Adsorption and Aggregation Behavior of Tetrasiloxane-tailed Gemini Surfactants with $(EO)_m$ Spacers

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2. General information

Infrared spectroscopy was performed with a Fourier Transform Infrared spectrometer (Hitachi 270-30). Proton nuclear magnetic resonance (\(^1\)H and \(^{13}\)C-NMR) spectroscopy was recorded in CDCl\(_3\) with a Varian INOVA-400MHz spectrometer. The \(^1\)H NMR spectra were recorded at 400 MHz, the \(^{13}\)C NMR spectra at 100 MHz. Since TMS cannot easily be used as internal standard because of the overlapping with other methyl signals, we used the residual protons of the solvent \(\delta^1\)H = 7.26 and \(\delta^{13}\)C = 77.00. The apparent coupling constants are given in Hertz. Elemental analyses were carried out by use of a PerkinElmer 2400 CHN analyzer.

3. Synthesis of Si-m-Si

N-(2-Aminoethyl)-3-Aminopropyltetrasiloxane (2)

The mixture of N-(2-Aminoethyl)-3-Aminopropyltrimethoxysilane (11.0 g, 0.05 mol), hexamethyldisiloxane (73.1 g, 0.9 mol), and tetramethyl ammonium hydroxide (0.468 g, 0.005 mol) 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 hexamethyldisiloxane was simultaneously distilled from the mixture. The liquid product was purified by fractional distillation. Yield: 23.9%, (Colorless liquid), boiling point (b. p.) 140 °C /3 mmHg.

IR (KBr): 3300 cm\(^{-1}\) (\(\nu\)(O–H)), 1467cm\(^{-1}\)(\(\nu\)(C–H) in –CH\(_2\)-), 1260cm\(^{-1}\)(\(\nu\)(Si–Me)), 1035–1146 cm\(^{-1}\) (\(\nu\)(C–O) and \(\nu\)(Si-O-Si)), 840 cm\(^{-1}\)(\(\nu\)(Si-Me\(_3\))), 760 cm\(^{-1}\)(\(\nu\)(Si-Me\(_3\))).

\(^1\)H NMR (CDCl\(_3\), 300 MHz)δ: 2.75(t, 2H, NCH\(_2\)CH\(_2\)N, J=5.7Hz), 2.62(t, 2H, NCH\(_2\)CH\(_2\)N, J=5.7Hz), 2.56(t, 2H, SiCH\(_2\)CH\(_2\)CH\(_2\)N, J=6.9Hz), 2.62(t, 2H, NCH\(_2\)CH\(_2\)N, J=5.7Hz), 2.56(t, 2H, SiCH\(_2\)CH\(_2\)CH\(_2\)N, J=6.9Hz), 1.48(m, 2H, SiCH\(_2\)CH\(_2\)), 1.23(s, 3H, NH\(_2\) and NH), 0.41(t, 2H, SiCH\(_2\), J=8.0Hz), 0.085(s, 27, Si(CH\(_3\))\(_3\)).

\(^{13}\)C-NMR(CDCl\(_3\), ppm) δ: 1.374(Si(CH\(_3\))\(_3\)), 11.574(SiCH\(_2\)), 23.573(SiCH\(_2\)CH\(_2\)), 32.573(SiCH\(_2\)CH\(_2\)).
41.437(SiCH₂CH₂CH₂N), 52.060, 52.429(NCH₂CH₂N)

Elemental analysis calculated for C₁₄H₄₀N₂O₃Si₄: C, 42.37; H, 10.16; N, 7.06. Found: C, 42.51; H, 10.40; N, 6.99.

**N-(2-Aminoethyl)-3-Aminopropyltetrasiloxane -N-glucosylamine (3)**

N-(2-Aminoethyl)-3-Aminopropyltetrasiloxane (1.98 g, 0.005 mol), was dissolved in 50 ml of dry methanol. D-(+)-gluconic acid δ-lactone (0.891 g, 0.005 mol) was added, and the mixture was heated to reflux temperature for 8 h. After cooling to room temperature and evaporation of the solvent the solid residue was gently crushed, washed several times with hexane at 25 °C, and dried under reduced pressure to a constant mass. The white solid 2.369 g, (yield 92%).

IR (KBr): 3300 cm⁻¹ (ν(O–H)), 1646 cm⁻¹ (ν(C=O) in amide), 1547 cm⁻¹ (δ(N–H) in amide), 1467 cm⁻¹ (ν(C=H) in –CH₂–), 1260 cm⁻¹ (ν(Si-Me₃)), 1035–1146 cm⁻¹ (ν(C–O), δ(O–H), and ν(Si-O-Si)), 840 cm⁻¹ (ν(Si-Me₃)), 760 cm⁻¹ (ν(Si-Me₃))

¹H-NMR(CDCl₃, ppm) δ: 0.082(s, 27H, Si(CH₃)₃), 0.387(t, 2H, SiCH₂), 1.484(s, 2H, SiCH₂CH₂CH₂), 2.565(d, 2H, SiCH₂CH₂CH₂N), 2.746(t, 2H, NCH₂CH₂N), 3.86(2H, NCH₂CH₂N), 4.53(s, 1H, H5), 4.30(s, 1H, H6), 3.74(m, 4H, H7+H8+H9+H9’)

¹³C-NMR(CDCl₃, ppm) δ: 1.743(Si(CH₃)₃), 11.734(SiCH₂), 22.776(SiCH₂CH₂), 38.459(SiCH₂CH₂CH₂N), 47.892 and 51.905 (NCH₂CH₂N), 173.82(C=O), 73.99(C₂), 72.46(C₄), 71.627(C₅), 70.517.09(C₆), 63.480(C₆)

Elemental analysis calculated for C₂₀H₃₀N₂O₉Si₄: C, 41.78; H, 8.77; N, 4.87. Found: C, 41.90; H, 8.40; N, 4.69.

**Oligo(Ethylene Oxide) Diglycidyl Ethers (5)**
A mixture of epichlorhydrin (23.4 mL, 0.3 mol), sodium hydroxide pellets (12.0 g, 0.3 mol), and tetrabutylammonium hydroxide sulfate (1.7 g, 0.005 mol) was vigorously stirred. Triethylene glycol (0.1 mol) cooled in ice was added dropwise. After the completion of addition, stirring was continued for another 45 min at 40 °C. The solid produced in the reaction process was filtered and washed with dichloromethane. The combined organic layer was washed with saturated ammonium chloride to neutrality and dried with anhydrous magnesium sulfate. The solvent and excess epichlorhydrin were distilled to give yellow oil. The residue was purified by Kugelrohr distillation under high vacuum to give colorless liquid 5c. (b.p. 202 °C/3 mmHg). Below figure is $^1$H-NMR spectrum of compound (5) in CDCl$_3$.

Compound 5a and 5a was synthesized using the same procedure as for compound 5c: Compound 5a (124 °C/3-5 mmHg) and Compound 5b (160 °C/3-5 mmHg). Below Figure 1 are $^1$H-NMR spectrum of compound (5) in CDCl$_3$.
Figure S1. $^1$H-NMR spectrum of Glycol Diglycidyl Ethers (5) in CDCl₃
Synthesis of Si-1-Si (6)

N-(2-aminoethyl)-3-aminopropyltetrasiloxane-N-glucosylamine 3 (2.875 g, 0.005 mol), and ethylene glycol diglycidyl ether 5a (0.0025 mol) was dissolved in 50 ml of dry methanol. The mixture was heated to reflux temperature for 8 h. After cooling to room temperature and evaporation of the solvent, washed several times with hexane at 25 ºC, and dried under reduced pressure to a constant mass. The wax liquid (3.08 g, yield: 93.0%)

IR (KBr): 3310 cm\(^{-1}\) (\(\nu\)(O–H)), 1650 cm\(^{-1}\) (\(\nu\)(C=O) in amide), 1552 cm\(^{-1}\) (\(\delta\)(N–H) in amide), 1465 cm\(^{-1}\) (\(\nu\)(C–H) in –CH\(_2–\)), 1260 cm\(^{-1}\) (\(\nu\)(Si-Me\(_3\))), 1035–1150 cm\(^{-1}\) (\(\nu\)(C–O), \(\delta\)(O–H), and \(\nu\)(Si-O-Si)), 840 cm\(^{-1}\) (\(\nu\)(Si-Me\(_3\))), 760 cm\(^{-1}\) (\(\nu\)(Si-Me\(_3\)))

\(^1\)H and \(^13\)C NMR analyses of Si-1-Si are given in the Figure S7 (H NMR) and Figure S8 (C NMR)

Elemental analysis calculated for C\(_{48}\)H\(_{114}\)N\(_4\)O\(_{22}\)Si\(_8\): C, 43.54; H, 8.68; N, 4.23. Found: C, 44.00; H, 8.60; N, 4.59.

Synthesis of Si-2-Si (7)

Si-2-Si was synthesized using the same procedure as for Si-1-Si, and it is also a wax liquid, with a yield of 92.3%

IR (KBr): 3300 cm\(^{-1}\) (\(\nu\)(O–H)), 1648 cm\(^{-1}\) (\(\nu\)(C=O) in amide), 1545 cm\(^{-1}\) (\(\delta\)(N–H) in amide), 1465 cm\(^{-1}\) (\(\nu\)(C–H) in –CH\(_2–\)), 1260 cm\(^{-1}\) (\(\nu\)(Si-Me\(_3\))), 1035–1150 cm\(^{-1}\) (\(\nu\)(C–O), \(\delta\)(O–H), and \(\nu\)(Si-O-Si)), 841 cm\(^{-1}\) (\(\nu\)(Si-Me\(_3\))), 760 cm\(^{-1}\) (\(\nu\)(Si-Me\(_3\)))

\(^1\)H and \(^13\)C NMR analyses of Si-2-Si are given in the Figure S9 (H NMR) and Figure S10 (C NMR)
Elemental analysis calculated for C_{50}H_{118}N_{4}O_{23}Si_{8}: C, 43.89; H, 8.69; N, 4.10; Found: C, 43.50; H, 8.40; N, 4.36.

**Synthesis of Si-3-Si (8)**

**Si-3-Si** was synthesized using the same procedure as for Si-1-Si, and it is also a wax liquid, with a yield of 94.3%

IR (KBr): 3300 cm\(^{-1}\) (\(\nu(O-H)\)), 1655 cm\(^{-1}\) (\(\nu(C=O)\) in amide), 1549 cm\(^{-1}\) (\(\delta(N-H)\) in amide), 1460 cm\(^{-1}\) (\(\nu(C-H)\) in \(-\text{CH}_2-\)), 1260 cm\(^{-1}\) (\(\nu(Si-Me_3)\)), 1035–1150 cm\(^{-1}\) (\(\nu(C-O)\), \(\delta(O-H)\), and \(\nu(Si-O-Si)\)), 840 cm\(^{-1}\) (\(\nu(Si-Me_3)\)), 760 cm\(^{-1}\) (\(\nu(Si-Me_3)\))

\(^1\)H and \(^{13}\)C NMR analyses of **Si-3-Si** are given in the Figure S11 (H NMR) and Figure S12(C NMR)

Elemental analysis calculated for C_{52}H_{122}N_{4}O_{24}Si_{8}: C, 44.23; H, 8.71; N, 3.97. Found: C, 44.52; H, 8.58; N, 3.69.

![Figure S2. \(^1\)H-NMR spectrum of 3-N-(2-aminoethyl)aminopropyltrimethoxysilane (1) in CDCl\(_3\)](image)
**Figure S3.** $^1$H-NMR spectrum of 3-N-(2-aminoethyl)aminopropyl]tetrasiloxane (2) in CDCl$_3$

**Figure S4.** $^{13}$C-NMR spectrum of 3-N-(2-aminoethyl)aminopropyl]tetrasiloxane (2) in
Figure S5. $^1$H-NMR spectrum of 3-N-(2-aminoethyl)aminopropyl]tetrasiloxane-N-glucosylamine (3) in CDCl$_3$

Figure S6. $^{13}$C-NMR spectrum of 3-N-(2-aminoethyl)aminopropyl]tetrasiloxane-N-glucosylamine (3) in CDCl$_3$
Figure S7. $^1$H-NMR spectrum of Si-1-Si (6) in CDCl$_3$

Figure S8. $^{13}$C-NMR spectrum of Si-1-Si (6) in CDCl$_3$
**Figure S9.** $^1$H-NMR spectrum of Si–2–Si (7) in CDCl$_3$

**Figure S10.** $^{13}$C-NMR spectrum of Si-3-Si (7) in CDCl$_3$
Figure S11. $^1$H-NMR spectrum of Si–1–Si (8) in CDCl$_3$.

Figure S12. $^{13}$C-NMR spectrum of Si–3–Si (8) in CDCl$_3$. 