added to an autoclave, with KI (0.9 g) as a catalyst. The reaction was maintained at 170 °C for 12 h under the microwave irradiation of 800 W. The crude product was filtered and vacuum distilled to remove the residual solvent. The other SiQC_nCl products were synthesized using a similar method.

SiQC₁₇Cl versions were prepared by adding sufficient stoichiometric molar concentrations of distilled water to SiQC₁₇Cl (0.005 mol) to target complete hydrolysis at 25 °C, with the assumption that negligible amounts of water were produced from condensation. Hydrolysis reactions were conducted at pH = 2.4 by adding 1 N HCl to the distilled water. Condensation reactions were conducted at pH = 8.5 by adding 1 N NaOH to the distilled water. The pH was adjusted while constantly monitoring the pH of the mixture with a combination pH electrode.

FTIR

Infrared Fourier transform (FTIR) spectra were recorded on a Bruker Model Tensor 27 spectrometer using KBr tablets. The infrared spectra of CPTMO, DCEAC₁₇, and SiQC₁₇Cl are shown in Fig. 2a and the infrared spectra of the other silicone surfactants (n = 15, 13, 11, 9) are shown in Fig. S1. The absorption peaks that appeared at 1741 cm⁻¹ represent the —COO— stretching vibration peak and those around 1088 cm⁻¹ represent the stretching vibration absorption peak of Si—OCH₃. The absorption peaks that appeared around 1367 cm⁻¹ represent the C—N characteristic absorption peak.

FTIR spectra of SiQC₁₇Cl after hydrolysis at pH = 2.4and after condensation at pH = 8.5 are shown in Fig. 2b. In the infrared spectrum of $SiQC_{17}Cl$, the absorption peaks that appeared at 1100 cm⁻¹ represent the Si-OCH₃ stretching vibration peak. The product SiQC₁₇Cl had an initial pH of approximately 5.3 and was reasonably stable toward hydrolysis and condensation. After the treatment of acidic solutions at pH = 2.4, the absorption peak that appeared at 950 cm⁻¹ represents Si-OH groups and the absorption peak at 1100 cm⁻¹ became wide, which showed that Si-O-Si groups began to form minimally and the wide peak shielded the absorption peak of Si-OCH₃. After the treatment of alkaline solutions at pH = 8.5, a wider absorption peak appeared at 1100 cm⁻¹, which showed that a large number of Si-O-Si groups formed. Therefore, changes in peaks showed that when the pH was lowered to 2.4, rapid hydrolysis occurred with



Fig. 2 (a) Infrared spectrum analysis of CPTMO, DCEAC₁₇, and SiQC₁₇Cl; (b) FTIR spectra of SiQC₁₇Cl after hydrolysis at pH = 2.4 and after condensation at pH = 7.5

minimal condensation; and when the pH was raised to 8.5, condensation of the silanol groups resulted in the formation of siloxane linkages.

¹H NMR

¹H nuclear magnetic resonance (¹H NMR) spectra were obtained on an AV III, Ascend 500 HD Bruker NMR spectrometer using CDCl₃ as a solvent. The ¹H NMR spectra of CPTMO, DCEAC₁₇, and SiQC₁₇Cl are shown in Fig. 3 and the ¹H NMR spectra of the other products (n = 15, 13, 11, 9) are shown in Fig. S2. The main structure of the intermediate DCEAC₁₇ was retained in the desired product SiQC₁₇Cl. It was worth mentioning that the Si-OCH₃ characteristic peak appeared in the position of shift $\delta = 3.5-3.6$. Therefore, it is inferred that the desired product was successfully synthesized. ¹H NMR (δ , ppm, 500 MHz, CDCl₃, TMS) **CPTMO**: $\delta_{0.69}$ (*m*, SiCH₂, 2H), $\delta_{1.80}$ (*m*, CH₂CH₂CH₂, 2H), $\delta_{3.45}$ (*t*, CH₂Cl, 2H), δ_{3.49} (d, SiOCH₃, 9H); DCEAC₁₇: δ_{0.81} (t, CH₂CH₃, 6H), $\delta_{1,20}$ (d, (CH₂)₁₄CH₃, 56H), $\delta_{1,54}$ (m, O=CCH₂CH₂, 4H), $\delta_{2,24}$ (t, O=CCH₂CH₂, 4H), $\delta_{2,28}$ (s, NCH₃, 3H), $\delta_{2.63}$ (*t*, NCH₂, 4H), $\delta_{4.09}$ (*t*, NCH₂CH₂, 4H); SiQC₁₇Cl: $\delta_{0.81}$ (t, CH₂CH₃, 6H), $\delta_{0.81}$ (m, SiCH₂, 2H), $\delta_{1.17}$ (m, $(CH_2)_{14}CH_3$, 56H), $\delta_{1.55}$ (s, O=CCH₂CH₂, 4H), $\delta_{1.80}$ (m, NCH₂CH₂CH₂, 2H), $\delta_{2.23}$ (t, O=CCH₂CH₂, 4H), $\delta_{2.65}$ (s, NCH₂CH₂CH₂, 2H), $\delta_{3.41}$ (s, NCH₃, 3H), $\delta_{3.50}$ (m, NCH₂CH₂O, 4H), $\delta_{3,60}$ (s, SiOCH₃, 9H), $\delta_{4,11}$ (m, NCH₂CH₂O, 4H).

Results and Discussion

Surface Activities of SiQC_nCl

To establish and compare the aggregation tendency and the ability to decrease surface tension of water, the static surface tension of cationic silicone surfactants (SiQC_nCl, n = 9, 11, 13, 15, 17) in aqueous solutions was measured. Figure 4 shows the surface tension (γ) versus logarithm of concentration $(\lg C)$ for the aqueous solutions of SiQC_nCl at 25 °C. The critical micelle concentration (CMC) and corresponding surface tension at the CMC (γ_{CMC}) for the silicone quaternary ammonium salts are listed in Table 1. In this work, the methoxysilane (Si-OCH₃) of SiQC_nCl would be hydrolyzed slowly into silanol groups (Si-OH) in aqueous solutions, and crosslinked to form siloxane (Si-O-Si) minimally. The results show that at 25 °C, the CMC and the surface tension at the CMC (γ_{CMC}) of SiQC_nCl aqueous solutions decrease with increasing length of hydrophobic chains.

The maximum excess surface concentration (Γ_{max}) and the area occupied by a single amphiphile molecule at the air/water interface (A_{\min}) can be calculated by the Gibbs adsorption isotherm [Eq. 1 and 2], which reflects the arrangement of surfactant molecules at the air/solution interface (Cao et al., 2015). An increase in A_{\min} or a decrease in Γ_{\max} means a denser arrangement of surfactant molecules at the surface of the solution (Gao et al., 2016; Olutaş and Acımış, 2014; Shi et al., 2011). The Gibbs adsorption isotherm equations are shown as follows:



Fig. 3 ¹H NMR analysis of CPTMO, DCEAC₁₇, and SiQC₁₇Cl



Fig. 4 Variation in the surface tension with the surfactant concentration for SiQC_nCl at 25 $^\circ\text{C}$

$$\Gamma_{\max} = -\frac{1}{nRT} \left(\frac{\partial \gamma}{\partial \lg C} \right) \tag{1}$$

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}} \tag{2}$$

where N_A is the Avogadro constant (6.02 × 10²³ mol⁻¹), γ denotes the surface tension, R is the ideal gas constant (8.31 J·mol⁻¹ K⁻¹), T is the absolute temperature (298.15 K), C is the concentration of surfactants in μ mol·L⁻¹, ($\partial \gamma / \partial lgC$) is the slope of the linear fit of the data below the CMC in the surface tension plots, and n is a constant that depends on the number of species constituting the surfactant that is adsorbed at the interface and the value of n in this study is considered to be 2 assuming that there exist only silicone quaternary ammonium salts in the absence of any other solutes.

 pC_{20} is regarded as a measure of the reducing efficiency of surface tension, and a higher value of pC_{20} indicates a greater ability for the reduction of surface tension, which is calculated by Eq. 3 (Rao et al., 2011):

$$pC_{20} = -\log C_{20} \tag{3}$$

where C_{20} is the concentration required to reduce the surface tension of pure water by 20 mN m⁻¹. The values of

 γ_{max} , A_{min} , and pC_{20} were obtained and summarized in Table 1. The structure of the molecules of surfactants affects their aggregation tendency and the surface properties significantly.

There are some important previous studies devoted to the discussion on the validity and application extensions of the Gibbs adsorption equation (Bermúdezsalguero et al., 2012; Bermúdezsalguero and Graciafadrique, 2011; Graciafadrique et al., 2002; Viades-Trejo et al., 2006; Viades-Trejo and Gracia-Fadrique, 2008). It was found that standard energies of adsorption and micellization differ by a positive constant, which provides strong evidence to support that the adsorption process is favored over the micellization process. And it validates that the calculation of surface molecular areas through the Gibbs adsorption equation is valid in the surface-saturated region. Surface saturation must precede micelle formation as demonstrated by a thermodynamic model, suggesting that micelles form as a consequence of surface saturation and that it is not a spontaneous process. What is more, neutron reflectivity together with surface tension experiments also demonstrate that the calculation of surface molecular areas through the Gibbs adsorption equation beyond the CMC is valid (Lu et al., 2000).

As is observed in Fig. 4, surface tension declines rapidly as the concentration increases, which suggests that the surfactant molecules are adsorbed at the interface of air and water. Then, a plateau appears in the $(\gamma - \lg C)$ plot and γ no longer decreases after the CMC meaning that the surface is saturated and the attractive forces are invested in micelle formation. The values of CMC were regarded as the concentrations at the intersection of the two linear regions of the γ -lgC plots (Bowers et al., 2004; Tan et al., 2013). In Table 1, it is shown that from $SiQC_9Cl$ to $SiQC_{17}Cl$, the $\Gamma_{\rm max}$ values increase, while the $A_{\rm min}$ values decrease with increasing hydrocarbon chain length. The pC_{20} values of SiQC_nCl with a longer chain are higher meaning that it has greater ability to reduce the surface tension. In the series of cationic silicone surfactants investigated, molecules with a longer carbon chain length (n = 15, 17) aggregate at lower concentrations, and their surface activity is better than D1821 as well as molecules with carbon chain lengths of

Table 1 Adsorption parameters of SiQC_nCl in aqueous solutions at 298.15 K

	CMC (μ mol L ⁻¹)	$\gamma_{\rm CMC} ({\rm mN} {\rm m}^{-1})$	$\Gamma_{\rm max} \times 10^{-10} ({\rm mol} {\rm cm}^{-2})$	A_{\min} (A ²)	<i>p</i> C ₂₀ 4.35
SiQC ₉ Cl	261.82 ± 3	37.92 ± 0.5	2.99	55.45	
SiQC ₁₁ Cl	81.47 ± 3	36.69 ± 0.5	3.40	48.87	4.71
SiQC ₁₃ Cl	46.67 ± 3	33.31 ± 0.5	3.68	45.16	5.06
SiQC ₁₅ Cl	36.98 ± 3	31.04 ± 0.5	4.20	39.52	5.18
SiQC ₁₇ Cl	21.98 ± 3	29.39 ± 0.5	4.64	35.74	5.52
D1821	44.46 ± 3	37.17 ± 0.5	6.89	24.12	4.98

n = 9, 11, and 13. A longer hydrophobic carbon chain causes the hydrophobic hydration, the driving force for micelle formation, to become stronger. What is more, the increased hydrophobic chain in surfactants becomes more flexible and more easily penetrates into the micelle core (Łudzik et al., 2018).

The surface tension reduction γ_{CMC} is a useful parameter that determines many interfacial properties of surfactants connected with packing density at the air/water interface, such as wettability and foaming properties (Grundke et al., 2008; Lin and Chen, 2006). The lower value of γ_{CMC} is achieved by the cationic silicone surfactants SiQC₁₇Cl and SiQC₁₅Cl with the longer hydrophobic carbon chains. It confirms the general trend that increasing the hydrophobic chain length causes the surfactant to reduce the surface tension to a greater extent (Silva et al., 2013). Comparison with the structure of SiQC₁₇Cl and D1821 indicates that a flexible Si—O—Si group in SiQC₁₇Cl enables the methyl groups to orient in low-energy configurations, with a higher surface activity (Schmaucks et al., 1992).

Results in Table 1 show that the area per molecule at the air/water interface A_{\min} for the cationic silicone surfactants (SiQC_nCl) increases with the increasing length of the carbon chain. And, it is clearly known that Amin of SiQCnCl is larger than that of D1821 ($A_{\min} = 24.12$), indicating a looser arrangement of the cationic silicone surfactant molecules at the air/water interface (Gentle and Snow, 1995). The quite low value of A_{\min} indicates that molecules at the interface are tightly packed. The area per molecule at the air/water interface is a consequence of a competition between attractive interactions from the tendency of nonpolar chains to minimize the contact with polar solvent and repulsive interactions between ionic head groups (Łudzik et al., 2018). The attraction between hydrocarbon tails causes the decrease of the parameter Amin whereas repulsion increases the value of A_{\min} . In our work, cationic silicone surfactant molecules with longer carbon chains (n = 15, 17) show better surface activity, and their performance is superior to that of the conventional surfactant D1821. This can be attributed to the flexible structure of double long chain and the electrostatic repulsion between quaternary ammonium cations, which causes the greater distance between the surfactant molecules and the silanol groups $[-Si(OH)_3]$ to be oriented parallel to the aqueous solution/air interface (Schmaucks et al., 1992; Tan et al., 2013).

TEM and DLS

Above the CMC, surfactants can self-assemble into a variety of ordered aggregates, thus minimizing the interfacial energy in the solutions (Gao et al., 2016; Li et al., 2014). The size of SiQC_nCl aggregates (10 mmol L^{-1}) in aqueous solutions was investigated through TEM and DLS.

Among them, the TEM images of silicone surfactants' aggregates in aqueous solutions are shown in Fig. 5. Spherical or ellipsoidal-like aggregates with diameters ranging from 300 to 900 nm were observed in the solution of silicone surfactants. The different morphologies show that the size of aggregates increases with increasing length of the carbon chain. The diameter of the aggregates is far greater than that of the micelles formed by low-molecular-weight surfactants, which normally lies in the range from 3 to 50 nm. And there was an association formed between the aggregates (Fig. 5a-a' and Fig. 5c-b'), which might promote the reaggregation between aggregates, thus increasing the size of the aggregates. The reason may be that the hydrolysis of trisiloxanes occurring in the aqueous solutions and the Si-OCH3 groups translated into Si-OH groups (Gong et al., 2012). Then, hydrogen bonds were produced and the interaction force increased between surfactant molecules. In addition, the crosslinking reaction of Si-OH between molecules also began to occur slowly. Thus, such an interesting phenomenon occurred. But, the regular aggregate morphology was not observed in D1821 aqueous solution and large groups of amorphous aggregates formed (Fig. 5f). Therefore, it is conjectured that the siloxane of silicone surfactants in aqueous solutions can also give the aggregates a stronger aggregation ability and a stable skeleton structure.

The size distribution of SiQC_nCl aqueous solutions (10 mmol L⁻¹) was investigated through DLS, and the hydrodynamic diameters are shown in Fig. 6. The varied sizes show that the aggregates exhibit monomodal functions. Learning from Fig. 6, we know that the size distribution of silicone surfactant solutions increases with the increase of the concentration (Fig. 6a) and the carbon chain length of SiQC_nCl (Fig. 6b). The particle sizes obtained by DLS measurements were slightly larger than that measured by TEM. It may be owing to the swelling action of aggregates that occurred in the aqueous solutions, which resulted in the increase of the hydrodynamic diameters.

Solubilization Capacity

The solubilization of sparingly soluble or insoluble organic compounds in the micellar solutions is an important application criterion (Paul and Mitra, 2005; Saito and Shinoda, 1967; Yang et al., 2013). As there is no solubilization when the concentration is lower than the CMC, an appropriate concentration of surfactants needs to be selected. In this study, solubilizing capacity was expressed as the amount of benzene solubilized in 10 mL SiQC_nCl solutions (1 mmol L⁻¹). The absorbance of the mixed benzene-surfactant solutions with different concentrations



Fig. 5 TEM images of the aggregates of silicone surfactants in aqueous solutions (10 mmol L^{-1}): (a) SiQC₉Cl, (b) SiQC₁₁Cl, (c) SiQC₁₃Cl, (d) SiQC₁₅Cl, (e) SiQC₁₇Cl, and (f) D1821

[composed of 10 mL SiQC_nCl solutions and benzene with a series of dosage (0.05, 0.1, 0.15, ..., 0.9 mL)] was determined using a ultraviolet-visible (UV-VIS) spectrophotometer and the results are shown in Fig. 7a.

As seen from Fig. 7a, the silicone surfactant with shorter carbon chains (n = 9, 11) shows a better solubilization performance, with a steep fall compared to the surfactants with long carbon chains ($n \ge 13$). It is well known that the essence of solubilization is an insoluble material

solubilizing into a micelle. And the solubilization position of benzene changes with the increase of solubilizing capacity: at first, benzene is adsorbed on the surface of the micelles (Fig. 7b-a'); then partitions into the micellar palisade layer (Fig. 7b-b'); and finally inside the micelles or interspersed with the surfactant molecules in the micelles (Fig. 7b-c'). It is a pity that the long double carbon chains also leads to poor solubility of the organic silicone quaternary ammonium salt itself, due to the lack of hydrophilic



Fig. 6 The size distribution of aggregates formed at 25 °C: (a) SiQC_nCl (n = 11, 17) solutions with different concentrations; (b) 10 mmol L^{-1} solutions of SiQC_nCl with different carbon chain lengths



Fig. 7 (a) Solubility test of benzene in the surfactant solutions; (b) Diagrammatic sketch of the solubilization process

groups. The results also reflect that the rational molecular design with functional groups is necessary and important.

Wettability

The contact angle is an important parameter to indicate the degree of wettability (Chaudhuri and Paria, 2009; Zdziennicka, 2009). A larger contact angle corresponds to lower wettability. The essence of wetting is liquid adherence to the solid surface (Salehi et al., 2008; Zdziennicka, 2010). A series of silicone quaternary ammonium salt solutions (10 mmol L^{-1}) were prepared to test the contact angles on the surface of different substrates. Water was chosen as the standard liquid. The measured contact angles are shown in Fig. 8a. It is shown that the addition of silicone surfactants

to water reduces the contact angles only slightly. The regularity of the results is similar to that shown in solubilization measurements, with short carbon chains (n = 9, 11, 13) showing the lowest contact angles. The cation of the cationic surfactant has a strong electrical effect with the solid surface that is negatively charged in the neutral water or weakly acidic, and the hydrophobic groups on the surface tend to be closely arranged (Fig. 8b). The results also showed that the larger the surface energy of the substrates, the smaller the contact angles with the same surfactant solutions.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is used to study the thermal stability of silicone materials. The changes in the



Fig. 8 (a) The contact angle photos of quaternary ammonium salt solutions (10 mmol L^{-1}) on the surface of different substrates; (b) Diagrammatic sketch of the cationic silicone surfactant adsorbed on the negatively charged surface of the substrates



Fig. 9 TGA and DTG curves of SiQC_nCl

physical and chemical properties of materials are measured as a function of the increasing temperature, which can also provide certain information about chemical phenomena of decomposition (Cui et al., 2015). The cotton fabrics treated with silicone surfactants needed to be cured at 130 °C; thus, the surfactants should exhibit excellent thermal stability to meet the requirements of fabric finishing. It can be seen from Fig. 9 that the thermal stability of SiQC_nCl shows good regularity, which is enhanced with the increase of the length of the carbon chains. Obviously, the thermogram of SiQC_nCl has only one decrease stage, which indicates that the products have a high purity. Along with the rise of temperature, thermal decomposition of long chain with diester groups occurred gradually. The siloxane moiety has partial ionic nature and high bond dissociation energy of the Si–O

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bond. The presence of siloxane groups in SiQC_nCl delays the degradation process, and the thermal stability is strengthened with the length of carbon chains. In addition, the residual ash of up to 500 °C may come from the Si-O bond, which has translated into SiO₂ residue (Schmaucks et al., 1992; Walsh, 1981).

Antibacterial Properties

The bactericidal activities of SiQC_nCl were evaluated by MIC and MBC tests against Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*), respectively. The lower the MIC and MBC values, the higher the antimicrobial activity of the agent. Previous studies have shown that there may exist three processes to inhibit the growth of bacteria or even kill bacteria: (i) cationic groups adsorbed onto the negative surface of bacteria; (ii) organic matter fused with cell wall and gradually penetrated it; and (iii) further combined with the cytoplasmic membrane and destroyed the cell membrane (Cloete, 2003; Liu et al., 2014).

The results of the antimicrobial test are summarized in Fig. 10. The silicone cationic surfactants all had different degrees of antibacterial properties against *S. aureus*, and *E. coli*, but the antibacterial effect on Gram-positive bacteria (*S. aureus*) was stronger than that on Gram-negative bacteria (*E. coli*). And with the carbon number n = 15, the cationic silicone surfactant shows the best antibacterial activity, which is equivalent to that of D1821 (Fig. S4, Supporting information 4).

Of course, the antibacterial properties against different types of bacteria mainly depend on the cell structures of bacteria (Chen et al., 2000; Kavoosi et al., 2013). It is known



Fig. 10 The MIC and MBC values of SiQC_nCl against E. coli and S. aureus

that the positively charged nitrogen atom of the quaternary ammonium salts has antibacterial activity (Rózga-Wijas et al., 2007). Gram-positive bacteria are bound by a comparatively thick cell wall made of peptidoglycan and the negatively charged teichoic acid; while gram-negative bacteria have an outer membrane and multilayer structure, which forms an additional barrier against other molecules (Li et al., 2011). For Gram-positive bacteria, quaternary ammonium salts were typically more easily adsorbed onto the bacteria by the electrostatic attractions between the cationic groups and the negatively charged cell wall, and diffused to the cytoplasmic membrane that would further damage the cell structure (Rózga-Wijas et al., 2007; Temiz et al., 2006). But for Gram-negative bacteria, excessive long carbon chains lead to a poor compatibility and adhesion of antibacterial agents on the surface of the bacteria. Therefore, the bactericidal effect of SiOC_nCl against Gram-negative bacteria was weaker than that on Gram-positive bacteria.

Treatment Process

A suitable emulsifier is essential for the process of the emulsification and the stability of the prepared emulsion. An orientated and accumulated monolayer film should be formed by emulsifier molecules, also with a good mechanical strength on the oil/water interface of the emulsion

droplets (Min et al., 2014). In this study, eight kinds of emulsifiers were selected to meet the requirements of emulsification and the environmental protection (Table 2). Finally, with the excellent performance and a high cloud point (83 °C), nonionic surfactant isomeric alcohol ethoxylates (1310) were used for the emulsification process of cationic silicone surfactant SiQC₁₅Cl. To a conical flask, SiQC₁₅Cl (10 g) and 1310 (1.5 g) were mixed and stirred for 20 min at 65 °C. And then, 5 wt.% HAc solution (4 g) was dripped in drops, which helped to adjust the pH. At last, 235 g of deionized water was added multiple times and homogenized for 20 min in a high-shearing homogenizer (5000 r min⁻¹) at a temperature of 65 °C. A uniform O/W emulsion with white blue light was prepared and used for the fabric-finishing process. The preweighted raw fabrics were soaked in the emulsion (weight ratio, fabrics/ bath = 1: 20) for 30 min at 65 °C and then rolled by the padder. Finally, the impregnated fabrics were dried at 100 °C for 120 s and cured at 130 °C for 90 s. The treated fabrics were kept in a dry container to balance for 24 h.

Scanning Electron Microscopy

Based on the analysis of the experimental results, the cationic silicone surfactant $SiQC_{15}Cl$, which has the best antibacterial properties, was selected for the treatment of cotton

 Table 2
 The effect on the emulsion process of different types of emulsifiers

emulsifier typ	pes	AEO-3	NP-10P	TX-10	1310	Tween-20	Tween-80	m(Tween-20)/m(Tween-80) = 1: 3
Stability	25 °C	_	_	_	_	_	_	-
	65 °C	-	_	+	+	_	_	_
Environment	ally friendly	+	-	-	+	+	+	+

Note: (Good: "+"; Poor: "-").



Fig. 11 (a) SEM photos of raw cotton fabrics and SiQC $_{15}$ Cl-treated cotton fabrics; (b) Bactericidal activities of treated cotton fabrics characterized by inhibitory zone diameters

fabrics. Then, the morphological structure of untreated and SiQC₁₅Cl-treated cotton fabrics were observed using scanning electron microscopy (SEM) (Fig. 11a). The surface of raw cotton fabrics was much rougher than the treated samples and there were more wrinkles on the surface. After treating the cotton fabric samples with the emulsions of SiQC₁₅Cl, a thin smooth film was coated on the surface of fibers and the folds were blocked. Besides, the surface of treated cotton fabrics became neat and smooth, also with an obvious improvement of softness. And the cationic silicone surfactant SiQC₁₅Cl has not affected the hydrophilicity of the fabrics, which can still achieve instant hydrophilicity.

Bactericidal Activities of Treated Cotton Fabrics

The growth and spread of bacteria on the textiles during use and storage negatively affect the wearers' health and comfort. The detrimental effects can be controlled by broad-spectrum antimicrobial finishing agent used in the treatment of textiles. In this study, the bactericidal activities of cotton fabrics treated with quaternary ammonium salts $SiQC_{15}Cl$ were investigated and characterized by inhibitory zone diameters.

against *S. aureus* and *E. coli* can be seen in Fig. 11b. And *S. aureus* is more sensitive to the SiQC₁₅Cl-treated cotton fabrics, followed by *E. coli*. The finished cotton fabrics have maintained some antibacterial properties, which can protect people's health effectively. Figure 12 described the reaction mechanism of the fab-

A large and clear inhibition zone on solid agar medium

ric finishing. Methoxysilane groups of SiQC₁₅Cl are hydrolyzed in the acidic aqueous medium and converted into silanol groups. The as-prepared emulsion is applied to the finishing of raw cotton fabrics. During the curing process, the silanol groups will be converted into siloxane entity and the crosslinking structure of Si-O-Si between molecules is formed at the elevated temperature. Hydrogen bonding, ionic crosslinked, ether crosslinking, and Van der Waals forces are formed between cotton fabrics and the cationic silicone softener. It could be concluded that, post-treatment with SiQC₁₅Cl results in remarkable changes in the surface properties, as confirmed by SEM. The extent of surface modification was expressed as smoothness and disappearing of ditches and grooves, as well as the location, the extent of distribution, and the degree of fixation of SiQC15Cl onto and/or within the cotton fabrics.



Fig. 12 Schematic illustration of film forming of SiQC₁₅Cl on the cotton fabrics

Conclusions

A series of novel cationic silicone surfactants SiQC_nCl (n = 9, 11, 13, 15, 17) containing ester bonds were synthesized using microwave irradiation technology. And the aggregation behavior of cationic silicone surfactants in the aqueous solutions was investigated systemically in this article. The CMC values of SiQC_nCl decreased with increasing length of hydrophobic chains and the corresponding surface tension (γ_{CMC}) also decreased at 25 °C. The morphology and sizes of SiQC_nCl aggregates in aqueous solutions above the CMC were measured through TEM and DLS. Spherical-like or ellipsoidal-like aggregates with diameters ranging from 300 to 900 nm were observed through TEM. It is also shown that the cationic silicone surfactants exhibit different degrees of antibacterial properties against Grampositive bacteria (S. aureus), but slightly poor to Gramnegative bacteria (E. coli). In this study, SiQC₁₅Cl was also used as finishing agents to treat the cotton fabrics and the morphological structure was observed using SEM. The cotton fabrics treated with SiQC₁₅Cl become neat and smooth,

also with an obvious improvement of softness. What is more, the finished cotton fabrics have maintained some antibacterial properties, which can protect people's health effectively. We hope that this work may help to design functional cationic silicone surfactants with novel structures and find more potential applications in colloid and interface science.

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

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