

Synthesis and Characterization of Glycoside-Based Trisiloxane Surfactant

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Abstract The synthesis of glycoside-based trisiloxane surfactants of the general formula $\text{Me}_3\text{SiOSiMeR}^1\text{OSiMe}_3$ ($\text{R}^1 = (\text{CH}_2)_3(\text{OCH}_2\text{CH}_2)_2\text{OR}^2$, $\text{R}^2 = \text{glycosyl}$) is described, and the surface activity properties of the surfactant are studied. Diethylene glycol monoallyl ether glycoside is synthesized by reacting the diethylene glycol monoallyl ether with glucose. The glycoside-based trisiloxane surfactant is prepared by hydrosilylation of the precursor glycoside with hydrogen-containing trisiloxane. The product is structurally characterized by IR, ^1H NMR and MS. The surface tension of an aqueous solution is reduced to approximately 20 mN m^{-1} at concentration level of $10^{-4} \text{ mol L}^{-1}$.

Keywords Synthesis · Characterization · Glycoside · Trisiloxane · Hydrosilylation

Introduction

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 attained using traditional hydrocarbon surfactants. Silicone surfactants are also known for their low physiological risk in cosmetic applications.

Trisiloxanes customarily considered to consist of two types, namely, “MD’M” and “M’DM”, where M is a trimethylsiloxy group $(\text{CH}_3)_3\text{-SiO}_{1/2-}$, D is $-\text{O}_{1/2}\text{Si}(\text{CH}_3)_2\text{O}_{1/2-}$, D’ is $-\text{O}_{1/2}\text{Si}(\text{CH}_3)\text{RO}_{1/2-}$, M’ is $-\text{O}_{1/2}\text{Si}(\text{CH}_3)_2\text{R}$, R is the hydrophilic head-group which is attached to the hydrophobic tail through a $-(\text{CH}_2)_3-$ spacer. The exceptional surface properties of the “MD’M” trisiloxanes, some having “super-wetting” ability, are attributed to their unique molecular architecture. They aroused the great interests of many scientific researchers [1–51]. The type of “MD’M” scattering at the air/water surface caused by the “umbrella” structure in a configuration where the methyl groups are closely packed and exposed to the air with surface tension values of approximately 21 mN m^{-1} being commonly achieved. By comparison, hydrocarbon surfactants generally have many $-\text{CH}_2-$ groups in their hydrophobic portions, which have an intrinsically higher surface energy than methyl groups.

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

However, the trisiloxane with the glycoside as the hydrophilic head-group has been only rarely reported in the literature [52, 53].

In this paper, we report the preparation of a glycoside-based trisiloxane surfactant and study the surface activity of this compound by measuring the equilibrium surface tension of the dilute aqueous solutions. The parameters studied include CAC (the critical aggregation concentration), pC_{20} (negative log of the surfactant molar concentration required to reduce the surface tension of the solvent by 20 mN m^{-1} , which is a measurement of the efficiency

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of adsorption), γ_{CAC} (the surface tension at the CAC), Γ_{m} (the maximum surface excess concentration at the air/water interface), a_m^s (the minimum area per surfactant molecule at the air/water interface), and the CAC/ C_{20} ratio (a measurement of the factors inhibiting aggregation relative to adsorption at the air/water interface), $\Delta G_{\text{agg}}^{\circ}$ (the standard free energy of aggregation), $\Delta G_{\text{ads}}^{\circ}$ (the standard free energy of adsorption).

Experimental Procedures

Preparation of Glycoside-Based Trisiloxane Surfactant

- (1) *Preparation of diethylene glycol monoallyl ether 1.* 4.0 g (0.1 mol) of NaOH and the solvent (dioxane) were introduced into a 500-mL reaction vessel. Then 7.6 g (0.1 mol) of allyl chloride and 21.2 g (0.2 mol) of diethylene glycol were added dropwise with rapid stirring at 50–55 °C. After the completion of the addition, stirring was continued for 6 h at 50–55 °C. The crude product was dried with magnesium sulfate. The solid material was filtered off. The solvent was distilled off and the residue was purified by column chromatography to give the compound in a yield of 82.5% and a purity of 99.2% (Agilent 7890A gas chromatography). The structure of the compound was confirmed by IR, ^1H NMR and MS.
- (2) *Preparation of diethylene glycol monoallyl ether glycoside 2.* 87.6 g (0.6 mol) of the diethylene glycol monoallyl ether and 18.0 g (0.1 mol) of the glucose anhydrous were introduced into a 500-mL round-bottomed flask and heated with stirring to a temperature of 110 °C. Then 0.6 g of the *p*-toluenesulfonic acid was then added and the stirring continued under reduced pressure and at 110 °C for 5 h. The clear mixture was neutralized with aqueous NaOH solution to neutrality and decolorized by activated carbon adsorption. The excess diethylene glycol monoallyl ether was distilled off in vacuum to give a vitreous product. An average degree of glycosidation of 1.1 was determined by ^1H NMR [54]. The structure of the compound was confirmed by IR and ^1H NMR.
- (3) *Preparation of glycoside-based trisiloxane 3.* First 32.4 g (0.1 mol) of the diethylene glycol monoallyl ether glycoside was introduced into a 500-mL round-bottomed flask and heated with stirring to a temperature of 80 °C and 0.4 g of a solution of 1 g of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 76 g of isopropanol (platinum content of the solution: 50 ppm) was added. Subsequently, 44.4 g (0.2 mol) of the 1,1,1,3,5,5,5-heptamethyltrisiloxane was added dropwise over the course of 30 min, during which the temperature rose to

100 °C. The mixture was stirred for 3 h and subsequently distilled under a reduced pressure and at 80 °C to give a viscous and clear product. The structure of the compound was confirmed by IR and ^1H NMR.

Characterization of the Glycoside-Based Trisiloxane Surfactant and Surface Activity Measurements

The proton nuclear magnetic resonance (^1H NMR) spectra were acquired on a 300 MHz Bruker DRX-300 NMR spectrometer. Samples were prepared in 5-mm OD tubes with deuterated solvents CDCl_3 or D_2O . Chemical shifts were referenced to tetramethylsilane. The infrared (IR) spectra were recorded on an Avater FT-IR Spectrometer Tensor 370 (KBr). The mass spectra were scanned on an Agilent 5975C instrument at 70 eV.

Aqueous solution equilibrium surface tension values were obtained by the Wilhelmy plate method using a Dataphysics tensiometer, model DCAT11. The CAC value was taken at the intersection of the linear portions of the plots of the surface tension against the logarithm of the surfactant concentration. Surfactant solutions were prepared with distilled, de-ionized water. Sample temperatures were stable to 25 ± 0.2 °C. Prior to measurements on surfactant solutions, the surface tension of the distilled, de-ionized water was measured. These water values were in the range of 72.3 ± 0.3 mN m^{-1} . Samples were aged 15 min prior to the surface tension measurement.

Results and Discussion

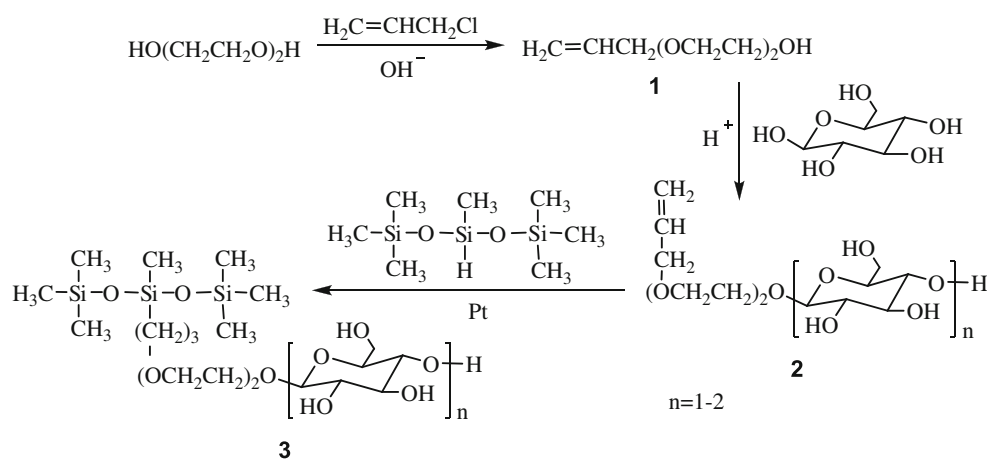
Preparation and Spectroscopic Characterization of the Glycoside-Based Trisiloxane Surfactant

The general formula and process of the glycoside-based trisiloxane surfactant is shown in Scheme 1. Herein, the diethylene glycol monoallyl ether **1** was prepared by the Williamson reaction in the aprotic solvent (dioxane). The more monoallyl ether was produced by using excess allyl chloride. The small amount of diallyl ether byproduct was separated and removed by column chromatography.

The diethylene glycol monoallyl ether glycoside **2** was prepared by glycosidation using *p*-toluenesulfonic acid catalyzed. The water formed in the glycosidation was distilled off in vacuum in time to promote the reaction continue. An average degree of glycosidation of 1.1 was obtained by using the excess diethylene glycol monoallyl ether.

The glycoside-based trisiloxane **3** was prepared by hydrosilylation using chloroplatinic acid as catalyst. The

Scheme 1 The general process of the glycoside-based trisiloxane surfactant



excess hydrogen-containing heptamethyl trisiloxane was added, which allowed the reaction to proceed to completion and distilled off after reaction.

These compounds were structurally characterized by their IR, $^1\text{H-NMR}$ and MS spectra. The details of these spectral characterizations were as follows. In all cases, the spectra acquired were consistent with the assigned structures of the compounds.

Diethylene glycol monoallyl ether 1

IR (KBr, ν , cm^{-1}): 3,380–3,400 (–OH), 2,850–2,950 (C–H), 1,652 (C=C), 1,030–1,100 (C–O–C); $^1\text{H NMR}$ (CDCl_3 , 300 MHz, δ ppm): 2.50 (s, 1H, –OH), 3.57–3.71 (m, 8H, $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-$), 4.00–4.02 (d, 2H, $\text{C}=\text{C}-\text{CH}_2-$), 5.15–5.30 (m, 2H, $\text{CH}_2=\text{C}-$), 5.85–5.94 (m, 1H, $\text{C}=\text{CH}-\text{C}-$); MS: $m/z = 41$ ($\text{CH}_2=\text{CHCH}_2-$), $m/z = 45$ ($-\text{CH}_2\text{CH}_2\text{OH}$), $m/z = 115$ ($\text{M} - \text{CH}_2\text{OH}$).

Diethylene glycol monoallyl ether glycoside 2

IR (KBr, ν , cm^{-1}): 3,350–3,450 (–OH in sugar), 2,910–2,930 (C–H), 1,645 (C=C), 1,020–1,100 (C–O–C), 840 (α -glycosidic bond), 886 (β -glycosidic bond); $^1\text{H NMR}$ (D_2O , 300 MHz, δ ppm): 3.15–3.85 (m, 8H, $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-$, and about 7H, glucose ring, overlap), 4.39, 4.84 (d, 1H, α , β -H in glycosidic bond), 3.96–3.98 (d, 2H, $\text{C}=\text{C}-\text{CH}_2-$), 5.14–5.27 (m, 2H, $\text{CH}_2=\text{C}-$), 5.80–5.89 (m, 1H, $\text{C}=\text{CH}-\text{C}-$).

Glycoside-based trisiloxane 3

IR (KBr, ν , cm^{-1}): 3,350–3,450 (–OH in sugar), 2,850–2,950 (C–H), 1,050–1,120 (C–O–C, Si–O–Si), 840 (α -glycosidic bond), 886 (β -glycosidic bond), 1,260, 840, 760 ($\text{Si}(\text{CH}_3)_3$), 2,150 (Si–H, disappeared), 1,645 (C=C, disappeared); $^1\text{H NMR}$ (D_2O , 300 MHz, δ ppm): 0.006 (s, 3H, Si– CH_3), 0.09 (s, 18H, $\text{Si}(\text{CH}_3)_3 \cdot 2$), 0.35–0.45 (t, 2H, Si– CH_2-), 1.45–1.55 (m, 2H, Si–C– CH_2-), 2.55–2.57

(t, 2H, Si–C– CH_2), 3.12–3.84 (m, 8H, $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-$, and about 7H, in sugar, overlap), 4.35, 4.82 (d, 1H, α , β -H in glycosidic bond).

Equilibrium Surface Tension Measurements

The equilibrium surface tension of dilute aqueous solutions of the glycoside-based trisiloxane surfactant was measured. For comparison, the 3-(polyoxyethylene-propyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (ethoxylated trisiloxane Silwet L-77 from GE, abbreviated as EOTS in what follows) was also listed. The minimum surface tension (γ_{CAC}) values were acquired by analyzing the plateau region of the plots. The critical aggregation concentrations (CAC) of the surfactants were acquired by analyzing the intersection point of the plateau region and the steeply downward sloping portion of the plots. The surface excess concentration (Γ_{max}) and the surface area per molecule (a_m^s) were acquired by analyzing the application of the Gibbs equation to the steeply downward sloping section of the plots. A summary of the data was compiled in Table 1 and in Fig. 1. These surfactants all reduced the surface tension of water to a minimum value of approximately 20 mN m^{-1} at concentrations of $10^{-4} \text{ mol L}^{-1}$.

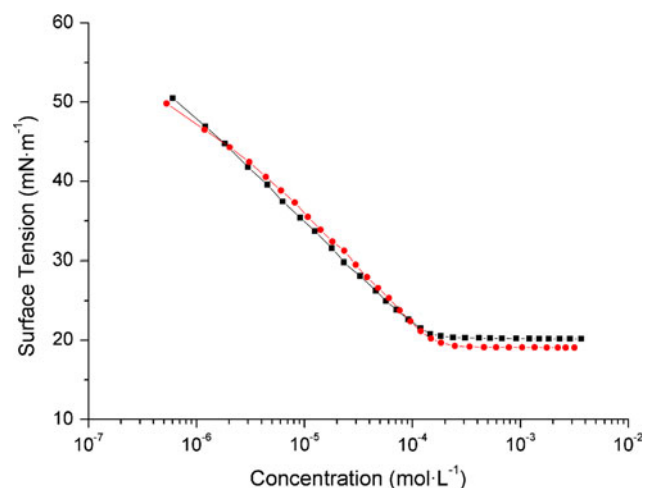
Inspection of the data in the Table 1 shows that the glycoside-based trisiloxane surfactant and EOTS significantly reduce the surface tension of the solution at low concentration, indicating that these molecules adsorb strongly at the air/water surface and they are highly effective aqueous surfactants, reducing the surface tension of water to approximate 20 mN m^{-1} .

The value of γ_{CAC} is significantly lower than those reported for organic glycosides [55] which are in the range of $30\text{--}40 \text{ mN m}^{-1}$ and is comparable to those reported for other trisiloxane surfactants [1–10].

The low surface tension of silicone surfactants has been attributed to both the preponderance of highly surface

Table 1 Aqueous surface activity of the glycoside-based trisiloxane surfactant

Compound	Glycoside-based trisiloxane	EOTS
CAC (mol·L ⁻¹)	1.30 × 10 ⁻⁴	1.68 × 10 ⁻⁴
γ _{CAC} (mN·m ⁻¹)	20.18	19.09
Γ _{max} (μmol·m ⁻²)	2.31	2.40
a _m ^s , 10 ² (nm·molecule ⁻¹)	71.89	69.19
ΔG _{agg} ^o (KJ·mol ⁻¹)	-32.14	-31.50
ΔG _{ads} ^o (KJ·mol ⁻¹)	-54.64	-53.61
pC ₂₀	6.32	6.19
CAC/C ₂₀	258.88	268.23

**Fig. 1** Plots of equilibrium surface tensions of aqueous solutions of trisiloxane surfactants versus log moles concentration. (closed squares), glycoside-based trisiloxane; (closed circles), ethoxylated trisiloxane EOTS

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.

When such a parallel orientation of the silicone backbone with respect to the water is adopted, it results in relatively large areas of molecular surface coverage and low CAC values.

Examination of Fig. 1 shows that the two plots have significant changes in slope as a minimum surface tension is reached. For most surfactants, this behavior implies that aggregation is occurring in bulk solution. For the organic glycosides mentioned in the previous section, the break points were considered to be the critical micelle concentrations.

Micelle formation by siloxane surfactants in aqueous solution has not been extensively investigated. Most of the studies to date report critical micelle concentrations (CMC) values from surface tension versus log surfactant concentration plots. Although the structure of the micelles formed was investigated in past few years, no conclusion was drawn on the tendency of these surfactants to form well-defined micelles [1–10].

Assuming that the changes in slopes of the surface tension versus log concentration curves in Fig. 1 represent the onset of surfactant aggregation, possibly into micelles, the CAC values for the surfactants are reported in Table 1.

Our interpretation of the plots is that aggregation is occurring in solution, not necessarily micellization, and that the CAC values can be determined by extrapolation. This type of extrapolation is universally applied to this type of plot to estimate critical aggregation concentration, and we use it uncritically here. Some caution is that the presence of a break point in the surface tension versus log concentration plot is only circumstantial evidence of aggregate formation.

The CAC values are determined from extrapolation to the break points in the surface tension versus log surfactant concentration curves (Fig. 1). The CAC values vary with the structure of the hydrophilic group.

The saturation adsorption values, Γ_{max}, at the air/water interface and the minimum area per surfactant molecule, a_m^s, at the air/water interface were obtained from the slope of the surface tension versus log concentration plots (Fig. 1) by using the approximate form of the Gibbs adsorption isotherm equations (Eqs. 1 and 2).

$$\Gamma_{\max} = -\frac{1}{2.303nRT} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad (1)$$

$$a_m^s = \frac{10^{16}}{N_A \Gamma_{\max}} \quad (2)$$

$$\Delta G_{\text{agg}}^o = RT \ln \left(\frac{CAC}{55.5} \right) \quad (3)$$

$$\Delta G_{\text{ads}}^o = RT \ln \left(\frac{C_\pi}{55.5} \right) - 6.022\pi a_m^s \quad (4)$$

where $R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$, $N_A = \text{Avogadro's number}$, Γ_{\max} is in mol cm^{-2} , and a_m^s is in $10^2 \text{ nm}^2 \text{ molecule}^{-1}$. In our solution, we can set $n = 1$. $\pi (= \gamma_0 - \gamma)$ is the surface pressure in the region of surface saturation and C_π is the molar concentration of surfactant in the aqueous phase at a surface pressure π (in mN m^{-1}).

In general, for both the known ionic and nonionic surfactants present, the value of the surface area per molecule, a_m^s , appears to be determined by the area occupied by the hydrated hydrophilic groups, rather than by the hydrophobic group, because the chains in typical ionic or

nonionic surfactants with hydrophilic groups at one end of the molecule do not lie flat on a surface but are rather somewhat tilted with respect to it.

The polar region of the silicone surfactant molecule determines the required surface area and the siloxane group is responsible for the distance between the molecules in the adsorption layer. Consequently, the measured or estimated required surface area per molecule depends on both the size of the siloxanyl group and the nature of the polar part of the surfactant molecule.

The excess of surface concentration (Γ_{\max}) decreases as a_m^s increases. The free energy of aggregation (ΔG_{agg}^0) (Eq. 3) and adsorption (ΔG_{ads}^0) (Eq. 4) of the glycoside-based trisiloxane surfactant and EOTS are negative value, indicating that the processes are thermodynamically favored.

The CAC/ C_{20} ratio is a measure of the tendency to form aggregates relative to the tendency to adsorb at the air/water interface. A higher CAC/ C_{20} ratio indicates that the hydrophobic groups are less suitably oriented for accommodating themselves in the interior of the aggregates. In general, for all type of surfactants, adsorption on the surface of an aqueous solution is preferred over the formation of aggregates. The larger CAC/ C_{20} values for the trisiloxane surfactants compared to conventional surfactants indicate that the trisiloxane surfactants have a greater preference to be adsorbed at the water/air interface relative to their preference to form aggregates than do the conventional surfactants. This might be due to the steric inhibition of convex aggregate formation by the silicone hydrophobic group of the trisiloxane surfactant.

Inspection of the data in the Table 1 and Fig. 1 shows that the aggregation and adsorption of the glycoside-based trisiloxane surfactant coincide with those of the EOTS.

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