

The Effects of the Organic Groups Attached at the Silicone Atoms of the Organosilane-Based Gemini Nonionic Surfactants on Their Surface Activities

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Abstract A novel trisiloxane gemini nonionic surfactant was synthesized by the reaction of 3-(diethoxy(methyl)silyl)propan-1-amine with hexamethyldisiloxane to get 3-(trisiloxane)propan-1-amine, which was further reacted with glutaroyl dichloride to form the surfactant molecule, N^1, N^5 -bis(3-(trisiloxane)propyl)glutaramide (**3**). Some related compounds were also prepared, including N^1, N^5 -bis(3-(trimethoxysilyl)propyl)glutaramide (**1**), and N^1, N^5 -bis(3-(diethoxy(methyl)silyl)propyl)glutaramide (**2**). All prepared compounds were analyzed by IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ to confirm their structures. Their interfacial activities, including surface tension and wetting ability, were measured. These surface activities were compared each other and a discussion was carried out on how the organic groups attached on the silicone atoms affect their surface tension and wetting ability. To explain the superior surface activities of the molecules **3**, a hypothesis was proposed about a cyclic hydrophobic core area that could be formed by the two hydrophobic chains and the linker of the gemini molecule due to the dispersion force (Van der Waals force) between the two trisiloxane moieties, which close the hydrophobic cycle inside the molecule.

Keywords Trisiloxane · Organosilane-based gemini nonionic surfactant · Surface activity · Wetting ability · Dispersion force · Hydrophobic interaction

Introduction

Organosilane surfactants, as small-molecules or polymers, are widely used as emulsifying agents and detergents in agrochemicals, waterborne coatings, mining, plastic foams, and personal care products due to their perfect interfacial properties such as low surface tension, excellent wetting and emulsifying properties, good compatibility with organic adducts, and biocompatibility [1–4]. These unusual surface properties are attributable to the inherent chemical nature of silicone atom and organic groups attached on it, exhibiting a hydrophobic behavior with high flexibility and easy orientation at interface.

Gemini surfactants with two polar heads and two hydrophobic chains linked by spacers, are a relatively new generation of surfactants. They have shown much better surface activities than those of their monomers, such as much lower surface tensions and critical micelle concentrations (CMC) [5–12]. Since they appeared in the early 1990s, they have attracted considerable interest of researchers.

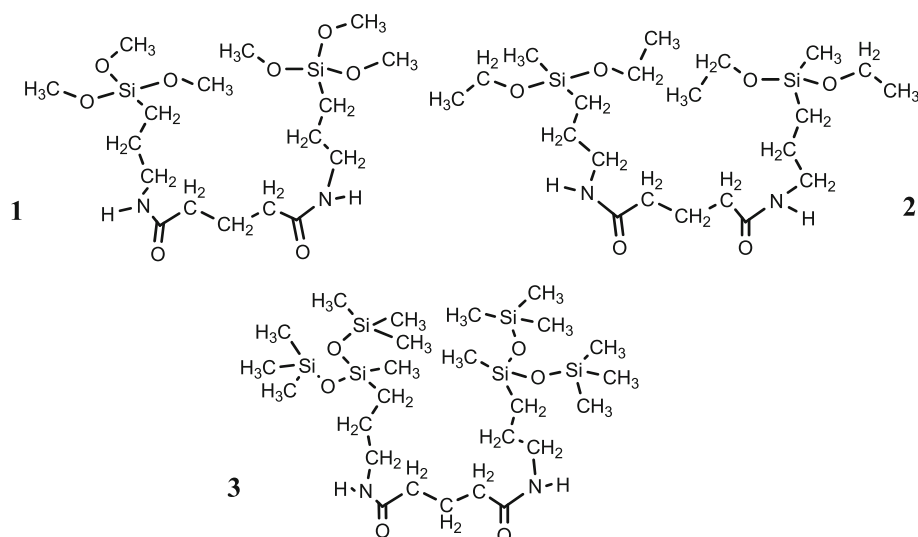
Prompted by the superior surface properties of organosilane type and gemini type surfactants, we undertook the research project to synthesize and characterize some organosilane-based gemini nonionic surfactant small molecules. They are an important type of surfactant molecules for academic research and industrial application. However, to the best of our knowledge, this kind of surfactant molecules have rarely been reported [13–15]. Therefore, it was deemed

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Scheme 1 The organosilane-based gemini nonionic surfactant molecules prepared



necessary to explore the interfacial activities of the organosilane-based gemini nonionic surfactants. We first used glutaroyl dichloride to link 3-trimethoxysilylpropylamine and 3-(diethoxy(methyl)silyl)propylamine to get N^1,N^5 -bis(3-trimethoxysilylpropyl)glutaramide (**1**) and N^1,N^5 -bis(3-(diethoxy(methyl)silyl)propyl)glutaramide (**2**), respectively. To improve their surface activities we desired to enhance the hydrophobicity of the silyl heads of surfactant molecules **1** and **2**. Of various silicone surfactants, perhaps the most impressive one is the trisiloxane type as reviewed by Hill [16]. The trisiloxane surfactants have been called “super spreader and wetter” [17], which can rapidly spread aqueous solution over hydrophobic surface and other low-energy substrates. Based on this knowledge we decided to modify the diethoxy(methyl)silyl moiety of molecule **2** to trisiloxane structure of molecule **3**. The three molecules were prepared as shown in Scheme 1.

These molecules **1**, **2** and **3** are organosilane-based gemini nonionic surfactants bearing the exactly same hydrophilic moiety but different functional groups attached on the silicone atoms of the hydrophobic portions. Their interfacial activities were measured, compared and discussed based on the trimethoxysilyl/diethoxy(methyl)silyl/trisiloxane different structural moieties.

Materials and Methods

Materials

The following four chemicals were purchased from Aladin Industrial Corporation (Shanghai, China): 3-(trimethoxysilyl)propan-1-amine (97 %), 3-(diethoxy(methyl)silyl)propan-1-amine (97 %), hexamethyldisiloxane (99 %) and tetramethylammonium hydroxide pentahydrate (97 %).

Glutaroyl dichloride was ordered from Tokyo Chemical Industry. All the above chemicals were used as received. The water used was doubly distilled. All other chemicals, triethyl amine, toluene, dichloromethane, anhydrous magnesium sulfate, were of analytical grade and were used without further purification.

Characterization

The prepared surfactant molecules were characterized by different chemical analysis methods. Fourier transform infrared (FTIR) spectra were recorded on a spectrometer of Thermo Nicolet Avatar 370 (USA). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured on a Bruker Ascend 600 MHz spectrometer, with chemical shifts recorded as ppm in CDCl_3 , TMS as internal standard. Surface tension was measured at 25 °C using an Auto Surface Tensiometer JK99C (Zongchen Digital Technical Equipment Co. Ltd (Shanghai, China).

Evaluation of Surface Activity

Surface Tension

The surfactant aqueous solution samples were freshly prepared with different concentrations for the measurements. Surface tensions of the three surfactant aqueous solutions with different concentrations were measured at 25 °C using the ring method [18]. The samples were dissolved in double-distilled water to get evenly dispersed solutions, with assistance of ultrasonic vibration when necessary. Noticeably, the trisiloxane dimmer, N^1,N^5 -bis(3-(trisiloxane)propyl)glutaramide (**3**) needed 25 min in the ultrasonic bath at 60 °C to be fully dissolved. It is less soluble/dispersible in water than other two surfactants. The

samples stand for 60 min at 25 °C before surface tension being measured. Each sample was measured three times, and the average value of the three was calculated and used as its surface tension. The CMC and γ CMC values were taken at the intersection of the linear portions of the plots of the surface tension against the logarithm of the surfactant concentration.

Wetting Ability

The wetting ability was measured according to the canvas descending method [19]. A canvas disk, 2.0 cm in diameter, was placed on the surfactant solution surface at room temperature, after some time, the disk was permeated by surfactant solution and started to sink. The wetting ability is determined by this period from being placed on the surface to starting to sink. The shorter the wetting time, the better is the wetting ability. The wetting ability was determined as the average value from three measurements. This procedure is actually a modification of the Draves wetting test [20].

Synthesis of Organosilane-Based Gemini Nonionic Surfactants

Preparation of N^1, N^5 -bis(3-(trimethoxysilyl)propyl)glutaramide (**1**): In a 50-ml of round bottom flask (RBF) with a magnetic stirrer bar were charged with 5 ml of toluene, 1.79 g of 3-(trimethoxysilyl)propan-1-amine (10.0 mmol), and 1.01 g of triethylamine (10.0 mmol) under nitrogen atmosphere. The mixture was stirred in an ice bath for 30 min. A solution of glutaroyl dichloride (0.845 g, 5.0 mmol, in 5 ml of toluene) was dropwise added over 30 min at cold. After the addition the reaction was stirred in ice bath for 1.5 h, then warmed up to room temperature, stirred for another 1.5 h. It was filtered under reduced pressure; the solid was washed with toluene (10 ml \times 3). The washings were combined with the filtrate, and volatiles were removed by evaporation under reduced pressure. The residue obtained was further dried at 55 °C in vacuo for 8 h. 2.03 g of orange-reddish slightly viscous liquid was obtained (89.4 % yield). IR: (film, cm^{-1}): 3,296–3,096 (N–H), 2,942–2,841 (CH_2 , CH_3), 1,645 (C=O), 1,086 (Si–O–C), 818 (Si–C). $^1\text{H-NMR}$, δ : 0.65 (t, $J = 6.4$ Hz, 4H, CH_2), 1.62 (m, 4H, CH_2), 1.96 (m, 2H, CH_2), 2.24 (t, $J = 7$ Hz, 4H, CH_2), 3.24 (q, $J = 6.7$ Hz, 4H, CH_2), 3.56 (s, 18H, CH_3), 6.01 (s, 2H, NH). ^{13}C NMR: 172.00, 50.09, 40.06, 41.59, 35.33, 23.76, 8.20.

Preparation of N^1, N^5 -bis(3-(diethoxy(methyl)silyl)propyl)glutaramide (**2**): The same procedure was used as that for preparing compound **1**. The reaction is shown in Scheme 2. An orange-reddish syrup, slightly viscous liquid was obtained with a yield of 90 %. IR: (film, cm^{-1}): 3,290–

3,082 (N–H), 2,972–2,927 (CH_2 , CH_3), 1,644 (C=O), 1,079 (Si–O–C), 820 (Si–C). ^1H NMR, δ : 0.12 (s, 6H, CH_3), 0.62 (t, $J = 3.2$ Hz, 4H, CH_2), 1.25 (t, $J = 2.8$ Hz, 12H, CH_3), 1.59 (m, 4H, CH_2), 1.95 (m, 2H, CH_2), 2.26 (t, $J = 7$ Hz, 4H, CH_2), 3.23 (q, $J = 6.9$ Hz, 8H, CH_2), 6.05 (s, 2H, NH). ^{13}C NMR: 171.95, 57.88, 56.48, 41.80, 35.35, 23.26, 22.17, 18.92, 11.26.

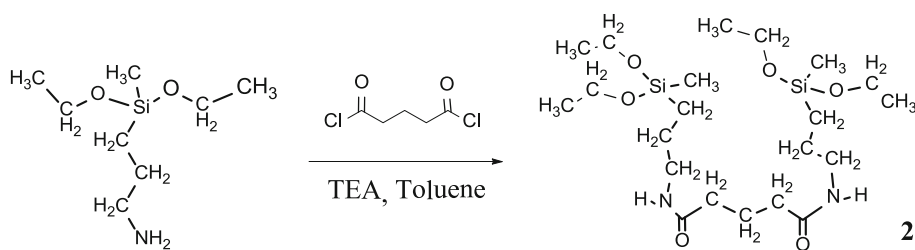
Preparation of N^1, N^5 -bis(3-(trisiloxane)propyl)glutaramide (**3**): A modified procedure from the reference [15] was used as follows. In a 50-ml of RBF were placed 8.12 g of hexamethyldisiloxane (50 mmol), 1.91 g of 3-(diethoxy(methyl)silyl)propan-1-amine (10 mmol) and 50 mg of tetramethylammonium hydroxide (TMAH) (0.27 mmol) under nitrogen atmosphere. The mixture was heated to reflux for 2 h, and then temperature was raised to 130 °C and kept for 30 min to decompose the TMAH catalyst. The excessive hexamethyldisiloxane and other volatiles were evaporated off in vacuo; the residue was cooled, washed with distilled water (10 ml \times 7), and dried in vacuo for 5 h. 1.92 g of light yellow oil was obtained with a yield of 68 %. To this compound (1.92 g, 6.9 mmol) in a 50-ml of RBF under nitrogen were added 5 ml of toluene and 0.69 g of triethyl amine (6.9 mmol). The mixture was stirred at 0 °C for 30 min, then a glutaroyl dichloride solution (0.59 g, 3.45 mmol in 5 ml of toluene) was slowly added over 30 min. After the addition it was continued stirring at cold for 1.5 h, then warmed up to room temperature and stirred for 1.5 h. It was then filtered. The solid was washed with toluene (10 ml \times 3). The washings were combined with the filtrate, and solvent was removed by evaporation under reduced pressure. The residue obtained was dried in vacuo at 55 °C for 8 h. 2.07 g of golden viscous liquid was obtained with a yield of 92 %. The synthesis is presented in Scheme 3. IR: 3,286–3,084 (N–H), 2,958 (CH_2), 1,643 (C=O), 1,075 (Si–O–C), 841 (Si–C). ^1H NMR, δ : 0.05 (s, 6H, CH_3), 0.09 (s, 36H, CH_3), 0.47 (t, $J = 4.2$ Hz, 4H, CH_2), 1.52 (m, 4H, CH_2), 1.96 (m, 2H, CH_2), 2.27 (t, $J = 6.4$ Hz, 4H, CH_2), 3.19 (t, $J = 2.8$ Hz, 4H, CH_2). ^{13}C NMR: 171.95, 41.83, 35.40, 23.41, 22.29, 14.90, 2.42, 0.12.

Results and Discussion

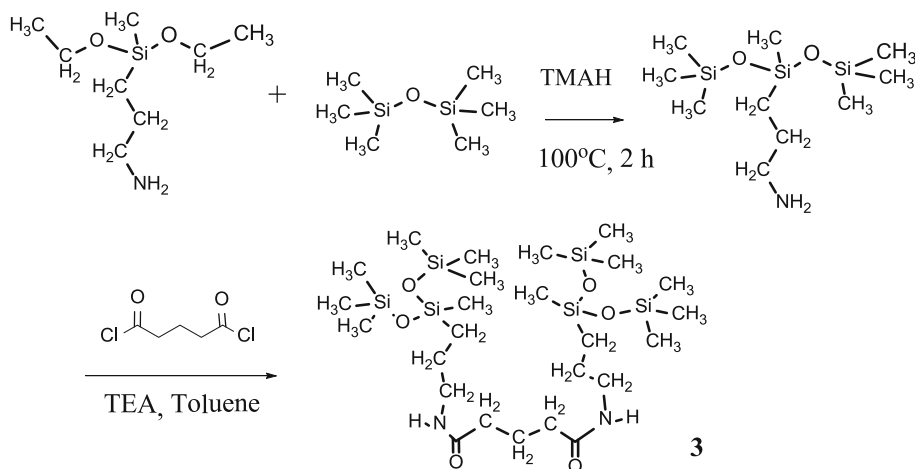
Synthesis and Spectroscopic Characterization of the Organosilane-Based Nonionic Surfactants

There are several procedures to make trisiloxane functional group from methoxysilyl or ethoxysilyl groups [15, 21–25]. Initially we used KOH as a catalyst to prepare the trisiloxane compound in hexamethyldisiloxane as solvent/reactant at 60 °C to react with 3-(diethoxy(methyl)silyl)propan-1-amine for 4 h. After removing

Scheme 2 Synthesis of siloxane-based gemini nonionic surfactant molecule **2**



Scheme 3 Synthesis of siloxane-based Gemini nonionic surfactant molecule **3**



excessive hexamethyldisiloxane and cooling to room temperature, the residue was washed with distilled water many times to reach pH7 and only about 40 % yield of trisiloxane product was obtained. Then we modified Fu Han's procedure [15] to use tetramethylammonium hydroxide (TMAH) as a catalyst. When the reaction was complete after stirred at reflux for 2 h, the catalyst was decomposed at 130 °C and the excessive hexamethyldisiloxane was removed under reduced pressure. The crude product was washed with water for fewer times to get pure product with 65–74 % yields, as shown in Scheme 3. The latter procedure is better because of its easier working-up, shorter reaction time and higher yield of the product.

Compared to other amidation of amine functional siloxanes [15, 26–30], our procedure for preparing compounds **1–3** with glutaroyl dichloride is much milder and more specific as shown in Schemes 2 and 3. The product yields are higher than 90 %. The by-product salt, triethyl amine (TEA) chloride formed in the reactions, is not soluble in toluene at room temperature, and can be easily removed by simple filtration after the reaction. Other solvents, such as THF and diethyl ether, always leave trace amounts of triethyl amine salt in the product, as we observed.

By examining the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of these compounds **1–3**, we observed that they were very pure, no triethyl amine or other impurities were present.

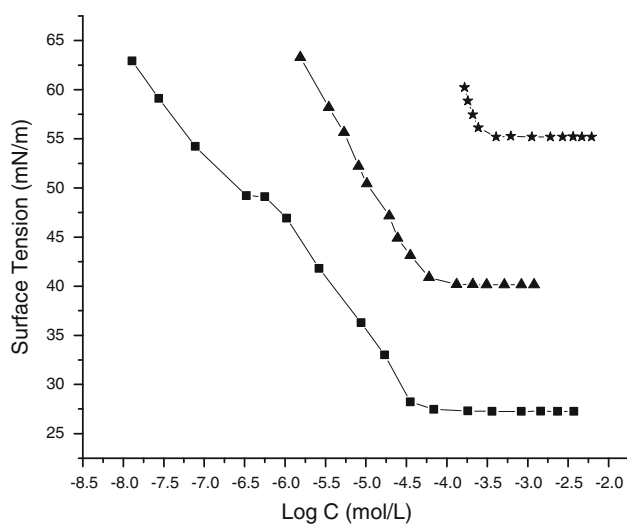


Fig. 1 Correlation of equilibrium surface tension of aqueous solutions of the three surfactant molecules and their log mole concentrations. (asterisks) N^1, N^5 -bis(3-(trimethoxysilyl)propyl)glutaramide (**1**), (filled triangles) N^1, N^5 -bis(3-(diethoxy(methyl)silyl)propyl)glutaramide (**2**); (filled squares) N^1, N^5 -bis(3-(trisiloxane)propyl)glutaramide (**3**)

Equilibrium Surface Tension of the Three Surfactant Molecules

The equilibrium surface tension of the three surfactants in water with different concentrations at 25 °C was measured. The data are illustrated in Fig. 1.

These molecules have the same type of hydrophilic heads while bearing different functional groups on the silicone atoms of the hydrophobic portions. All three surfactants reduced surface tension of water gradually from one level to another. It was found that the interfacial activity of the surfactants is sensitive to the functional groups attached on the silicone atoms. When all three groups are methoxyl on the silicone atom of N^1,N^5 -bis(3-(trimethoxysilyl)propyl)glutaramide (**1**), its surface tension γ_{CMC} at CMC is high (55.19 mN/m), although it is a dimer/gemini surfactant. This is probably due to the fact that methoxyl groups are able to form hydrogen bonds with water molecules well, so that molecule 1 could disperse in water and have fewer tendencies to move to the water/air interface to form a hydrophobic film to reduce water surface tension. For N^1,N^5 -bis(3-(diethoxy(methyl)silyl)propyl)glutaramide (**2**) the functional groups on the silicone atom are diethoxymethyl which has much less chance to form a hydrogen bond with water. Its surface tension is much lower than that of molecule **1**. The γ_{CMC} value of molecule 1 is remarkably reduced from 55.19 to 39.43 mN/m when the trimethoxyl group on the silicone atom changed to diethoxymethyl for molecule **2**. The most impressive change is those γ_{CMC} values are further greatly reduced to 27.25 mN/m when the hydrophobic head became trisiloxane for the surfactant molecule **3**. This is probably attributable to the trisiloxane structure: the two silicone atoms, connect to the central silicone atom of the trisiloxane via ether bonds, each attached three methyl groups. These trimethylsilyl structure motifs are highly hydrophobic, compatible and attracted each other via dispersion force to form an even and continuous film at the water/air interface.

For molecule **3** shown in Scheme 1, it seems that a cyclic hydrophobic core area could be formed by the two hydrophobic chains and the linker of gemini molecule due to dispersion force (Van der Waals force) between two trisiloxane moieties, which close the hydrophobic cycle inside the molecule.

Although dispersion force is a weak intermolecular force, it plays an important role in forming some particular three-dimensional structural motifs. The leucine zipper is an example [31]. This parallel alpha helices, a super-secondary structure of protein, are bound together by the dispersion force generated by hydrophobic interactions between isopropyl groups (side chains of leucines) on one helix with the isopropyl groups of leucines on the other strand every second turn. This dispersion force sticks two alpha helices together [32].

In our case, the two methyl-silicone-methyl moieties interact with other methyl-silicone-methyl groups would generate similar or even stronger dispersion force as isopropyl with isopropyl interaction does in the leucine

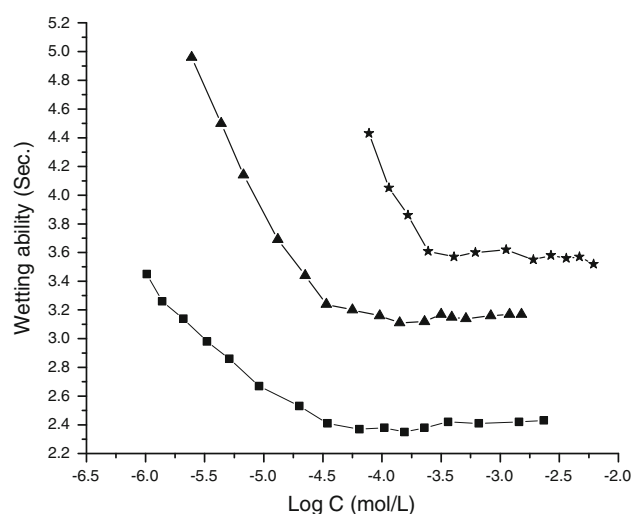


Fig. 2 Wetting ability of the three surfactant molecules. (asterisks) N^1,N^5 -bis(3-(trimethoxysilyl)propyl)glutaramide (**1**), (filled triangles) N^1,N^5 -bis(3-(diethoxy(methyl) silyl) propyl)glutaramide (**2**); (filled squares) N^1,N^5 -bis(3-(trisiloxane)propyl)glutaramide (**3**)

zipper situation. If the interaction between two trisiloxane groups is strong enough to close the hydrophobic cycle, the hydrophobic volume formed may partially account for the superior surface activities of trisiloxane gemini nonionic surfactant molecule **3**. For molecules **1** and **2**, they cannot form cyclic hydrophobic core areas because there are not enough intermolecular forces between two trimethoxysilyls or two diethoxymethylsilyls to attract them together to close the hydrophobic cycles.

Wetting Abilities of the Three Surfactant Molecules

The wetting abilities were also measured and the results were presented in Fig. 2.

We observed the canvas used in the experiment was made non-wetting by a ‘waxing’ chemical treatment. When the canvas disks contact with the surfactant solution, the liquid spreads and penetrates to displace air on the disk surface area. The ability of the liquid to wet the canvas disks is dependent on how well the liquid can ‘stick’ to the canvas surface. This sticking ability is mainly a dispersion force because wax consists of high molecular weight hydrocarbons. Here the wetting effectiveness of the three surfactants was determined by comparing the minimum wetting time achievable by each of them.

As shown in Fig. 2 N^1,N^5 -bis(3-(trimethoxysilyl)propyl)glutaramide (**1**) took approximately 3.6 s of the minimum time for the canvas disks to get wet and sink, while N^1,N^5 -bis(3-(diethoxy(methyl) silyl) propyl)glutaramide (**2**) and N^1,N^5 -bis(3-(trisiloxane)propyl)glutaramide (**3**) needed 3.2 and 2.4 s to sink, respectively. These results are consistent with those of surface tension, i.e., the stronger

hydrophobicity of the silicone-head, the better surface activity of the surfactant. Especially noticeable is the trisiloxane surfactant molecule **3**, which reduces the sinking time to about 2.4 s. Obviously, the trisiloxane moiety replacement tremendously improved the interfacial activity of the surfactant molecule **2**. Interestingly, the curves in Figs. 1 and 2 have similar shapes and tendencies, i.e., as the concentrations increase, surface tension/wetting time decrease until the CMC is reached, where surfactants begin to aggregate into micelles in the bulk aqueous solution. Indeed, the lowering of a surface tension is a necessary step toward wetting.

Wetting ability is important in surfactant applications, such as coating, cleaning, emulsion polymerization, pesticide formulation, skin care and color cosmetics, etc. Therefore, N^1, N^5 -bis(3-(trisiloxane)propyl)glutaramide (**3**) may have potentially a lot of practical applications.

Conclusions

Of the three prepared organosilane-based gemini nonionic surfactant molecules, the trisiloxane type molecule **3** has superior surface activity, i.e., it exhibits the lowest surface tension and the best wetting ability. This is attributable to the structure of the trisiloxane, two trimethylsilyl connecting with a central silicone atom via ether bonds. It is highly hydrophobic, compatible and flexible, capable of forming a continuous film at the water/air interface. Molecule **2** has a moderate surface activity due to the diethoxymethyl functional groups attached on silicone atom, which is quite hydrophobic. Molecule **1** has a high surface tension and requires a long time to wet canvas because trimethoxysilyl functional groups can easily form hydrogen bonds with water.

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