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A gemini-type superspreader: synthesis, spreading behavior and superspreading mechanism

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Abbreviations

Fourier transform infrared spectroscopy (FTIR)

¹H nuclear magnetic resonance spectroscopy (¹H NMR)

Transmission electron microscopy (TEM)

Atomic force microscopy (AFM)

Dynamic light scattering (DLS)

Critical aggregation concentration (CAC)

Corresponding surface tension (γ_{CAC})

Surface excess concentration (Γ_{max})

Occupied area per surfactant molecule (A_{CAC})

Standard free energy of aggregation ($\Delta G_{\text{mic}}^{\theta}$)

Standard free energy of adsorption ($\Delta G_{\text{ads}}^{\theta}$)

Advancing contact angle (θ)

Spreading radius (r),

Wetted area (S(t))

Velocity of spreading (dr/dt)

Liquid volume (V)

Spreading time (t)

Spreading exponent (n)

Critical wetting concentration (CWC)

Hydrophilic-lipophilic balance (HLB)

Length of the spacer (s)

Numbers of ethoxy units (CH₂-CH₂-O-) (n(EO))

Liquid/vapor (L/V)

Solid/vapor (S/V)

Solid/liquid

(S/L)

ABSTRACT

This paper describes the facile microwave-assisted synthesis of a series of trisiloxane gemini superspreaders, as well as their surface and aggregation properties and superspreading behavior on plant leaf surfaces. The molecular structures of the trisiloxane gemini surfactants were characterized by Fourier transform infrared spectroscopy (FTIR) and ^1H nuclear magnetic resonance spectroscopy (^1H NMR). The obtained thermodynamic parameters showed that an increase in the spacer group (CH_2) resulted in decreases in the critical aggregation concentration (CAC), corresponding surface tension (γ_{CAC}), and surface excess concentration (Γ_{max}) but increases in the occupied area per surfactant molecule (A_{CAC}) and absolute values of the standard free energies of aggregation ($\Delta G_{\text{mic}}^\theta$) and adsorption ($\Delta G_{\text{ads}}^\theta$). An increase in ethoxy units ($\text{CH}_2\text{-CH}_2\text{-O-}$) resulted in increases in the CAC, γ_{CAC} , and A_{CAC} but decreases in Γ_{max} and the absolute values of $\Delta G_{\text{mic}}^\theta$ and $\Delta G_{\text{ads}}^\theta$. The transmission electron microscopy and dynamic light scattering results showed that the average sizes of the aggregates of superspreader solutions increased with an increasing number of spacer units (CH_2) but decreased with an increasing number of ethoxy units ($\text{CH}_2\text{-CH}_2\text{-O-}$). The dynamic spreading behavior results demonstrated that the average spreading velocity increased with increasing spacer chain length, and the dependence of the maximum spreading velocity on the ethoxy chain length was nonmonotonous with a maximum at $n(\text{EO}) = 8.68$. The optimal HLB value was essential to obtaining good superspreading behavior, and the substrate wettability (hydrophobic rice plant and hydrophilic mango plant surfaces) greatly influenced the superspreading. The synergistic effects from the precursor film and Marangoni effect existed in the proposed superspreading model.

KEYWORDS: Surfactant; Superspreader; Microwave-assisted synthesis; Superspreading mechanism.

1. INTRODUCTION

Superspreaders have attracted considerable interest in scientific and industrial communities due to their fascinating rapid spreading properties over large areas of difficult-to-wet substrates. Trisiloxane-based surfactants, known as ‘superspreaders’, are commonly employed in numerous applications for which enhanced wetting is of the utmost importance [1,2]. These surfactants are widely used as adjuvants to promote the rapid spreading of water-soluble herbicides on the surfaces of waxy leaves [3]. Generally, the epicuticular wax on a leaf acts as a substantial barrier to wetting. Water alone tends to bead-up and roll off the leaf, which can make spray applications ineffective. Because superspreaders reduce the surface tension of water and induce a surface tension gradient, they enable spray solutions to rapidly and completely wet waxy leaf surfaces, thereby increasing the amount of spray retained on the leaf. As a result, superspreaders can increase the reliability of spray applications by improving the delivery of agrochemicals [4].

Since the discovery of superspreaders in the 1960s by Schwartz and Reid [5], the underlying reasons for the superiority of trisiloxane-based surfactants over conventional surfactants in reducing the equilibrium contact angles of water droplets on hydrophobic surfaces and enabling complete wetting have not been established and remain under discussion, despite their importance to many technological applications [6]. The surface tension of aqueous superspreader solutions at the critical aggregation concentration (CAC) is relatively low (20-25 mN/m) [7,8], but not lower than that of fluorosurfactants (18-28 mN/m) [9]. However, trisiloxane-based surfactants promote the rapid spreading of water droplets over hydrophobic surfaces and even wet them completely. Hydrophobic surfaces are only partially wetted by the adsorption of general surfactants onto a liquid/vapor (L/V) or solid/liquid (S/L) interface. Therefore, the structure and surface activity of the surfactant molecule itself, the phase behavior and structures of the surfactant aggregates in bulk solutions, the physicochemical properties of the substrates and several other parameters can strongly influence the superspreading behavior [10]. Over the years, scientists have struggled to provide a comprehensive understanding of superspreading behavior. However, the superspreading mechanism is very complicated and is not clearly understood. Hill [11] and Ananthapadmanabhan [12] declared that the superspreader molecules' unique molecular structure with a “hammer-like” shape plays a key role. Ruckenstein [13] and Karapetsas et al. [14] proposed that the mechanism was related to the fast adsorption of surfactants at the L/V and S/L interface from the liquid bulk. Furthermore, the role of bilayer aggregation in the bulk was elucidated by Ananthapadmanabhan [12] and Venzmer [15]. Additionally, Chengara et al. [16] claimed that a surface tension gradient causing Marangoni flow was the driving force for the superspreading process. Lin et al. [17] and Churaev [18] noted that the existence of a thin water precursor film in contact with the leading edge of the droplet plays a significant role. Keurentjes et al. [19] stated that surfactants adsorbed onto a hydrophobic surface expose their polar head groups to the solution, whereas in the case of a more hydrophilic surface, surfactant molecule bilayers might form, rendering the surface more hydrophilic. Moreover, Zhang and Han [20] and Rafai et al. [21] noted that spreading was driven by capillary forces dominated by Marangoni forces with a spreading exponent n above 0.25.

Overall, a detailed understanding of the superspreading mechanism is far from complete. Herein, considerable efforts were made to design and synthesize a series of novel trisiloxane-based superspreaders to understand their spreading behavior over substrates. Gemini surfactants are a class of surfactants characterized by two polar head groups connected by various types of

spacers to two hydrophobic tails [22]. These surfactants have evoked intense interest, both academic and industrial, because of their unique properties compared to conventional single-headed and single-tailed surfactants, including lower CAC values (by approximately an order of magnitude), increased surface activity and lower surface tension at the CAC [22]. Many studies have investigated the relationship between the molecular structure of gemini surfactants and their properties [22-25]. However, research on the effect of the structural variation of gemini surfactants on superspreading behavior is still rare. In this work, a series of gemini surfactants with different structures were designed and synthesized by adopting the spacer and polar head groups to obtain improved superspreading ability. A schematic representation of gemini surfactants as superspreaders is given in Fig. S1. The effects of the molecular structure on the surface activities and aggregation properties of superspreaders were investigated by evaluating thermodynamic parameters, including the CAC, γ_{CAC} , Γ_{max} , A_{CAC} , $\Delta G_{\text{mic}}^{\theta}$, and $\Delta G_{\text{ads}}^{\theta}$. The relationships between the molecular structure and spreading behavior were investigated by analyzing the contact angle, $r(t)$, S , dr/dt , n , and CWC. The influences of the HLB value and different substrate wettability on the superspreading behavior are also discussed. Finally, a possible superspreading model is given to illustrate the superspreading mechanism.

2. EXPERIMENTAL

2.1. Materials

1,1,1,3,5,5,5-Heptamethyltrisiloxane (HMTS) was purchased from the Runhe Organicsilicone New Material Co., Ltd. (Ningbo, Zhejiang Province, China). Hexachloroplatinic acid (H_2PtCl_6), tetramethylammonium bromide (TMAB), sulfuric acid, acrylic acid (AA), ethylene glycol diglycidyl ether (EGDE), 1,4-butanediol diglycidyl ether (BDGE), and 1,6-hexanediol diglycidyl ether (HDGE) were procured from Sigma Aldrich (China). Polyethylene glycol (PEG-200, PEG-400, and PEG-600) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Hexane, cyclohexane, ethyl acetate, and toluene were of analytical grade. Silwet L-77, a commercial superspreader supplied by GE Healthcare Life Sciences (Canada), is a chemical mixture of polyalkyleneoxide-modified heptamethyltrisiloxane (84%) and allyloxypolyethyleneglycol methyl ether (16%). The leaves of rice plants and mango trees were supplied by the planting base of Guangzhou University.

2.2. Preparation of the gemini-type superspreader

Trisiloxane-based gemini-type surfactants were synthesized by a three-step process (see Fig. S1 in the Electronic Supplementary Information) in a microwave reactor (XH-100B, Peking, China) at a power of 300 W. The hydrosilylation reaction (Fig. S1, step a) of HMTS with AA was performed with a catalyst (H_2PtCl_6). The requisite amounts of AA, H_2PtCl_6 (20 ppm, based on the mass of HMTS), and toluene (50 wt.% in total weight) were added to a dried 100-ml round-bottom flask in the microwave reactor equipped with a thermometer, magnetic stirrer, reflux condenser and nitrogen inlet/outlet, and the reaction mixture was stirred for 5 min. Thereafter, a requisite amount of HMTS (molar ratio of HMTS:AA equal to 1:1.2) was added into the above mixture, which was then heated at 80 °C with stirring for 6 h. The intermediate product (A) was obtained, fractionated and further purified three times using hexane. The intermediate products (B-m: B-1, B-2, and B-3) were synthesized by the ring-opening reaction (Fig. S1, step b) of A and glycol diglycidyl ether (EGDE, BDGE, and HDGE, respectively) using 1:1 molar ratios of the epoxy group and carboxyl group in the presence of TMAB catalyst (1 wt.% based on the glycol diglycidyl ether mass) [26,27]. The ring-opening reaction was

carried out at 110 °C for 5 h. The requisite amounts of the obtained B-m products, PEGs (preferable molar ratios of B-m and PEGs equal to 1:2.1) and sulfuric acid (3 wt.% based on the mass of the reactants) as the catalyst were mixed and added to the round-bottom flask, and the condensation reaction (Fig. S1, step c) of the B-m products with the PEGs in toluene (50 wt.% in total weight) was maintained at 110 °C for 1 h in a decompression device. Then, the mixture was cooled, the solvents were removed by distillation, and the products were further purified by recrystallization from a mixture of cyclohexane and ethyl acetate (v/v = 1/1) three times. The reaction products, namely the gemini-type surfactants ($S_m(\text{EO})_n$: $S_2(\text{EO})_{4.14}$, $S_2(\text{EO})_{8.68}$, $S_2(\text{EO})_{13.23}$, $S_4(\text{EO})_{4.14}$, $S_4(\text{EO})_{8.68}$, $S_4(\text{EO})_{13.23}$, $S_6(\text{EO})_{4.14}$, $S_6(\text{EO})_{8.68}$, and $S_6(\text{EO})_{13.23}$; m and n represent the number of CH_2 groups in the spacer and the number of $\text{CH}_2\text{-CH}_2\text{-O}$ groups, respectively), were finally obtained from the reaction of B-1, B-2, and B-3 with PEG-200, PEG-300 and PEG-400, respectively. The structures of the starting reactant (HMTS), intermediate product (A, B-m), and reaction products ($S_m(\text{EO})_n$) were confirmed and analyzed by Fourier transform infrared spectroscopy (FTIR) and ^1H nuclear magnetic resonance spectroscopy (^1H NMR), and these data are included in the Electronic Supplementary Information (Figs. S2 and S3, respectively).

2.3. Characterization and measurements

The structures of HMTS, A, B-m, and $S_m(\text{EO})_n$ were characterized by FTIR from KBr discs on a Bruker Vector 33 FTIR spectrometer (Bruker Instruments, Germany) over the range 4000-400 cm^{-1} . The structures of A, B-m, and $S_m(\text{EO})_n$ were further characterized by ^1H NMR on a Bruker Avance NMR-500 MHz spectrometer using CD_3CN and CDCl_3 as solvents. A Krüss K122 tensiometer (Krüss, Germany) was used to measure the surface tension of the aqueous $S_m(\text{EO})_n$ solutions with varying concentrations at 298.15 K. Each value of the surface tension was the average of five replicates, with less than 1% variation. The dynamic surface tension of the aqueous superspreader solution (1 mmol/L) was further determined using a bubble pressure tensiometer (BP 100, Krüss, Germany). A gas bubble was formed from a capillary (SH2031) with an inner diameter of 0.227 mm. The measurement was performed from 5 ms to 100000 ms, and the instrument was calibrated before each new measurement using double-distilled water surface tension standards with corresponding surface tension values of 72.1 mN/m at 25 °C. The microstructures of the surfactant aggregates were observed by transmission electron microscopy (TEM; JEM-2100, JEOL, Japan) with 2 wt.% uranyl acetate negative staining. The particle size distribution of the aggregates was determined by dynamic light scattering (DLS) (ZS Nano ZS 90, Malvern Co.). To study the spreading behavior of the droplet of the superspreaders on the surface of the rice/mango plant leaves, the dynamic contact angle was measured using a droplet shape analyzer (DSA30, Krüss, Germany) with a precision degree of 0.01° that was connected to two CCD cameras. The samples (leaves) were fixed using double-sided adhesive tape onto a clinic stage, and the vertical and horizontal CCD cameras monitored the droplet shape and dynamic contact angle individually. The temperature of these experiments was maintained at 25 ± 1 °C, and the environmental humidity was maintained at $50 \pm 5\%$. The dynamic contact angles were obtained from the side view of the horizontal CCD camera. The droplet spread radius and area were directly determined using the true image of the droplet shape, and image analysis was performed with ImageJ software. To minimize the deviations, twenty pieces of plant leaves were measured for each parallel experiment, and each data point for the dynamic contact angle was the average of the above replicates. Every experiment was repeated at least five times until the reproducibility was satisfactory to ensure

minimal relative error, and each data point was the average of the above replicates. The morphologies of the surfaces of the plant leaves was observed by field emission scanning electron microscopy (FE-SEM, ZEISS-SUPRA55, Germany) at an acceleration voltage of 2 kV. Moreover, the surface roughness was investigated by atomic force microscopy (AFM, Dimension® Edge™, Bruker) in the tapping mode using an RTESP tip. Two-dimensional and three-dimensional topographic images were acquired by scanning sizes measuring 20 $\mu\text{m} \times 20 \mu\text{m}$. R_a and R_q denote the arithmetic averages of the absolute values of the surface height deviations solved based on the mean plane and the root mean square average of the height deviations based on the mean image data plane, respectively.

3. RESULTS AND DISCUSSION

3.1. Surface activities and aggregation properties of surfactants in aqueous solution

The surface activity of $S_m(\text{EO})_n$ in aqueous solutions was evaluated by measuring the equilibrium surface tension at 298.15 K. A plot of the surface tension vs the logarithm of different molar concentrations of surfactants is depicted in Fig. 1. The surface tension clearly decreased rapidly with increasing concentration and finally reached a plateau, where the concentration transition point corresponds to the CAC, indicating aggregate formation [28]. Two dashed fitted lines were drawn to identify the CAC and the corresponding surface tension (γ_{CAC}) through determination of the breakpoint between the two fitted straight lines. The obtained parameters for the as-prepared gemini surfactants are summarized in Table 1. The surface tension at the same concentration increased as $S_6(\text{EO})_{4.14} < S_4(\text{EO})_{4.14} < S_2(\text{EO})_{4.14} < S_6(\text{EO})_{8.68} < S_4(\text{EO})_{8.68} < S_2(\text{EO})_{8.68} < S_6(\text{EO})_{13.23} < S_4(\text{EO})_{13.23} < S_2(\text{EO})_{13.23}$, and the same trend was obtained for the CAC: $S_6(\text{EO})_{4.14} (3.84 \times 10^{-5} \text{ mol/L}) < S_4(\text{EO})_{4.14} (3.95 \times 10^{-5} \text{ mol/L}) < S_2(\text{EO})_{4.14} (4.08 \times 10^{-5} \text{ mol/L}) < S_6(\text{EO})_{8.68} (9.75 \times 10^{-5} \text{ mol/L}) < S_4(\text{EO})_{8.68} (1.06 \times 10^{-4} \text{ mol/L}) < S_2(\text{EO})_{8.68} (1.21 \times 10^{-4} \text{ mol/L}) < S_6(\text{EO})_{13.23} (1.84 \times 10^{-4} \text{ mol/L}) < S_4(\text{EO})_{13.23} (2.08 \times 10^{-4} \text{ mol/L}) < S_2(\text{EO})_{13.23} (2.11 \times 10^{-4} \text{ mol/L})$. The corresponding γ_{CAC} values increased as $S_6(\text{EO})_{4.14} (21.00 \text{ mN/m}) < S_4(\text{EO})_{4.14} (21.37 \text{ mN/m}) < S_2(\text{EO})_{4.14} (21.61 \text{ mN/m}) < S_6(\text{EO})_{8.68} (22.25 \text{ mN/m}) < S_4(\text{EO})_{8.68} (22.42 \text{ mN/m}) < S_2(\text{EO})_{8.68} (22.56 \text{ mN/m}) < S_6(\text{EO})_{13.23} (23.62 \text{ mN/m}) < S_4(\text{EO})_{13.23} (23.69 \text{ mN/m}) < S_2(\text{EO})_{13.23} (24.10 \text{ mN/m})$. These results indicate that the CAC and γ_{CAC} depend little on the length of the spacer (m), e.g., the CAC ($4.08 \times 10^{-5} \text{ mol/L}$) and γ_{CAC} (21.61 mN/m) of $S_2(\text{EO})_{4.14}$ (m = 2) were similar to the CAC ($3.84 \times 10^{-5} \text{ mol/L}$) and γ_{CAC} (21.00 mN/m) of $S_6(\text{EO})_{4.14}$ (m = 6). The CAC and γ_{CAC} of $S_m(\text{EO})_n$ slightly decreased with an increasing number m (m = 2, 4 or 6, respectively) of $-\text{CH}_2-$ groups in the spacer because of the increased molecular hydrophobicity, easily reducing the surface tension and forming aggregates. For comparison, the CAC and γ_{CAC} depended on the numbers of ethoxy units (n(EO)), e.g., the CAC ($4.08 \times 10^{-5} \text{ mol/L}$) and γ_{CAC} (21.61 mN/m) of $S_2(\text{EO})_{4.14}$ (n(EO) = 4.14) were much lower than the CAC ($2.11 \times 10^{-4} \text{ mol/L}$) and γ_{CAC} (24.10 mN/m) of $S_2(\text{EO})_{13.23}$ (n(EO) = 13.23). The CAC and γ_{CAC} of $S_m(\text{EO})_n$ significantly increased as n increased (n(EO) = 4.14, 8.68, or 13.23) due to increased molecular hydrophilicity resulting in an increase in the hydrogen bonding force between ethoxy groups and water molecules and a decrease in aggregate formation. Similar results were reported in the literature [29,30]. Notably, these γ_{CAC} values were significantly lower than those of hydrocarbon-based surfactants (30-40 mN/m) [31] and were similar to those reported for other trisiloxane surfactants (20-25 mN/m) [7,8] and fluorosurfactants (18-28 mN/m) [9], which might be attributed to the two hydrophobic trisiloxane groups of the gemini surfactant molecules better facilitating the self assembly into aggregates and more efficiently decreasing the surface tension than the corresponding

monomeric surfactants. Moreover, other physicochemical parameters (Γ_{CAC} , A_{CAC} , ΔG_{mic}^{θ} , and ΔG_{ads}^{θ}) related to surface activity were calculated according to previous studies [32-35]. The variables Γ_{max} and A_{CAC} are also related to m and n , and an increase in the spacer group (CH_2) resulted in a slight decrease in Γ_{max} and an increase in A_{CAC} . Compared to a short spacer (e.g., $m = 4$), a long spacer (e.g., $m = 6$) created a longer distance between the two connected head groups, resulting in a loose distribution in the L/V interface, a decrease in Γ_{max} and an increase in A_{CAC} . An increase in $n(EO)$ apparently resulted in a decrease in Γ_{max} and an increase in A_{CAC} . Therefore, the surfactant molecules with more ethoxy units were much more loosely packed in the L/V interface potentially because the additional hydrophilic ethoxy chains could not lay vertically at the L/V interface but were rather tilted or curled. In addition, both ΔG_{mic}^{θ} and ΔG_{ads}^{θ} were negative, indicating that the $S_m(EO)_n$ products were able to spontaneously form aggregates in solution and adsorb at the L/V interface. The values of ΔG_{ads}^{θ} were more negative than ΔG_{mic}^{θ} , indicating that the gemini surfactants more easily exhibited adsorption than micellization. Namely, the surfactant molecules tended to saturate at the surface first before starting the micellization process. An increase in the spacer group (CH_2) resulted in an increase in the absolute values of ΔG_{mic}^{θ} and ΔG_{ads}^{θ} , and an increase in ethoxy units (CH_2-CH_2-O-) apparently resulted in a decrease in the absolute values of ΔG_{mic}^{θ} and ΔG_{ads}^{θ} . Increased molecular hydrophobicity of the gemini surfactant made it easier to form aggregates and absorb in the L/V interface, whereas increased hydrophilicity had the opposite effect.

The morphologies of the gemini surfactant aggregates in the aqueous $S_m(EO)_n$ solutions at a CAC of 8 were investigated by TEM. As shown in Fig. 2(a-i), the surfactant molecules self-assembled into spherical morphologies or nearly spherical aggregates with a range of diameters from approximately 120 to 350 nm, and a small amount of partial particles was mutually coherent with each other. The hydrodynamic size distributions of the aggregates formed by $S_m(EO)_n$ in aqueous solution were calculated from the DLS measurements shown in Fig. 3 and are summarized in Table 1. The intensity-weighted distribution curves of the aqueous $S_m(EO)_n$ solutions reveal a monomodal function with an average diameter centered at approximately 200 nm. The sizes of the micelles were also dependent on the chain lengths of the hydrophobic and hydrophilic spacers. On the one hand, the average sizes of the aggregates increased as the hydrophobic spacer increased (e.g., from 209.09 nm for $S_2(EO)_{4,14}$ ($m = 2$) and 216.95 nm for $S_4(EO)_{4,14}$ ($m = 4$) to 237.04 nm for $S_6(EO)_{4,14}$ ($m = 6$); from 205.50 nm for $S_2(EO)_{8,68}$ ($m = 2$) and 215.56 nm for $S_4(EO)_{8,68}$ ($m = 4$) to 234.91 nm for $S_6(EO)_{8,68}$ ($m = 6$); and from 195.34 nm for $S_2(EO)_{13,23}$ ($m = 2$) and 214.68 nm for $S_4(EO)_{13,23}$ ($m = 4$) to 229.89 nm for $S_6(EO)_{13,23}$ ($m = 6$)) likely due to the progressive penetration of the spacer into the hydrophobic core of the micelle, which allowed the surfactant molecules to pack tighter and form larger aggregates, which was reflected in the increase in diameter. On the other hand, the average sizes of the aggregates decreased with increasing length of the hydrophilic ethoxy chains (e.g., from 209.09 nm for $S_2(EO)_{4,14}$ and 205.5 nm for $S_2(EO)_{8,68}$ to 195.34 nm for $S_2(EO)_{13,23}$; from 216.95 nm for $S_4(EO)_{4,14}$ and 215.56 nm for $S_4(EO)_{8,68}$ to 214.68 nm for $S_4(EO)_{13,23}$; and from 237.04 nm for $S_6(EO)_{4,14}$ and 234.91 nm for $S_6(EO)_{8,68}$ nm to 229.89 nm for $S_6(EO)_{13,23}$) potentially due to the strong interaction between the hydrophilic ethoxy chains and water molecules lowering the hydrophobicity of the surfactant molecules and resulting in less favorable micellization, which was reflected in the decrease in diameter [36,37]. Furthermore, some large aggregates (sizes of approximately 300-350 nm) coexisted with small spherical micelles. The formation of partial, large, complex aggregates might have been due to the further assembly of small aggregates in close proximity induced by hydrogen bonding or van der Waals interactions among the

hydrophilic shells with a number of ethoxy chains [32,38,39]. The formation of dumbbell-like aggregates (see Fig. 2(g)) between two nearby small aggregates further confirms the possibility of the formation of large aggregates (see the schematic drawing in Fig. 3).

3.2. Dynamic spreading behavior of the surfactants on plant leaf surfaces

The dynamic surface tension was further measured to investigate the adsorption of the superspreader molecules at the liquid-vapor interface, as illustrated in Fig. 4. The whole spreading process can be characterized by three stages. (i) The initial short-term stage, during which the surface tension remains almost constant, takes approximately 30 ms. (ii) The second rapid stage consists of the surface tension decreasing from its initial value (approximately 71 mN/m) to its lowest value (< 30 mN/m). We refer below to the duration of this stage as “the adsorption time”. In particular, the surface tensions of $S_6(\text{EO})_{8.68}$, $S_4(\text{EO})_{8.68}$, $S_2(\text{EO})_{8.68}$ and Silwet L-77 reached their lowest values in 10 s, which indicates that the superspreader molecules could rapidly adsorb from the bulk to the interface in the short-time regime. (iii) In the third stage, the surface tension remains almost constant, which indicates that the adsorption has reached equilibrium. This stage was undetectable for $S_6(\text{EO})_{4.14}$, $S_4(\text{EO})_{4.14}$, $S_2(\text{EO})_{4.14}$, $S_6(\text{EO})_{13.23}$, $S_4(\text{EO})_{13.23}$, and $S_2(\text{EO})_{13.23}$ because their second stage was relatively slow. In addition, the adsorption time of the spreaders increased in the following order: $S_6(\text{EO})_{8.68} < S_4(\text{EO})_{8.68} < \text{Silwet L-77} < S_2(\text{EO})_{8.68} < S_6(\text{EO})_{4.14} < S_4(\text{EO})_{4.14} < S_2(\text{EO})_{4.14} < S_6(\text{EO})_{13.23} < S_4(\text{EO})_{13.23} < S_2(\text{EO})_{13.23}$. A shorter adsorption time corresponds to a faster migration rate of the superspreaders. In addition, the surface tension at 100 s increased in the following order: $S_6(\text{EO})_{4.14}$ (21.68 mN/m) $< S_4(\text{EO})_{4.14}$ (21.98 mN/m) $< S_2(\text{EO})_{4.14}$ (22.43 mN/m) $< S_6(\text{EO})_{8.68}$ (22.77 mN/m) $< S_4(\text{EO})_{8.68}$ (23.37 mN/m) $< S_2(\text{EO})_{8.68}$ (23.84 mN/m) $< \text{Silwet-77}$ (24.59 mN/m) $< S_6(\text{EO})_{13.23}$ (26.42 mN/m) $< S_4(\text{EO})_{13.23}$ (26.80 mN/m) $< S_2(\text{EO})_{13.23}$ (27.90 mN/m), which is consistent with the above obtained equilibrium surface tension.

Fig. 5 shows the dynamic contact angles of droplets of the spreaders on the surfaces of rice and mango leaves to reveal the dynamic spreading behavior. As observed from Fig. 5(a), all droplets displayed a rapid spreading phenomenon, especially $S_6(\text{EO})_{8.68}$, $S_4(\text{EO})_{8.68}$, and $S_2(\text{EO})_{8.68}$. In the first ten seconds, the dynamic contact angles sharply decreased from the initial contact angle (θ_0) in the fast spreading stage. Hence, the spreading speeds decreased and relaxed to the final contact angles (θ_∞), after which no apparent spreading occurred. In contrast, the θ_0 of pure water on rice and mango leaves was 130.7° and 88.7° , respectively, and neither contact angle subsequently changed much. Therefore, this spreading process can also be characterized in two stages: rapid short-term spreading followed by slow long-term spreading. A similar spreading process was reported by Bahr et al. [40]. The general spreading behavior of a surfactant solution is usually attributed to a positive spreading coefficient created by considerable reduction of the tension at the L/V and S/V interfaces due to the surfactant's ability to absorb at the interface. However, the lowest surface tension value (e.g., 21.00 mN/m for $S_6(\text{EO})_{4.14}$) of the surfactant solution did not guarantee the fastest spreading, but $S_6(\text{EO})_{8.68}$ (with a surface tension of 22.25 mN/m) showed the best spreading behavior. Similar results were reported in the literature [10]. Hence, rapid spreading behavior is complex and not simply related to the surface tension or the “hammer-like” molecular structure reported by Hill [11], but rather to the synergistic effects of many factors. To more clearly illustrate the spreading behavior, the spreading kinetics of aqueous $S_m(\text{EO})_n$ solutions were further investigated by calculating the droplet spreading radius ($r(t)$), spreading area ($S(t)$), and spreading rate (dr/dt). $r(t)$ and by directly determining $S(t)$ using the true image. As shown in Fig. 5(b-c) for the

$S_m(\text{EO})_n$ solutions, a significant difference was observed in the $r(t)$ and $S(t)$ of the droplet spreading on the rice leaf compared to pure water, the latter of which showed only a small change in its $r(t)$ and $S(t)$. At a fixed surfactant concentration, $r(t)$ and $S(t)$ increased significantly faster in approximately the first ten seconds and subsequently increased slowly, ultimately becoming nearly flat at a maximum value at one minute. $r(t)$ and $S(t)$ depended on both the hydrophobic spacer chain length and the hydrophilic ethoxy chain length. On the one hand, the dependence of $r(t)$ and $S(t)$ on the spacer length was monotonous for the same ethoxy chain length in that $S_m(\text{EO})_n$ products with different spacer chain lengths on the surface of the rice leaf increased with an increasing spacer chain length in the following order: $S_m(\text{EO})_n$ ($m = 2$) < $S_m(\text{EO})_n$ ($m = 4$) < $S_m(\text{EO})_n$ ($m = 6$) (e.g., for the maximum spreading radius: $S_2(\text{EO})_{4.14}$ (3.51 mm) < $S_4(\text{EO})_{4.14}$ (3.74 mm) < $S_6(\text{EO})_{4.14}$ (3.85 mm), $S_2(\text{EO})_{8.68}$ (4.35 mm) < $S_4(\text{EO})_{8.68}$ (4.60 mm) < $S_6(\text{EO})_{8.68}$ (5.47 mm), and $S_2(\text{EO})_{13.23}$ (2.60 mm) < $S_4(\text{EO})_{13.23}$ (2.79 mm) < $S_6(\text{EO})_{13.23}$ (2.91 mm); and for the maximum spreading area: $S_2(\text{EO})_{4.14}$ (38.79 mm²) < $S_4(\text{EO})_{4.14}$ (43.83 mm²) < $S_6(\text{EO})_{4.14}$ (46.67 mm²), $S_2(\text{EO})_{8.68}$ (59.38 mm²) < $S_4(\text{EO})_{8.68}$ (66.43 mm²) < $S_6(\text{EO})_{8.68}$ (94.00 mm²), and $S_2(\text{EO})_{13.23}$ (21.20 mm²) < $S_4(\text{EO})_{13.23}$ (24.44 mm²) < $S_6(\text{EO})_{13.23}$ (26.68 mm²)). The $r(t)$ and $S(t)$ of $S_6(\text{EO})_{8.68}$ and $S_4(\text{EO})_{8.68}$ on the rice leaf were larger than those of Silwet L-77 (4.44 mm and 61.82 mm², respectively), which indicates that $S_6(\text{EO})_{8.68}$ and $S_4(\text{EO})_{8.68}$ possess good superspreading behavior. On the other hand, the dependence of $r(t)$ and $S(t)$ on the ethoxy chain length was nonmonotonous with a maximum at $n(\text{EO}) = 8.68$ for the same spacer chain length, with both increasing in the following order for the $S_m(\text{EO})_n$ products with different ethoxy chain lengths on the surface of the rice leaf: $S_m(\text{EO})_n$ ($n(\text{EO}) = 13.23$) < $S_m(\text{EO})_n$ ($n(\text{EO}) = 4.14$) < $S_m(\text{EO})_n$ ($n(\text{EO}) = 8.68$) (e.g., for the maximum spreading radius: $S_2(\text{EO})_{13.23}$ (2.60 mm) < $S_2(\text{EO})_{4.14}$ (3.51 mm) < $S_2(\text{EO})_{8.68}$ (4.34 mm), $S_4(\text{EO})_{13.23}$ (2.79 mm) < $S_4(\text{EO})_{4.14}$ (3.74 mm) < $S_4(\text{EO})_{8.68}$ (4.60 mm), and $S_6(\text{EO})_{13.23}$ (2.91 mm) < $S_6(\text{EO})_{4.14}$ (3.85 mm) < $S_6(\text{EO})_{8.68}$ (5.47 mm); and for the maximum spreading area: $S_2(\text{EO})_{13.23}$ (21.20 mm²) < $S_2(\text{EO})_{4.14}$ (38.79 mm²) < $S_2(\text{EO})_{8.68}$ (59.38 mm²), $S_4(\text{EO})_{13.23}$ (24.44 mm²) < $S_4(\text{EO})_{4.14}$ (43.83 mm²) < $S_4(\text{EO})_{8.68}$ (66.43 mm²), and $S_6(\text{EO})_{13.23}$ (26.67 mm²) < $S_6(\text{EO})_{4.14}$ (46.67 mm²) < $S_6(\text{EO})_{8.68}$ (94.00 mm²)). The same trend was found in dr/dt (see Fig. 5(d)): dr/dt in the initial stage was higher than in the later stage. The dependence of the maximum dr/dt on the spacer length was monotonous for the same ethoxy chain length. The maximum dr/dt of the $S_m(\text{EO})_n$ products on the rice leaf increased with increasing spacer chain length in the following order: $S_2(\text{EO})_{4.14}$ (0.827 mm/s) < $S_4(\text{EO})_{4.14}$ (0.866 mm/s) < $S_6(\text{EO})_{4.14}$ (1.320 mm/s), $S_2(\text{EO})_{8.68}$ (1.238 mm/s) < $S_4(\text{EO})_{8.68}$ (1.243 mm/s) < $S_6(\text{EO})_{8.68}$ (1.802 mm/s), and $S_2(\text{EO})_{13.23}$ (0.764 mm/s) < $S_4(\text{EO})_{13.23}$ (0.894 mm/s) < $S_6(\text{EO})_{13.23}$ (1.043 mm/s). The dependence of the maximum dr/dt on the ethoxy chain length was nonmonotonous for the same spacer chain length with a maximum at $n = 8.68$. Both increased for the $S_m(\text{EO})_n$ products with different ethoxy chain lengths in the following order: $S_m(\text{EO})_n$ ($n(\text{EO}) = 13.23$) < $S_m(\text{EO})_n$ ($n(\text{EO}) = 4.14$) < $S_m(\text{EO})_n$ ($n(\text{EO}) = 8.68$) (e.g., $S_2(\text{EO})_{13.23}$ (0.764 mm/s) < $S_2(\text{EO})_{4.14}$ (0.827 mm/s) < $S_2(\text{EO})_{8.68}$ (1.238 mm/s), $S_4(\text{EO})_{13.23}$ (0.894 mm/s) < $S_4(\text{EO})_{4.14}$ (0.866 mm/s) < $S_4(\text{EO})_{8.68}$ (1.243 mm/s), and $S_6(\text{EO})_{13.23}$ (1.043 mm/s) < $S_6(\text{EO})_{4.14}$ (1.320 mm/s) < $S_6(\text{EO})_{8.68}$ (1.802 mm/s)). The dr/dt for $S_m(\text{EO})_n$ increased in the following order: $S_2(\text{EO})_{13.23}$ (0.0203 mm/s) < $S_4(\text{EO})_{13.23}$ (0.0224 mm/s) < $S_6(\text{EO})_{13.23}$ (0.0245 mm/s) < $S_2(\text{EO})_{4.14}$ (0.0345 mm/s) < $S_4(\text{EO})_{4.14}$ (0.0380 mm/s) < $S_6(\text{EO})_{4.14}$ (0.0398 mm/s) < $S_2(\text{EO})_{8.68}$ (0.0475 mm/s) < $S_4(\text{EO})_{8.68}$ (0.0513 mm/s) < $S_6(\text{EO})_{8.68}$ (0.0625 mm/s). The dependence of the average dr/dt on the spacer length was monotonous for the same ethoxy chain length. The average dr/dt of the $S_m(\text{EO})_n$ products on the surface of the rice leaf increased with increasing spacer chain length in the

following order: $S_m(\text{EO})_n$ ($m = 2$) < $S_m(\text{EO})_n$ ($m = 4$) < $S_m(\text{EO})_n$ ($m = 6$) (e.g., $S_2(\text{EO})_{4.14}$ < $S_4(\text{EO})_{4.14}$ < $S_6(\text{EO})_{4.14}$, $S_2(\text{EO})_{8.68}$ < $S_4(\text{EO})_{8.68}$ < $S_6(\text{EO})_{8.68}$, and $S_2(\text{EO})_{13.23}$ < $S_4(\text{EO})_{13.23}$ < $S_6(\text{EO})_{13.23}$). A faster migration rate of surfactant molecules from the bulk solution to the L/V or S/L interface may improve the dr/dt as a result of the increased molecular hydrophobicity with increasing spacer chain length. The dependence of the average dr/dt on the ethoxy chain length was nonmonotonous with a maximum at $n = 8.68$ for the same spacer chain length, with both increasing in the following order for the $S_m(\text{EO})_n$ products with different ethoxy chain lengths: $S_m(\text{EO})_n$ ($n(\text{EO}) = 13.23$) < $S_m(\text{EO})_n$ ($n(\text{EO}) = 4.14$) < $S_m(\text{EO})_n$ ($n(\text{EO}) = 8.68$) (e.g., $S_2(\text{EO})_{13.23}$ < $S_2(\text{EO})_{4.14}$ < $S_2(\text{EO})_{8.68}$, $S_4(\text{EO})_{13.23}$ < $S_4(\text{EO})_{4.14}$ < $S_4(\text{EO})_{8.68}$, and $S_6(\text{EO})_{13.23}$ < $S_6(\text{EO})_{4.14}$ < $S_6(\text{EO})_{8.68}$). The spreading behavior is dependent on the proper ethoxy chain length, namely, the synergism between solubility and hydrophobicity. Compared to $S_m(\text{EO})_n$ ($n(\text{EO}) = 8.68$), the lower solubility of a shorter hydrophilic ethoxy chain ($n(\text{EO}) = 4.14$) is unfavorable for the migration rate of surfactant molecules despite its greater hydrophobicity. The lower hydrophobicity of a longer hydrophilic ethoxy chain ($n(\text{EO}) = 13.23$) is unfavorable for the migration rate of surfactant molecules despite its higher solubility. This phenomenon is consistent with the results obtained by Ivanova et al. [41], according to which more hydrophilic surfactants with $n(\text{EO}) = 6, 8$ demonstrated a lower wetting ability on different polymeric substrates compared to surfactants with shorter EO chains with $n(\text{EO}) = 3, 4$. Hence, the HLB of the surfactants plays a very crucial role in the spreading behavior. In our experiments, the HLB of the surfactants was calculated by Griffin's method [42,43]: $\text{HLB} = 20 \cdot M_h/M$, where M_h is the molecular mass of the hydrophilic portion of the molecule and M is the molecular mass of the whole molecule. The HLB values of $S_m(\text{EO})_n$ are listed in Table 1. Notably, the HLB values of $S_6(\text{EO})_{8.68}$, $S_4(\text{EO})_{8.68}$, and $S_2(\text{EO})_{8.68}$, which possessed good spreading ability, were 10.10, 10.28, and 10.47, respectively, which is consistent with an earlier study that found an HLB value of approximately 10 for the surfactant with the best spreading behavior [20]. The HLB of the trisiloxane ethoxylate surfactant, Silwet L-77, was also approximately 10. Therefore, an optimal HLB of approximately 10 is necessary to achieve good spreading.

In addition to the spacer chain length, ethoxy chain length and optimal HLB value, the superspreading behavior was also significantly influenced by the surfactant concentration. According to earlier research [44], trisiloxane surfactants have a CWC and undergo a transition from partial spreading (below the CWC) to complete spreading (above the CWC) on some moderately hydrophobic surfaces, which results in a "superspreading" behavior. This suggests that the CWC is correlated with the beginning of the superspreading process [7]. Herein, plots of the final contact angles of droplets of $S_m(\text{EO})_n$ solutions vs the logarithm of the concentrations are depicted in Fig. 6. Each final contact angle was the average of five measurements, with less than 1% variation. The final contact angle gradually decreased with increasing surfactant concentration until a plateau was reached. Two dashed fitted lines were drawn to identify the CWCs by determining the points of intersection of the fitted straight lines. The obtained CWCs increased in the following order: $S_6(\text{EO})_{8.68}$ (0.268 mmol/L) < $S_4(\text{EO})_{8.68}$ (0.364 mmol/L) < $S_2(\text{EO})_{8.68}$ (0.436 mmol/L) < $S_6(\text{EO})_{4.14}$ (0.495 mmol/L) < $S_4(\text{EO})_{4.14}$ (0.556 mmol/L) < $S_2(\text{EO})_{4.14}$ (0.589 mmol/L) < $S_6(\text{EO})_{13.23}$ (0.615 mmol/L) < $S_4(\text{EO})_{13.23}$ (0.671 mmol/L) < $S_2(\text{EO})_{13.23}$ (0.737 mmol/L). This trend is the opposite of the trend in the average dr/dt for the $S_m(\text{EO})_n$ products. For the droplets of surfactant solution, a better spreading ability corresponded to a lower CWC, and the CWCs were three or even ten times higher than the corresponding CACs. The obtained CWCs for the $S_m(\text{EO})_n$ products were of the same order of magnitude as the CWC of the trisiloxane surfactant T₇ (0.40 mmol/L) and trisiloxane surfactant

T₈ (0.70 mmol/L) [7]. Hence, the superspreading behavior was associated with the concentration above the CWC based on the Marangoni mechanism because the surface tension gradient tended to be most significant at an intermediate concentration [4].

Moreover, the Marangoni effect on the superspreading phenomenon for different molecular structures of surfactant was further analyzed by calculating the spreading exponent. The obtained data for the evolution over time of the droplets based on the radius were fitted by the power law $r \sim t^N$, where r is the radius of the spreading area, t is the spreading time and N is the spreading exponent. The analysis of the spreading exponent followed the analysis presented in [10]. The spreading exponent N of the S_m(EO)_n products at a CAC of 8 (above the CWC) followed an order of S₆(EO)_{8.68}@mango ($N = 0.521$) > S₆(EO)_{8.68}@rice ($N = 0.454$) > S₄(EO)_{8.68}@rice ($N = 0.411$) > Silwet L-77@rice ($N = 0.396$) > S₂(EO)_{8.68}@rice ($N = 0.392$) > S₆(EO)_{4.14}@rice ($N = 0.357$) > S₄(EO)_{4.14}@rice ($N = 0.345$) > S₂(EO)_{4.14}@rice ($N = 0.331$) > S₆(EO)_{13.23}@rice ($N = 0.268$) > S₄(EO)_{13.23}@rice ($N = 0.259$) > S₂(EO)_{13.23}@rice ($N = 0.247$), suggesting that N was related to the molecular structure of the surfactant and the substrate wettability. Capillary forces play a significant role in spreading at $N = 0.10$ [40,45,46]. Marangoni forces are considered to be responsible for spreading at $N \geq 0.25$ [21,47,48]. Therefore, Marangoni forces were mainly responsible for this superspreading. Moreover, the Marangoni effect was related to the molecular structure of the surfactant and substrate wettability as well as the concentration of surfactant, which was also considered in the literature [21,22]. Some authors have reported that the obtained CWCs were independent of the surface energies of the substrates on which a droplet of solution spreads [45,49]. However, in this work, the effects of two substrates with different wetting abilities (hydrophobic rice leaf and hydrophilic mango leaf) on the spreading behavior are discussed. The initial contact angles were 44.4° and 37.5° for S₆(EO)_{8.68} on the rice and mango leaves (see Fig. 5(a)), respectively. S₆(EO)_{8.68} completely spread on the mango and rice leaves with final contact angles of 1.4° and 0.6°, respectively. Although there was very little difference in the final contact angles on the rice and mango leaves, the corresponding spreading radius and areas were greatly influenced (5.47 mm and 94.00 mm² for rice and 7.01 mm and 154.58 mm² for mango, respectively). Additionally, the average dr/dt for S₆(EO)_{8.68} on the mango leaf (0.084 mm/s) was higher than that on the rice leaf (0.062 mm/s). S₆(EO)_{8.68} exhibited better superspreading behavior on the mango leaf than on the rice leaf.

The varying wettabilities of the substrates significantly affected the superspreading behavior and were greatly influenced by the surface morphology, including the surface energy. Fig. 7 shows images of the rice and mango leaves obtained using SEM and AFM. SEM revealed that the morphology of the rice plant leaf as a hierarchical 3-D structure constructed by combining micro- and nanostructures. The surface of the rice leaf contained sub-millimeter-scale grooves and was patterned with arrays with widths ranging between 100-200 μm. The partially enlarged image indicates that the plant surface was randomly distributed with the cylindrically tapered micropapillae, which were superimposed by a dense distribution of waxy nanoplatelets. The micropapillae were 3-5 μm high and 4-8 μm wide. An epicuticular wax layer covered the surface. From the AFM images, the rice leaf had a fairly rough surface with R_q and R_a of 1.25 μm and 1.01 μm, respectively. The hierarchical 3-D structure agreed with that of the lotus leaves and is believed to have contributed to the hydrophobicity of the rice plant leaf. In contrast, there was a relatively smooth 2-D wax layer on the surface of the mango leaf in the absence of 3-D wax crystals. The surface of the mango leaf contained cuticula crusts and randomly distributed elliptical stomata (lengths of the long and the short axes were 4.8 μm and

2.9 μm , respectively, and the distance between stomata was $\sim 20 \mu\text{m}$). Compared with the rice plant leaf, the mango leaf presented a rather smooth surface with R_q and R_a of 0.304 μm and 0.235 μm , respectively, which was believed to contribute to the hydrophilicity of the mango leaf. According to the aforementioned data, the velocity and exponent of spreading for $S_6(\text{EO})_{8.68}$ at a CAC of 8 on the mango leaf surface was greater than that on the rice leaf, confirming that the substrate wettability indeed influenced the superspreading behavior.

Despite significant experimental efforts and molecular dynamics simulations [1,4,7,13,15,16,49,50-53], the precise mechanisms underlying superspreading remain unknown to date, and more work is needed to elucidate the various aspects of superspreading. It is now clear that the combined effects of different factors may hold the key to elucidating the superspreading mechanism. Based on our work and earlier studies, a possible spreading mechanism on hydrophobic vs. hydrophilic substrates is proposed in Fig. 8. The varying dynamics of the spreading processes proceed as follows. When the surfactant concentration is greater than the CWC, a favorable condition for aforementioned superspreading, some surfactant molecules are oriented at the L/V interface of a liquid droplet [29,30,54], while other molecules generally integrate themselves into aggregates typically consisting of spherical micelles with the hydrophobic portion inside the core and the hydrophilic portion towards the water interface. Once the droplet contacts the substrates, the droplet immediately relaxes. The ways in which the surfactant molecules are rapidly adsorbed onto the hydrophobic and hydrophilic substrates varies. The hydrophobic part of the molecule is inclined to be adsorbed on the surface of a hydrophobic substrate from the L/V interface to the contact line (see Fig. 8(a)). By contrast, the hydrophilic part of the molecule is prone to be adsorbed on the surface of the hydrophilic substrate (see Fig. 8(c)). At the end of relaxation, a contact angle is formed, which is referred to as the initial contact angle (θ_0). Obviously, the initial contact angles were greatly influenced by the aforementioned molecular structure of the superspreader and substrate (e.g., $\theta_0 = 64.5^\circ$ for $S_2(\text{EO})_{4.14}$ @rice, $\theta_0 = 44.5^\circ$ for $S_6(\text{EO})_{8.68}$ @rice, and $\theta_0 = 37.6^\circ$ for $S_6(\text{EO})_{8.68}$ @mango), in addition to the concentration. The phenomenon of a decreasing initial contact angle of the droplet with increasing concentration was mentioned by Starov et al. [50]. The initial contact angles depend on the interface tension and surface roughness (e.g., $R_q = 1.25 \mu\text{m}$ for the rice leaf surface, $R_q = 0.304 \mu\text{m}$ for the mango leaf surface). The duration of the above stage is in the range of milliseconds, which was stated in the literature [50]. Afterwards, the droplet begins to spread on the substrate. A water film of a molecularly thin precursor is generated and spreads in a capillary rise geometry from the droplet at the S/V interface prior to spreading to the droplet's edge (see Figs. 8(b) and (d)). Popescu et al. [55] proposed that this thin precursor water film results from the competition between the gain in entropy and the balance of the attractive interactions occurring between fluid particles for water molecules and substrate particles and the attractive interactions among the fluid particles. The boundary particles in the front of the film consecutively transit over the raised part of the uneven surface away from the droplet to move forward. The particles need to tackle a potential barrier, which changes greatly depending on the difference in roughness. Thus, the shape of the precursor film during spreading was affected by the two types of substrates described above. The low-energy substrates (hydrophobic) with a molecularly thin precursor film were compared to the high-energy substrates (hydrophilic) with a terraced-shaped precursor water film, as shown in Figs. 8(b) and (d), respectively. The latter substrate type contained five such molecular layers, considering the macroscopic part of the droplet as a reservoir, which was confirmed by the literature [56]. Furthermore, the thicknesses of the films in both cases significantly changed in

the particular S/L system: ranging from several (molecular size) to hundreds of angstroms. The radius of the film $R(t)$ grew in proportion to $\sqrt{t}$, which was proposed in the literature [57]. In the meantime, the surfactants at the leading edge could be instantly adsorbed onto the precursor film from the L/V and S/L interfaces from the bulk, as suggested by Popescu et al. [55] and further confirmed by Theodorakis et al. [53] through molecular dynamics simulations. As a result, a decrease in the local surface concentration of the surfactant led to a larger surface tension at the perimeter instead of at the apex. This further resulted in a surface tension gradient along the direction of the arrow between the precursor film and droplet surface, and the gradient formed the Marangoni effect along the direction of the precursor film on the substrate surface. The central droplet surface therefore moved outwards and spread onto the substrate until the gradient reduced. A detailed discussion of theoretical arguments supporting the Marangoni effect mechanism together with experimental evidence has been given in previous studies [16,49,51]. The formation of surface tension gradients resulting in the Marangoni effect was also observed in numerical simulations [55]. The Marangoni effect was clearly the driving force for the superspreading process because all the spreading exponents n were above 0.25 in our experiments. A greater Marangoni driving force with a higher spreading exponent results in a more rapid superspreading process. As mentioned above, the Marangoni effect was related to the surfactant concentration, molecular structure of the surfactant (e.g., $S_6(EO)_{8.68}$ had a maximum Marangoni effect) and substrate wettability: more attractive interactions occurred between the water fluid particles and the substrate particles on a more hydrophilic substrate surface, and the particles in the film tended to proceed forward by hopping to the raised portion of the bulged part when the substrate had a less rough surface of both the boundary and the fluid. In this case, the precursor water film is more likely to be generated. In contrast, more hydrophobic and rougher surfaces are not detrimental to the generation of the precursor water film. With the spreading of the droplets, the contact angle gradually decreased, the areas of the L/V and S/L interfaces continually expanded, and the surfactants were continually depleted by the adsorption of aggregates to the area of expansion. For continued spreading in the superspreading process, maintaining a positive spreading velocity is crucial. A faster migration rate of surfactant molecules from the bulk solution to the L/V or S/L interface may improve the spreading velocity, and surfactant diffusion could be the rate-determining step for the superspreading process mentioned by Venzmer [15]. As mentioned previously, the spreading in our experiment above the CWC proceeds in two stages. The spreading velocity in the first short and fast stage is far higher than the second slow stage. The fast stage of spreading is probably determined by the fast adsorption of surfactant molecules at the L/V interface. The slow stage could be explained by the reduction of the spreading rate due to the competition between the rate of surfactant adsorption at the L/V interface and the rate of molecule depletion due to the expansion of this interface in the course of spreading. The Marangoni drive can be retained until the disappearance of aggregates as a reservoir for the surfactants. Finally, the Marangoni drive disappears, and the liquid droplet becomes a water film covering the substrate. In conclusion, the superspreading mechanism greatly depends on the integrated effects of the precursor water film and the Marangoni effect in the presence of a suitable molecular structure or HLB.

4. Conclusions

A series of novel trisiloxane gemini surfactants ($S_m(EO)_n$) were designed and synthesized to study the relationship between molecular structure and superspreading properties. Surfactants

possessing a good spreading ability were obtained by a three-step reaction under microwave irradiation. The FTIR and ^1H NMR results confirmed the successful preparation of the $\text{S}_m(\text{EO})_n$ products. The effects of molecular structure on the surface and aggregation properties of the $\text{S}_m(\text{EO})_n$ products were investigated in aqueous solution, and the $\text{S}_m(\text{EO})_n$ products had good surface-active properties. An increase in the spacer group (CH_2) resulted in a decrease in the CAC, γ_{CAC} , and Γ_{max} but an increase in A_{CAC} and the absolute value $\Delta G_{\text{mic}}^\theta$ and $\Delta G_{\text{ads}}^\theta$. An increase in ethoxy units ($\text{CH}_2\text{-CH}_2\text{-O-}$) resulted in an increase in the CAC, γ_{CAC} , and A_{CAC} but a decrease in Γ_{max} and the absolute value $\Delta G_{\text{mic}}^\theta$ and $\Delta G_{\text{ads}}^\theta$. The TEM and DLS results showed that the formed aggregates of surfactant solutions at a CAC of 8 were spherical or nearly spherical in shape with an average diameter of approximately 200 nm. The average sizes of the aggregates increased with increases in the spacer (CH_2) but decreased with an increasing number of ethoxy units ($\text{CH}_2\text{-CH}_2\text{-O-}$). The dynamic spreading parameters were evaluated to investigate the dynamic spreading phenomenon on rice and mango leaf substrates. These parameters included the contact angle, $r(t)$, $S(t)$, dr/dt , n , and CWC, which depended on the hydrophobic spacer chain length and the hydrophilic ethoxy chain length. The maximum spreading radius, wetted area, average spreading velocity, spreading exponent, and CWC for the $\text{S}_m(\text{EO})_n$ products on the surface of the rice leaf increased with an increasing spacer chain length. The dependence of the maximum spreading velocity on the ethoxy chain length was nonmonotonous with a maximum at $n(\text{EO}) = 8.68$. The CWC for the $\text{S}_m(\text{EO})_n$ products (0.2-0.8 mmol/L) were of the same order of magnitude as that of the trisiloxane surfactants T_7 (0.40 mmol/L) and T_8 (0.70 mmol/L). The droplets of $\text{S}_m(\text{EO})_n$ went through fast and slow stages, and $\text{S}_6(\text{EO})_{8.68}$, with an HLB value of approximately 10, showed the best spreading ability. Therefore, an optimal HLB of approximately 10 was crucial to achieving good spreading. The spreading exponent N obtained by calculation ($\text{S}_6(\text{EO})_{8.68}@\text{mango}$ ($N = 0.521$) > $\text{S}_6(\text{EO})_{8.68}@\text{rice}$ ($N = 0.454$) > $\text{S}_4(\text{EO})_{8.68}@\text{rice}$ ($N = 0.411$) > $\text{Silwet L-77}@\text{rice}$ ($N = 0.396$) > $\text{S}_2(\text{EO})_{8.68}@\text{rice}$ ($N = 0.392$) > $\text{S}_6(\text{EO})_{4.14}@\text{rice}$ ($N = 0.357$) > $\text{S}_4(\text{EO})_{4.14}@\text{rice}$ ($N = 0.345$) > $\text{S}_2(\text{EO})_{4.14}@\text{rice}$ ($N = 0.331$) > $\text{S}_6(\text{EO})_{13.23}@\text{rice}$ ($N = 0.268$) > $\text{S}_4(\text{EO})_{13.23}@\text{rice}$ ($N = 0.259$) > $\text{S}_2(\text{EO})_{13.23}@\text{rice}$ ($N = 0.247$) was related to not only the molecular structure of the surfactant but also the substrate wettability. The spreading velocity of $\text{S}_6(\text{EO})_{8.68}$ on the mango leaf was higher than that on the rice leaf, indicating that the substrate with a hydrophilic and relatively smooth surface (based on SEM and AFM images) presented a better spreading ability than that on a hydrophobic or relatively rough surface. Moreover, the Marangoni forces were considered to be responsible for the spreading, with exponent values above 0.25. After a comprehensive analysis of our work combined with the previously reported literature, a possible spreading mechanism was proposed, which illustrated that the synergistic effects of the precursor water film and Marangoni effect played important roles in the superspreading mechanism on the premise of an appropriate molecular structure or HLB. This work provides a basis for the molecular structure design of superspreaders and furthers our understanding of the superspreading mechanism.

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Conflicts of Interest

All authors declare no conflicts of interest.

ACCEPTED MANUSCRIPT

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Figure Legends

Fig. 1 Plots of the equilibrium surface tension of aqueous S_mEO_n solutions as a function of the concentration at 298 K.

Fig. 2 TEM images (a-i) of the S_mEO_n surfactants

Fig. 3 DLS of the S_mEO_n surfactants.

Fig. 4 Dynamic surface tension for spreader solutions at 298 K as a function of time.

Fig. 5 Evolution of the dynamic contact angle (a), radius (b), wetted area (c), and velocity of spreading droplets of aqueous superspreaders (S_mEO_n) on the surface of plant leaves.

Fig. 6 Dependence of the final contact angle on the surfactant concentration for droplets of S_mEO_n solutions on rice leaves.

Fig. 7 SEM and AFM images of the rice (a and c, respectively) and mango (b and d, respectively) leaves.

Fig. 8 Schematic representation of a possible spreading mechanism on a hydrophobic (a-b) vs. hydrophilic (c-d) substrate.

Tables

Table 1 Parameters of the aggregation and adsorption of $S_m(EO)_n$ at 298 K.

Surfactants	γ_{CAC} (mN/m)	CAC (mol/L)	Γ_{max} ($\mu\text{mol}/\text{m}^2$)	A_{CAC} ($\text{\AA}^2/\text{molecule}$)	ΔG_{mic}^θ (kJ/mol)	ΔG_{ads}^θ (kJ/mol)	Particles size	HLB
$S_2(EO)_{4.14}$	21.61	4.08×10^{-5}	1.19	139.30	-35.01	-77.26	209.09	7.08
$S_2(EO)_{8.68}$	22.56	1.21×10^{-4}	1.13	146.98	-32.32	-76.05	205.50	10.47
$S_2(EO)_{13.23}$	24.10	2.11×10^{-4}	1.08	153.22	-30.94	-75.11	195.34	12.45
$S_4(EO)_{4.14}$	21.37	3.95×10^{-5}	1.17	142.23	-35.09	-78.43	216.95	6.91
$S_4(EO)_{8.68}$	22.42	1.06×10^{-4}	1.11	149.22	-32.64	-77.17	215.56	10.28
$S_4(EO)_{13.23}$	23.69	2.08×10^{-4}	1.06	156.54	-30.97	-76.49	214.68	12.27
$S_6(EO)_{4.14}$	21.00	3.84×10^{-5}	1.16	143.00	-35.16	-79.05	237.04	6.75
$S_6(EO)_{8.68}$	22.25	9.75×10^{-5}	1.07	154.52	-32.85	-79.02	234.91	10.10
$S_6(EO)_{13.23}$	23.62	1.84×10^{-4}	1.03	160.63	-31.28	-78.05	229.89	12.10

Figure Legends

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HIGHLIGHTS:

- The trisiloxane-based gemini-surfactant is a promising superspreader.
- The molecular structure and substrate wettability influenced the superspreading.
- The optimal HLB value was essential to obtaining good superspreading behavior.
- The synergistic effects of the precursor film and Marangoni effect existed in superspreading.