# Synthesis and Characterization of Glucosamide-Based Trisiloxane Gemini Surfactants

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**ABSTRACT:** A new family of glucosamide-based trisiloxane gemini surfactants of the general formula $(CH_2OCH_2)_n$ $(Me_3SiOSiMeR^1OSiMe_3)_2$ (where $R^1 = (CH_2)_3NR^2(CH_2)_2NHCO$ $(CHOH)_4CH_2OH$; $R^2 = CH_2CH(OH)CH_2OCH_2$; and $n = 0, 1$, or 2) was prepared and characterized, both structurally and as aqueous surfactants. The monomer was prepared by amidation of the precursor amine functional trisiloxane with D-gluconic acid δ-lactone. Gemini surfactants were then prepared by the alkylation of the precursor secondary amine with oligoethylene glycol diglycidyl ethers. They were structurally characterized by proton and ^{13}C nuclear magnetic resonance and elemental analysis. Members of this family reduced the surface tension of water to approximately 21 mN/m at concentration levels of $10^{-5}$ mol/L. These gemini compounds showed two critical aggregation concentration values. This behavior resulted from the formation of premicellar aggregates before true micelles were formed.

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**KEY WORDS:** Characterization, gemini, glucosamide, premicellar aggregates, surface tension, synthesis, trisiloxane.

In recent years, silicone surfactants have attracted considerable interest because of their many technical applications. Owing to their unique molecular structure compared with that of normal hydrocarbon surfactants, they have excellent surface-active properties for special purposes. They can also reduce the surface tension of water to lower values than can be obtained using traditional organic surfactants. Furthermore, because of their bulkiness and molecular structure, the adhesion forces between the individual molecules in interfacial films are small; for this reason, the compounds act as good wetting agents. Silicone surfactants are also known for their low physiological risk in cosmetic applications.

In contrast, sugar-based surfactants have been known for many years. In recent years, they have begun to be produced on an industrial scale and their use has gradually increased because of their valuable properties, such as good dermatological compatibility, excellent biodegradability, and the absence of toxic effects.

Over a decade ago, gemini (dimeric) surfactants, a new class of surfactants consisting of two hydrophobic chains and two hydrophilic headgroups connected by a relatively short (rigid or flexible) spacer, were developed. These dimeric compounds show improved surfactant properties compared with monomeric surfactants. Gemini surfactants have attracted considerable interest, since these compounds have much smaller critical micelle concentration (CMC) values, much greater efficiency in reducing surface tension than expected, and better aggregation behavior. Gemini surfactants have been generating increasing interest owing to their tunable molecular geometry and their superior performance in applications (the CMC of the gemini is very low, so less gemini may be needed to reduce the surface tension of the solution).

The unique surfactant properties of gemini surfactants have prompted investigations by a number of researchers. Those that have been studied in greatest depth, in terms of their physicochemical behavior, have been the cationic gemini surfactants (1–13), although research on anionic (14–24), zwitterionic (25), and nonionic (26–35) dimeric surfactants also has been conducted.

The aforementioned properties of gemini surfactants prompted us to design and synthesize a new type of amphiphilic molecule composed of two glucosamide-based trisiloxane molecules linked through a spacer. Our use of glucosamide-based trisiloxane as a monomer was due mainly to the biodegradability of the glucosamide and the superior interfacial tension of the trisiloxane.

In this paper, we report on the preparation of a family of glucosamide-based trisiloxane gemini surfactants. The surface activity of these dimeric compounds was studied by measuring the equilibrium surface tension of their dilute aqueous solutions.

## EXPERIMENTAL PROCEDURES

*Preparation of glucosamide-based trisiloxane gemini surfactants.* Four trisiloxane surfactants (compounds **I–IV**) were prepared and analyzed. Table 1 lists the complete and abbreviated structures of these compounds.

*(i) Preparation of amine functional trisiloxanes.* Amine functional trisiloxanes were prepared by the base-catalyzed reaction of a silane monomer, $[(CH_3O)_2Si(Me)(CH_2)_3NH(CH_2)_2NH_2]$,

**TABLE 1**
**Structures and Abbreviations of Glucosamide-Based Trisiloxane Gemini Surfactants**

| Compound structure | Abbreviation[a] | Designation |
|---|---|---|
| $(Me_3SiO)_2Si(Me)(CH_2)_3NH(CH_2)_2NHCO(CHOH)_4CH_2OH$ | MDM | I |
| $(CH_2OCH_2)_2[(Me_3SiO)_2Si(Me)(CH_2)_3NCH_2CH(OH)-$ $(CH_2)_2NHCO(CHOH)_4CH_2OH)]_2$ | MDM-1-MDM | II |
| $(CH_2OCH_2)_3[(Me_3SiO)_2Si(Me)(CH_2)_3NCH_2CH(OH)-$ $(CH_2)_2NHCO(CHOH)_4CH_2OH)]_2$ | MDM-2-MDM | III |
| $(CH_2OCH_2)_4[(Me_3SiO)_2Si(Me)(CH_2)_3NCH_2CH(OH)-$ $(CH_2)_2NHCO(CHOH)_4CH_2OH)]_2$ | MDM-3-MDM | IV |

[a]The abbreviations use the common notation for silicone polymers (M = $Me_3SiO$, D = $MeSiO$).

and $(Me_3Si)_2O$. In a typical preparation, a silane monomer, a fivefold molar excess of $(Me_3Si)_2O$, and a catalytic amount of tetramethyl ammonium hydroxide (TMAH) were charged to a 500-mL reactor vessel. The mixture was heated for 2 h at 90°C under nitrogen atmosphere, with stirring. The resulting quaternary ammonium hydroxide was then deactivated by heating for 30 min at 130°C, and the excess $(Me_3Si)_2O$ was simultaneously distilled from the mixture. The liquid product was purified by fractional distillation [boiling point (b.p.) 130°C/3 mm Hg; purity >98%]. The structure of the compound was confirmed by $^1H$ and $^{13}C$ nuclear magnetic resonance (NMR).

*(ii) Preparation of glucosamide-based trisiloxanes.* The amine functional compound and a equal mole of D-gluconic acid δ-lactone were added to a three-necked bottle equipped with a refluxing condenser and mechanical stirrer. The mixture was heated to reflux temperature in methanol. After 6 h, the solvent was removed and the viscous oil obtained was dispersed in *n*-pentane. The mixture was dried at room temperature. A white powder or ointment-like product was obtained. The structure of the compound was confirmed by $^1H$ and $^{13}C$ NMR.

*(iii) Preparation of oligoethylene glycol diglycidyl ethers.* Epichlorohydrin, a equal mole of sodium hydroxide pellets, 5 mol% of tetrabutyl ammonium hydrogen sulfate (based on diols), and 10% water (based on sodium hydroxide) were added to a three-necked bottle equipped with a dropping funnel and mechanical stirrer. One-sixth mole of oligoethylene glycol (based on epichlorohydrin) was added dropwise, with rapid stirring, at 40°C. After the addition was completed, stirring was continued for 1 h at 40°C, and the solid material was filtered off. The combined organic solution was dried with magnesium sulfate. The excess epichlorohydrin was distilled off, and the residue was purified by distillation in vacuum to give colorless liquids (b.p. 124, 158, and 204°C/5 mm Hg, respectively; purity >98%). The structures of the compounds were confirmed by $^1H$ and $^{13}C$ NMR.

*(iv) Preparation of dimeric compounds.* The oligoethylene glycol diglycidyl ether and a twofold mole of glucosamide-based trisiloxane were dissolved in dry methanol. The mixture was heated to reflux temperature for 8 h. The solvent was then removed under reduced pressure, and the flask and the viscous liquid were washed with *n*-pentane. After drying, a thick syrup was obtained. The structures of the compounds were confirmed by $^1H$ and $^{13}C$ NMR and by elemental analysis.
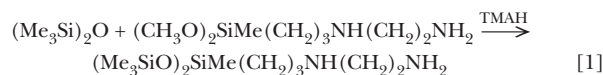
*Characterization of the glucosamide-based trisiloxane gemini surfactants and measurements of surface activity.* Proton and $^{13}C$ NMR spectra were acquired on a Bruker DRX-300 NMR spectrometer (Zurich, Switzerland). Samples were prepared in 5-mm o.d. tubes with deuterated solvent ($CDCl_3$). Chemical shifts were referenced to tetramethylsilane. Elemental analysis data were determined on a Vario EL analyzer (Frankfurt, Germany).

Equilibrium surface tension values of the surfactants in aqueous solution were obtained by the Wilhelmy plate method using a model K12 Krüss tensiometer (Hamburg, Germany). Prior to measurement, the surface tension of the distilled, deionized water was measured; these values were in the range of 72.3 ± 0.3 mN/m. Surfactant solutions were then prepared with this water, and the samples were aged 15 min prior to surface tension measurement. Sample temperatures were stable to 25 ± 0.2°C.
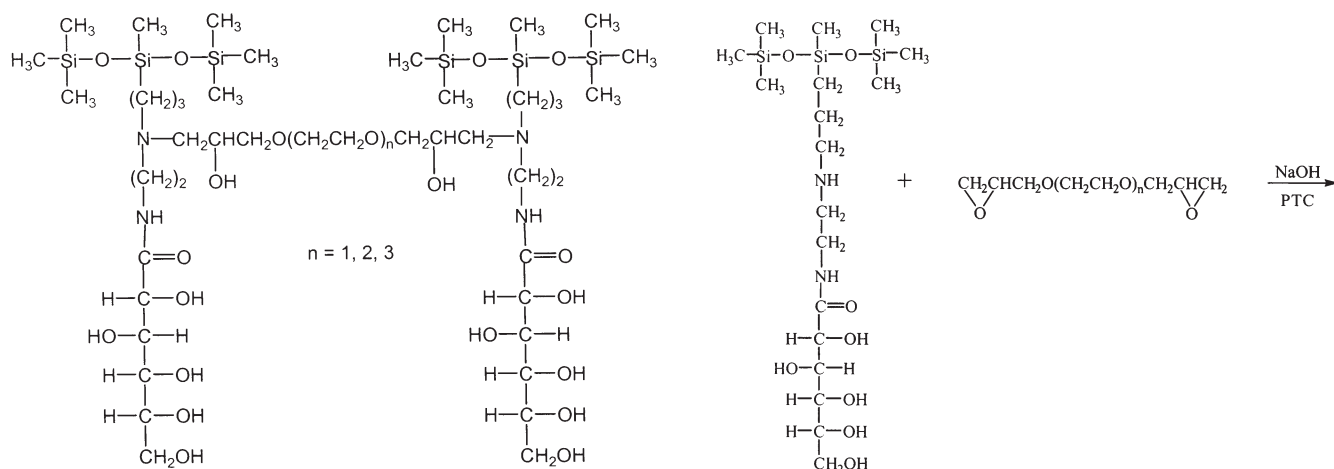
## RESULTS AND DISCUSSION

*Preparation and spectroscopic characterization of glucosamide-based trisiloxane gemini surfactants.* The general formula of these gemini surfactants is shown in Scheme 1. The glucosamide-based trisiloxane surfactant monomer was first prepared by the two-step process described in Equation 1 and Scheme 2. Three gemini surfactants were then prepared by the three-step process described by Equation 1 and Schemes 2 and 3. The compounds obtained were thick, syrupy, or viscous liquids.

Equation 1 describes the synthesis of the amine intermediate. The reaction was carried out under conditions of strong base catalysis at 90–100°C.

$$(Me_3Si)_2O + (CH_3O)_2SiMe(CH_2)_3NH(CH_2)_2NH_2 \xrightarrow{TMAH}$$
$$(Me_3SiO)_2SiMe(CH_2)_3NH(CH_2)_2NH_2 \quad [1]$$

The D-gluconic acid δ-lactone was ring-opened by nucleophilic attack of the primary amine (Scheme 2). The amidation of the primary amine proceeded in the presence of methanol at reflux temperature. The reaction conditions were moderate. In all cases the amide of the primary amino

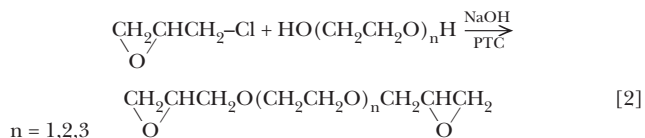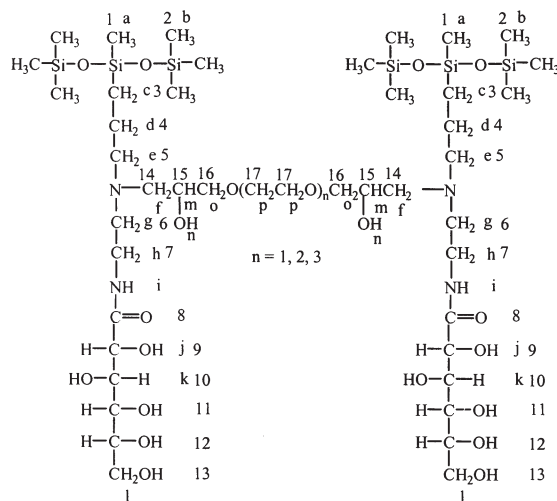**SCHEME 1**

n = 1, 2, 3

**SCHEME 2**

MeOH →

**SCHEME 3**

$$CH_2CHCH_2O(CH_2CH_2O)_nCH_2CHCH_2 \xrightarrow[PTC]{NaOH}$$

n = 1, 2, 3
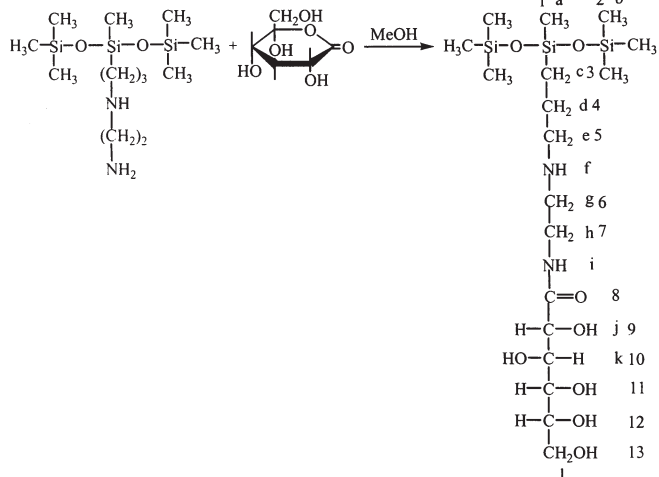
function was formed, whereas the secondary amino group did not yield a considerable amount of by-products. The amidation of amine functional siloxanes has been reported previously by Wagner and colleagues (36–42).

Equation 2 describes an easy one-step synthesis of the oligoethylene glycol diglycidyl ethers from oligoethylene glycols and epichlorohydrin under phase-transfer conditions (PTC) in the presence of sodium hydroxide. The reaction was carried out under conditions of rapid stirring at 40°C.

$$CH_2CHCH_2-Cl + HO(CH_2CH_2O)_nH \xrightarrow[PTC]{NaOH}$$

$$CH_2CHCH_2O(CH_2CH_2O)_nCH_2CHCH_2 \qquad [2]$$

n = 1,2,3

As expected, the epoxides alkylated the secondary amino function of the glucosamide-based trisiloxane quantitatively under the conditions applied. These amides reacted with the epoxy compounds, yielding the corresponding tertiary amines. In examining the spectra of the products, we found

no major signals for carbon atoms attached to the new ether bridges (etherified hydroxyl groups). The presence of a secondary amino group allowed the possibility of synthesizing dimeric compounds. Different gemini surfactants were obtained by careful choice of the spacer. By choosing the spacer carefully, the existing possibilities for the design of gemini surfactants could be extended considerably.

These compounds were structurally characterized by their ^{1}H and ^{13}C NMR spectra and by elemental analysis. These data are shown in Tables 2–4. In all cases, the spectral data and the result of elemental analysis were consistent with the assigned structures of the compounds.

*Equilibrium surface tension measurements.* The equilibrium surface tension of dilute aqueous solutions of surfactants **I–V** (Table 1) were measured. The data are compiled in Table 5 and illustrated in Figure 1. All four surfactants reduced the surface tension of water to a minimum value of approximately 21 mN/m at concentrations of $10^{-5}$ mol/L.

The values of the minimum surface tension (where CAC refers to critical aggregation concentration) ($\gamma_{CAC}$) are significantly lower than those reported for organic glucosamide gemini surfactants (33,34) and are comparable to

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**TABLE 2**
**$^1$H NMR Data ($\delta$ ppm) for the Glucosamide-Based Trisiloxane Dimeric Compounds[a]**

| H-atom | I | II | III | IV |
|---|---|---|---|---|
| a | 0.005 | −0.036 | −0.041 | −0.049 |
| b | 0.069 | 0.038 | 0.035 | 0.028 |
| c | 0.40 | 0.31 | 0.30 | 0.29 |
| d | 1.47 | 1.37 | 1.36 | 1.35 |
| e | 2.57 | 2.43 | 2.43 | 2.43 |
| f | 4.71 | 2.60 | 2.60 | 2.58 |
| g | 2.75 | 2.89 | 2.88 | 2.90 |
| h | 3.38 | 3.39 | 3.40 | 3.38 |
| i | 7.25 | 7.72 | 7.73 | 7.71 |
| j | 4.35–5.05 | 4.45–5.55 | 4.45–5.35 | 4.50–5.40 |
| k | 3.55–3.90 | 3.63–3.95 | 3.66–3.90 | 3.65–3.90 |
| l[b] | 4.11/4.29 | 4.10/4.25 | 4.09/4.25 | 4.08/4.24 |
| m | | 3.63–3.95 | 3.66–3.90 | 3.65–3.90 |
| n | | 4.45–5.55 | 4.45–5.35 | 4.50–5.40 |
| o | | 3.47 | 3.47 | 3.46 |
| p | | 3.59 | 3.59 | 3.58 |

[a]The structures of compounds **I–V** are listed in Table 1. NMR, nuclear magnetic resonance.
[b]Slash indicates two peaks.

**TABLE 3**
**$^{13}$C NMR Data ($\delta$ ppm) for the Glucosamide-Based Trisiloxane Dimeric Compounds[a]**

| C-atom | I | II | III | IV |
|---|---|---|---|---|
| 1 | 0.24 | −0.24 | −0.30 | −0.25 |
| 2 | 2.50 | 1.93 | 1.87 | 1.93 |
| 3 | 15.54 | 15.07 | 15.01 | 15.07 |
| 4 | 23.12 | 18.96 | 19.08 | 19.10 |
| 5 | 52.67 | 57.87 | 57.82 | 57.89 |
| 6 | 48.57 | 53.26 | 53.16 | 53.23 |
| 7 | 39.05 | 37.27 | 37.17 | 37.22 |
| 8 | 174.56 | 173.28 | 173.26 | 173.30 |
| 9 | 74.57 | 74.07 | 74.04 | 74.11 |
| 10 | 71.19 | 70.55 | 70.34 | 70.40 |
| 11 | 72.26 | 72.56 | 71.54 | 71.62 |
| 12 | 74.57 | 74.07 | 72.53 | 72.85 |
| 13 | 64.09 | 63.58 | 63.47 | 63.58 |
| 14 | | 56.53 | 56.43 | 56.58 |
| 15 | | 68.12 | 68.00 | 68.12 |
| 16 | | 72.56 | 71.54 | 71.62 |
| 17 | | 70.55 | 70.34 | 70.40 |

[a]The structures of compounds **I–V** are listed in Table 1. For abbreviation see Table 2.

**TABLE 4**
**Elemental Analysis Data (%) on the Glucosamide-Based Trisiloxane Dimeric Compounds[a]**

| Compound | | I | II | III | IV |
|---|---|---|---|---|---|
| N | Calc. | 5.59 | 4.77 | 4.59 | 4.43 |
| | Found | 5.75 | 4.68 | 4.46 | 4.16 |
| C | Calc. | 43.16 | 44.94 | 45.29 | 45.61 |
| | Found | 42.26 | 44.21 | 44.14 | 44.54 |
| H | Calc. | 8.86 | 8.74 | 8.76 | 8.77 |
| | Found | 8.32 | 8.44 | 8.37 | 8.70 |

[a]The structures of compounds **I–V** are listed in Table 1.

those reported for other low molecular weight silicone surfactants, many of which contain the trisiloxane backbone (43–47). However, the $\gamma_{CAC}$ values are not much lower than those of the corresponding monomer.

**TABLE 5**
**Aqueous Surface Activity[a] of the Glucosamide-Based Trisiloxane Gemini Surfactants**

| Compound | $\gamma_{CAC}$ (mN/m) | CAC (mol/L) | $A_m$ (Å$^2$/molecule) | $\Delta G$ (kJ/mol) |
|---|---|---|---|---|
| I | 21.0 | $5.36 \times 10^{-4}$ | 38.4 | −28.63 |
| II | 20.5 | $1.94 \times 10^{-5}$ | 72.2 | −36.85 |
| III | 20.6 | $2.92 \times 10^{-5}$ | 72.5 | −35.84 |
| IV | 20.7 | $3.34 \times 10^{-5}$ | 72.8 | −35.51 |

[a]CAC, critical aggregation concentration; $\gamma_{CAC}$, minimum surface tension; $A_m$, area per surfactant molecule at the air–water interface at surface saturation; $\Delta G$, standard free energy of micellization.

The average surface tension value of 21 mN/m for the aqueous solutions of these surfactants was considerably (10–20 mN/m) lower than that commonly achieved with hydrocarbon-based surfactants. It is comparable to the surface tension of high molecular weight homopolymeric poly(dimethylsiloxane) (20.6 mN/m) at 25°C. The low surface tension of poly(dimethylsiloxane) has been attributed to both the preponderance of highly surface-active methyl substituents and a flexible polymer backbone, which allows the methyl groups to orient in low-energy configurations. By comparison, hydrocarbon surfactants generally have many methylene groups in their hydrophobic portions, which have an intrinsically higher surface energy than methyl groups. The surface tension values of these surfactants suggest that the siloxane portion lies flat on the water surface, exposing the methyl groups to the air.

A dramatic change in the slopes of the surface tension vs. log mole surfactant concentration curves is generally interpreted as the onset of surfactant aggregation into micelles in a bulk aqueous solution. Inspection of the curves in Figure 1 suggests that the surfactants are forming micelles.
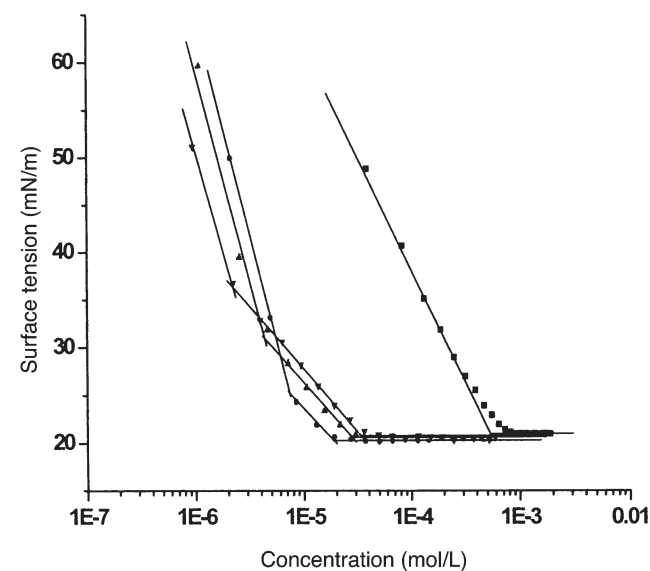


**FIG. 1.** Plots of the equilibrium surface tension of aqueous solutions of glucosamide functional trisiloxane gemini surfactants vs. log mole concentration. (■) MDM (**I**); (●) MDM-1-MDM (**II**); (▲) MDM-2-MDM (**III**); (▼) MDM-3-MDM (**IV**). See Table 1 for compound structures and their abbreviations.

For comparison, CAC values for the monomer were also included. Compared with the monomer, the gemini surfactants showed very small CAC values. This indicates that these double-chain compounds aggregated easily compared with the single-chain compound. Micellization took place at a concentration of about $10^{-5}$ M, about two orders of magnitude lower than that of the monomer. This extraordinary ability to aggregate is a common feature of gemini surfactants.

The gemini compounds showed two CAC values in their surface tension curves. This implies a different aggregation process for geminis than for conventional surfactants. This aberrant behavior may be due to the existence of premicellar aggregates in these compounds. This type of aberrant behavior in gemini molecules has been observed by other investigators and has sometimes been explained on the basis of the formation of premicellar aggregates (dimers, trimers, oligomers) (48–50).

Values for the slope of the surface tension vs. log concentration plots (Fig. 1) were obtained by using the approximate forms of the Gibbs adsorption isotherm equations (Eqs. 3 and 4),

$$\Gamma = -\frac{1}{2.303 \, nR \, T} \left(\frac{\partial \gamma}{\partial \log C}\right)_T \qquad [3]$$

$$A_m = \frac{1}{N\Gamma} \qquad [4]$$

where $R$ is the gas constant ($8.3144 \, \mathrm{J \, mol^{-1} K^{-1}}$), $N$ is Avogadro's number, $\Gamma$ is the surface excess concentration in $\mathrm{mol/cm^2}$, and $A_m$ is the area per surfactant molecule at the air–water interface in $10^2 \, \mathrm{nm^2/molecule}$. In our solution, no electrolyte is present; therefore, we can set $n$ as 1.

As expected, and as confirmed by the $A_m$ values in Table 5, increasing the number of oxyethylene units in the spacer increased the area per molecule of the surfactant at the interface, but this increase was slight.

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