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ORIGINAL ARTICLE

Synthesis and Properties of a Hydrolysis Resistant Cationic Trisiloxane Surfactant

Ru-xian Luo · Ping-ping Liu · Yao-bin Chen

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Abstract In order to improve the hydrolysis resistant ability (HRA) of trisiloxane surfactants, a new kind of quaternary ammonium salt cationic trisiloxane surfactant (QASCTSS) was synthesized in three steps and investigated. The chemical structure of QASCTSS was characterized by Fourier transform infrared spectroscopy and proton nuclear magnetic resonance. Compared with normal trisiloxane surfactants, QASCTSS exhibits a lower surface tension, especially under strong acid or alkaline conditions. This was attributed to the protection for Si–O backbone from the quaternized side chain, and some improvement in HRA is seen in acidic conditions with ethyl instead of methyl side chains on the quaternary structure.

Keywords Silicone · Trisiloxane · Quaternary ammonium salt · Hydrolysis resistant ability · Cationic surfactant

Introduction

The hydrolysis resistant ability (HRA) of trisiloxane surfactants is important in many technological applications, such as coatings, cosmetics, and agriculture. Trisiloxane is a relatively new class of surfactant, which has proven to be more effective in reducing surface tension than conventional surfactant, and to exhibit superspreading performance [1–3]. The development and applications of trisiloxane surfactants has attracted great interest. Numerous studies have been undertaken in polyether modified trisiloxane surfactants, but this class of nonionic trisiloxane surfactants currently exhibits poor resistance to hydrolysis [4], and this shortcoming limits its application, such as in agricultural adjuvants, because they are likely to lose their efficacy as pesticide emulsifiers during transportation or storage. Therefore, the development of hydrolysis resistant superspreading surfactants is an important issue.

Many investigations have been undertaken to improve the HRA of these trisiloxane surfactants. Knoche [5] discussed the HRA of Silwet L-77, and observed that some of them hydrolyze rapidly when placed in an aqueous environment where the pH value is below 5.0 or above 9.0, and that they are stable for only 40 days even in a neutral aqueous environment (pH 7.0). Policello [6] investigated a kind of hydrolysis-resistant trisiloxane surfactant that can be stable for 3 months in an aqueous environment where the pH is at 4.0 and 11.0. But unfortunately, the structure of silicon compounds is too special, difficult to mass produce, limiting the promotion of trisiloxane surfactants. Retter [7] discussed that the polar groups of quaternary ammonium salt trisiloxane surfactants formed micelles that can protect Si–O backbone from hydrolyzing, thus, it can improve its HRA. Han [8–10] prepared the glucosamide-based trisiloxane gemini surfactants, but studies on cationic trisiloxane surfactants (especially the quaternary ammonium salt cationic trisiloxane surfactants) have rarely been reported [11, 12]. Despite these efforts, the HRA of trisiloxane surfactants is not sufficient for commercial applications.

The aforementioned properties of trisiloxane surfactants prompted us to design and synthesize a new type of hydrolysis resistant cationic trisiloxane surfactant (QASCTSS). In order to contribute to expend the application of

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R. Luo · P. Liu (✉)
School of Chemical and Environmental Engineering,
Wuyi University, Jiangmen 529020, Guangdong, China
e-mail: wyuchemys09lpp@126.com

Y. Chen
Jiangmen Kanhoo Industry Co., Ltd, Jiangmen 529040,
Guangdong, China

trisiloxane surfactants into agricultural adjuvant and personal products, we used the reactant 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD^HM) as a chemical raw material.

In this paper, the synthesis, interfacial properties and hydrolysis resistant performance of this kind of quaternary ammonium salt cation trisiloxane surfactant are reported in detail.

Experimental Procedures

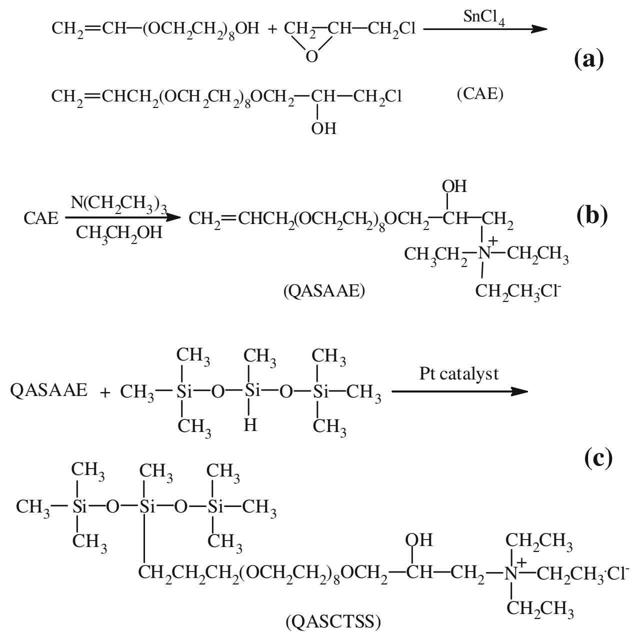
Materials

1,1,1,3,5,5,5-heptamethyltrisiloxane (MD^HM) was purchased from the Zhejiang Run he New Material Co., Ltd., China. Allyl polyoxy-ethylene ether (average molar mass about 410 g mol^{-1}) was purchased from the Zhejiang Huang ma Chemical Industry Group Co., Ltd., China. Chloroplatinic acid was purchased from the Guangdong Shantou Dahao Fine Chemicals Co., Ltd., China. All the above chemicals were used as received. All other chemicals were of analytical grade. All solutions were prepared with ultra-pure water with an electrical resistivity of 18.2 MΩ cm.

Synthesis

The synthesis route to QASCTSS is shown in Scheme 1. The specific methods are described as follows:

Procedure (a) was carried out in accordance with Ref. [13], a 250-mL, four-necked glass flask was equipped with reflux condenser, thermometer and stirrer and internally purged with nitrogen gas. The flask was charged with 1.0 mol allyl polyoxyethylene ether and proper quantities of tin tetrachloride as a catalyst, and then was heated to 120 °C for about 30 min in vacuum. When the temperature dropped to 70 °C, 1.4 mol epichlorohydrin was added dropwise over 1–2 h to the flask, after which the contents were stirred for 2 h at that temperature. The resulting reaction solution was subjected to distillation under reduced pressure to remove the epichlorohydrin which had not reacted completely; a yellowish liquid product, CAE, was attained.



Scheme 1 Synthesis route to QASCTSS

Procedure (b): A 250-mL, three-necked glass flask was equipped with reflux condenser, thermometer and stirrer. The flask was charged with 1.0 mol of the product of procedure (a) (CAE) and 1.05 mol triethylamine in the presence of anhydrous ethanol as solvent. The mixture was heated to 85 °C for about 15 h, a yellow viscous liquid product (QASAAE) was obtained after removing the ethanol by reduced pressure distillation.

Procedure (c): A 250-mL, four-necked glass flask was equipped with reflux condenser, thermometer and stirrer and internally purged with nitrogen gas. The flask was charged with 1.0 mol the product of procedure (b) (QASAAE) and 1.03 mol 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD^HM) in the presence of toluene as solvent. The mixture was heated to 80 °C and charged with 6 mg L^{-1} Pt catalyst, stirring was continued for 6 h at this temperature. The resulting reaction solution was subjected to distillation under reduced pressure to remove the toluene; a yellowish liquid product QASCTSS was obtained.

Structural Characterization

Infrared spectroscopy was performed using a Magna-550 Fourier transform infrared (FT-IR) spectrometer. The surfactants were directly smeared onto a KBr plate. Proton nuclear magnetic resonance (^1H NMR) spectra were acquired on a 400 MHz Bruker Avance-400 NMR spectrometer. Samples were prepared with deuterated solvents $CDCl_3$. Chemical shifts were referenced to tetra methyl silane. The details of these spectral characterizations are shown in Figs. 1, 2 and Table 1. In all cases, the spectra acquired were consistent with the assigned structures of the compounds.

Equilibrium Surface Tension Measurements

All the surfactant solutions were prepared with ultra-pure water and used to determinate the CMC value within 1 h after having been prepared at ambient temperature. Prior to measurements on surfactant solutions the surface tension of the ultra-pure water was measured. These water values

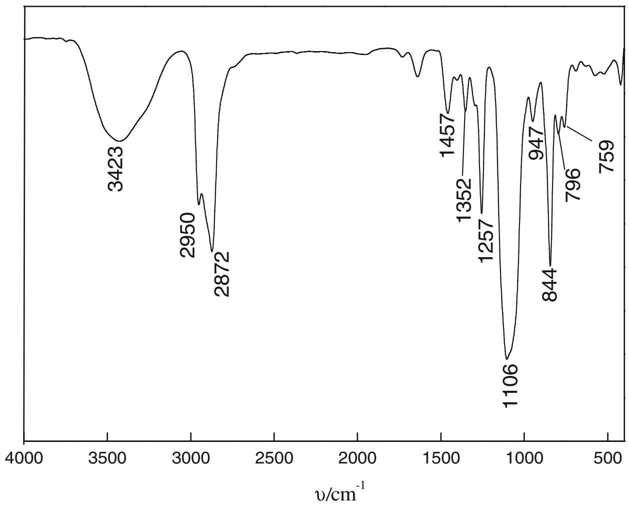


Fig. 1 FT-IR spectrum of QASCTSS

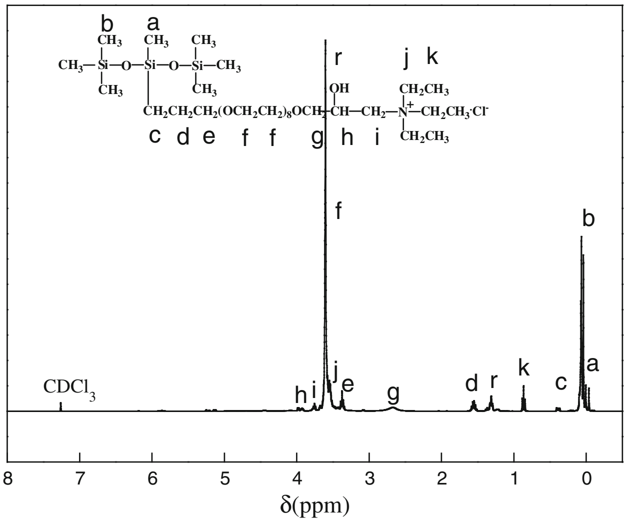


Fig. 2 ^{1}H-NMR spectrum of QASCTSS

Table 1 ^{1}H-NMR spectral data (δ) of QASCTSS

H-atom	a	b	c	d	e	f	g
δ (ppm)	−0.039	0.039	0.304	1.584	3.374	3.603	2.672

h	i	j	k	r	$CDCl_3$
3.939	3.732	3.507	0.883	1.294	7.265

were in the range of 71.7 ± 0.3 mN m^{-1}. The equilibrium surface tension values of dilute aqueous solutions of QASCTSS were measured. The data are plotted in Fig. 3.

Hydrolysis Resistant Ability Determination

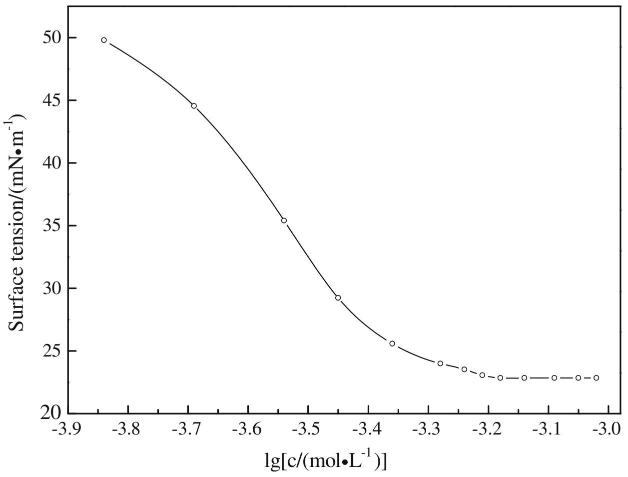


Fig. 3 Plots of equilibrium surface tensions values of aqueous solutions of QASCTSS versus logarithm of molar concentration

The hydrolysis resistant ability (HRA) of surfactants was determined by preparing 0.1 wt% solutions (pH 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0 and 12.0). In order to accelerate the hydrolysis, the solutions were heated for 30 min at 50 °C, and then their surface tension values were measured after they had cooled slowly to ambient temperature.

Results and Discussion

Structural Characterization

The compounds were structurally characterized by their FT-IR (infrared) and ^{1}H-NMR spectra. In the FT-IR spectra, the major absorptions of use in characterization were (1) 2,950 and 2,872 cm^{-1} C–H stretching (alkyl); (2) 3,423 cm^{-1} stretching vibration peak of –OH; (3) 1,257, 844 and 759 cm^{-1} characteristic absorption peak of $–O–Si(CH_3)_3$; (4) 1,100–1150 cm^{-1} and 1,020–1,080 cm^{-1} stretching vibration overlap caused by asymmetric peak of Si–O–Si; (5) 1,352–947 cm^{-1} characteristic absorption peak of $–(CH_2CH_2O)n–$; (6) 1.457 cm^{-1} deformation vibration absorption $–N(CH_2CH_3)_3$ of quaternary ammonium salt.

Figure 1 shows FT-IR spectra of QASCTSS synthesized through the hydrosilylation of 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD^{H}M) with active hydrogen and QASAAE using chloroplatinic acid as a catalyst.

In the ^{1}H-NMR spectra of QASCTSS, the chemical shifts of the various peaks were consistent with the assigned structures of the compound. For example, the 200-MHz ^{1}H-NMR spectrum of QASCTSS is displayed in Fig. 2 and the chemical shifts tabulated in Table 1, along with the proposed peak assignments based on chemical shifts. In general, reference to our previously published spectroscopic data on structurally similar QASPETSS aided in routine compound structure and purity verification [11].

This smearing-out effect is the most apparent for the peaks assigned to the two unique methylene groups bound to the nitrogen center (e H and j H in Fig. 2). Rao et al. [14] noted a similar phenomenon in the ^{1}H-NMR spectrum of cetyltrimethylammonium bromide in D_2O. As in our case, the peak in question was that assigned to the methylene group bound directly to the quaternary ammonium nitrogen. They ascribed this smearing out ("broadening") to a temperature-dependent coupling of the methylene protons to the quadrupole moment of ^{14}N.

Interfacial Properties

Aqueous solution equilibrium surface tension values were obtained by using an adaptation of the maximum bubble pressure method by controlling the speed of dropping water. The critical micelle concentration (CMC) values were taken at the intersection of the linear portions of the plot of the surface tension against the logarithm of the surfactant concentration. The surface tension of the intersection point is called the surface tension of surfactant solution at CMC (γ_{CMC}).

According to the literature [15–19], the surface tension of an aqueous solution containing a siloxane wetting agent is less than that of a conventional surfactant, because of the silicone existing in the hydrophobic part. It has also been suggested that these could form micelles with a lower concentration of the aqueous solution.

Inspection of the data in Fig. 3 shows that the QASCTSS significantly reduced the surface tension of the solution at low concentration, indicating that these molecules adsorbed strongly at the air/water interface and they are highly effective aqueous surfactants, reducing the surface tension of water to approximate 22.84 mN m^{-1} at concentrations of 6.66×10^{-4} mol L^{-1}.

The equilibrium surface tensions of dilute aqueous solutions of all of the surfactants prepared were measured. The CMC values of the surfactant were estimated at the breaking point of the plot. The surface excess concentration ($\Gamma_{\max}$) and the surface area per molecule (a_m^s) were calculated by applying Gibbs' equations (Eqs. 1 and 2) in the steeply downward section just below the CMC. The standard free energy of micellization ($\Delta_{\min}G^{\theta}$) of trisiloxane surfactants was calculated by Eq. 3 [9, 10, 13, 20].

$$\Gamma_{\max} = -\frac{1}{2.303nRT}\left(\frac{\partial \gamma}{\partial \lg c}\right)T \tag{1}$$

$$a_m^s = \frac{10^{16}}{N_A \Gamma_{\max}} \tag{2}$$

$$\Delta G_{mic}^{\theta} = RT \ln\left(\frac{\mathrm{CMC}}{55.5}\right) \tag{3}$$

where $R = 8.3144$ J mol^{-1} K^{-1}, N_A is Avogadro's number, $\Gamma_{\max}$ and a_m^s are in mol m^{-2} and nm^2 molecule^{-1}, respectively. For cationic surfactant, $n = 2$ [21]. All of the data of γ_{CMC}, CMC, $\Gamma_{\max}$, a_m^s and $\Delta_{\min}G^{\theta}$ are listed in Table 2.

In general, the value of the surface area per molecule (a_m^s) appears to be determined by the area occupied by the hydrated hydrophilic groups, rather than by the hydrophobic groups [22]. As can be seen from Table 2, the a_m^s value of QASCTSS is 0.44 nm^2. It indicates that the adsorbed molecules form a tight monolayer on the surface. It indicates that the a_m^s value of QASCTSS is only depended on the "umbrella" conformation and size of trisiloxane surfactants. It belongs to poly methyl groups arrayed closed on the water surface. The negative value of the free energy of micellization ($G_{\mathrm{mic}}^{\theta}$) indicates that the processes are thermodynamically favored.

Hydrolysis Resistant Ability Determination

The lower the surface tension values of different surfactants solutions with the same time at the same pH value, the stronger is the HRA of the surfactant. On this basis, we proposed to measure the change of surface tension values characterizing the HRA of different surfactants indirectly.

The molecular structures of three tested trisiloxane surfactants (QASCTSS, QASPETSS [11], and NPTSS) are shown in Table 3.

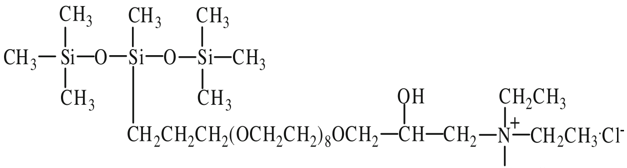
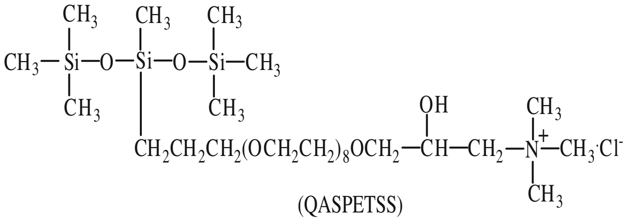
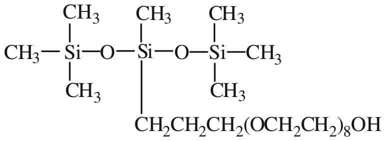
The surface tension values of three kinds of trisiloxane surfactants are shown in Fig. 4.

In a dilute aqueous solution, the surface tension value after heating at 50 °C for 30 min is strongly pH dependent. According to Fig. 4, the HRA of cationic trisiloxane surfactants is obviously superior to that of the nonionic ones. No matter if the environment is acid or alkaline, the HRA of NPTSS is the worst. Only in the pH 7.0–8.0 range, are the surface tension values of NPTSS almost equivalent with QASCTSS and QASPETSS; otherwise, the latter is largely lower than the former's. It indicates that cationization is an effective method to improve the HRA of trisiloxane surfactant. The reasonable explanation is that polar groups of quaternary ammonium salt trisiloxane surfactant formed micelles increasing the steric hindrance for the water molecule to attack the Si atom that can protect the Si–O backbone from hydrolyzing, thus, it can improve its HRA [7].

Table 2 Aqueous surface activity of QASCTSS

γ_{CMC} (mN m^{-1})	CMC (mol L^{-1})	$\Gamma_{\max}$ (mol m^{-2})	a_m^s (nm^2)	$\Delta_{\min}G^{\theta}$ (kJ mol^{-1})
22.84	6.66×10^{-4}	3.6×10^{-6}	0.44	−28.1

Table 3 The molecular structure of three tested trisiloxane surfactants

Name	Molecular structure
QASCTSS Cationic trisiloxane surfactants	 $(CH_3)_3Si-O-Si(CH_3)[CH_2CH_2CH_2(OCH_2CH_2)_8OCH_2-CH(OH)-CH_2-N^+(CH_2CH_3)_3\cdot Cl^-]-O-Si(CH_3)_3$ (QASCTSS)
QASPETSS Cationic trisiloxane surfactants	 $(CH_3)_3Si-O-Si(CH_3)[CH_2CH_2CH_2(OCH_2CH_2)_8OCH_2-CH(OH)-CH_2-N^+(CH_3)_3\cdot Cl^-]-O-Si(CH_3)_3$ (QASPETSS)
NPTSS Non-ionic polyoxyethylene trisiloxane surfactant (Silwet 408)	 $(CH_3)_3Si-O-Si(CH_3)[CH_2CH_2CH_2(OCH_2CH_2)_8OH]-O-Si(CH_3)_3$ (NPTSS)

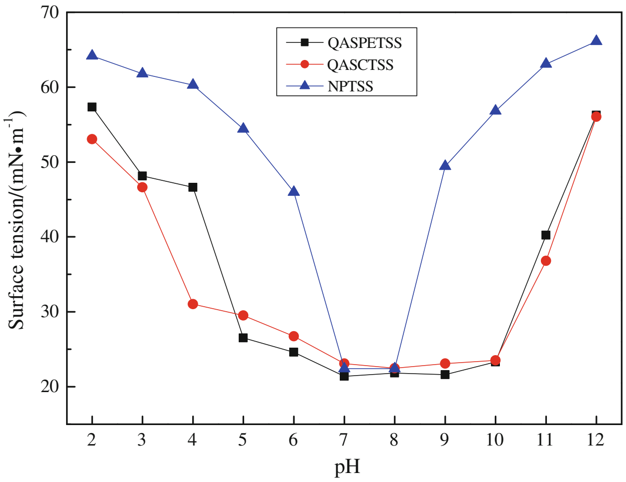


Fig. 4 Effect of pH on the hydrolytic stability of QASCTSS, QASPETSS and NPTSS

Figure 4 also show that the HRA of QASCTSS is stronger than QASPETSS, especially in acidic conditions (pH 4.0). It indicated that the HRA of the same type of quaternary ammonium salt cationic trisiloxane surfactants increases as the length of alkyl group. The larger the attached hydrophobic group is, the stronger is the HRA of the quaternary ammonium salt cationic trisiloxane surfactant, and consequently the more difficult it is for the water molecule to attack the Si atom.

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Author Biographies

Ru-xian Luo is an associate professor of applied chemistry. He received a Ph.D. in industrial catalytics in 1995 from the School of Chemistry, South China University of Technology, People's Republic of China. His research involves the synthesis and application of surfactants.

Ping-ping Liu is an undergraduate student at Wuyi University. Her research involves the synthesis and application of surfactants.

Yao-bin Chen received an M.Sc. in applied chemistry from Wuyi University. He works at Jiangmen Kanhoo Industry Co., Ltd. His research involves the synthesis and application of surfactants.