Synthesis and Properties of Multiarmed Geminis

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Three families of multiarmed and multicationic gemini surfactants, having pentaerythritol, dipentaerythritol, or adamantane cores, were synthesized and examined for their colloidal properties in water. Geminis with four or six six-carbon chains are highly water-soluble and do not self-assemble. But surface tension and conductivity measurements show that the geminis with four or six eight-carbon chains form micelles in the 3−6 mM range (compared to 0.5 M for a corresponding surfactant with a single chain). According to dynamic light scattering, these micelles are small (<30 Å diameter); no evidence of dendritic growth below 25 mM is evident. Geminis with four or six 12-carbon chains are too water-insoluble to examine for micelle formation. It is concluded the outward projection of the hydrocarbon chains in water greatly enhances the propensity of the surfactants to self-assemble. Micellar growth is seemingly restricted by chain pairing, chain looping, and associative ring formation. Since the aggregates have, despite these effects, greater residual water−hydrocarbon contact than found in typical micelles, water solubility of surfactants having longer chains is impaired.

Introduction

Kary Mullis, a Nobel laureate of "polymerase chain reaction" fame, wrote recently: "Probably the most important scientific development of the twentieth century is that economics has replaced curiosity as the driving force behind research".[1] As with many such generalizations, the message seems overblown. Perhaps a more accurate statement would be that economics has increasingly joined (but, fortunately, not yet replaced) curiosity as a major driving force. Gemini surfactants, having a structure shown in Chart 1, are a case in point. We were first prompted to synthesize geminis (and, indeed, to coin the name) out of curiosity over how preventing intramolecular chain−chain association via long, rigid spacers (e.g., a stilbene unit) would affect self-assembly in water.[2,3] Later on, many other investigators, focusing on more flexible spacers, began patenting geminis for their potential commercial utility.[4] Economic considerations had joined curiosity to generate a vibrant field of research. Although the field is still young, short reviews of the progress to date are already available.[4−6]

It was a simple extension of our work and that of others[7] to wonder about the behavior of surfactants with four or more hydrocarbon tails (which we loosely also include in the gemini family). This led to our synthesizing three series of compounds based on pentaerythritol (PE), dipentaerythritol (DPE), and adamantane (AD). Each possesses multiple water-solubilizing quaternary nitrogens bearing hydrocarbon chains of varying length. Scheme 1 gives three examples with labels that include a number indicating the chain length of the tails. Do these compounds abruptly self-assemble at a critical micelle concentration (CMC)? If so, how big are the micelles? And how do the surfactants affect the surface tension of water? Such questions are addressed after first discussing how the compounds were synthesized.

Synthesis

The synthesis of the PE, DPE, and AD surfactants is described in Scheme 2, parts A, B, and C, respectively. More straightforward attempts to attach long-chain tertiary amines to the PE core via the tetrabromo (Aldrich), tetramesylate,[8] and tetratriflate derivatives of pentaerythritol failed, thus accounting for the tetraester approach seen in Scheme 2. Since spontaneous ester hydrolysis was a concern, we invariably checked our geminis by NMR for this potential problem. It turns out that PE-8, for example, exhibited no hydrolysis after standing in D_2O for 24 h at room temperature and 4 h at 55 °C. Perhaps steric hindrance, arising from bulky groups on both sides of the ester, stabilizes the compounds. Of the compounds examined, only PE-12 and DPE-12 hydrolyzed slowly, but their water solubility was too low for practical purposes anyway. Curiously, PE-8 and other geminis are much more labile in CD_3OD, transesterifying in less than 7 h at room temperature; thus, alcoholic solvents were always avoided in purification schemes.

Synthetic details are given in the Experimental Section. Recrystallization or multiple washings with acetone gave geminis as white solids of correct structure and satisfactory purity as judged by ^{1}H and ^{13}C NMR and by elemental analysis. Yields ranged from good to excellent, although no attempt was made to optimize them.

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[1] Mullis, K. *Dancing Naked in the Mind Fields*; Panthem Books: New York, 1998.

[2] Menger, F. M.; Littau, C. A. *J. Am. Chem. Soc.* **1991**, *113*, 1451.

[3] Menger, F. M.; Littau, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 10083.

[4] Rosen, M. J.; Tracy, D. J. *J. Surfactants Deterg.* **1998**, *1*, 52/7.

[5] Rosen, M. J. *CHEMTECH* **1993**, *23*, 30.

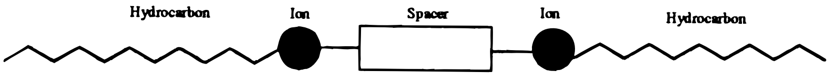
[6] Menger, F. M.; Keiper, J. S. Review to be published in *Angew. Chem.* This review covers a history of geminis, including their early synthesis, as well as a multitude of papers published from all over the world.

[7] Sumida, Y.; Masuyama, A.; Maekawa, H.; Takasu, M.; Kida, T.; Nakatsuji, Y.; Ikeda, I.; Nojima, M. *Chem. Commun.* **1998**, 2385. See also refs 4−6.

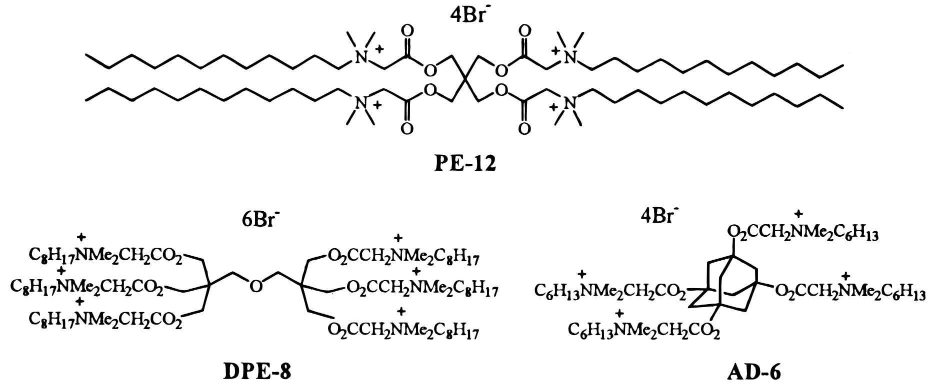
[8] Turkevich, B. M. *Farm. Zh. (Kiev)* **1962**, *17*, 14; *Chem. Abstr.* **1963**, *59*, 1471.

10.1021/jo9912350 CCC: $18.00

Chart 1



Scheme 1



PE-12

DPE-8

AD-6

Scheme 2

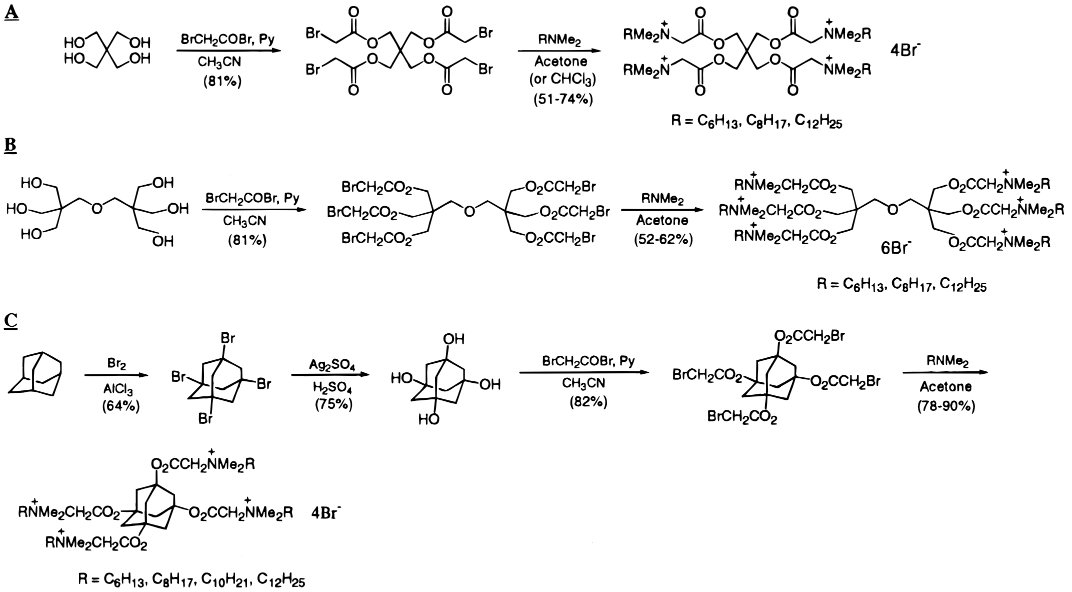


Table 1. Solubilities of Geminis in Chloroform and Water[a]

gemini	$CHCl_3$	H_2O
PE-6	>0.5 M	>0.5 M
PE-8	>0.5 M	30–50 mM
PE-12	>0.5 M	<0.2 mM
DPE-6	0.3–0.5 M	>0.5 M
DPE-8	>0.5 M	50–100 mM
DPE-12	0.3–0.5 M	<0.1 mM
AD-6	<0.1 mM	>0.5 M
AD-8	0.5–1 mM	50–80 mM
AD-10	1–3 mM	2–3 mM
AD-12	3–5 mM	<0.1 mM

[a] At 23 °C in units of molarity and micromolarity.

Properties

Solubility. Solubility is a surprisingly difficult parameter to determine accurately.[9] In our case, we were content to define only solubility ranges in chloroform and water (Table 1). Although often omitted from descriptions of surfactants, solubilities are important because they reveal overall "hydrophobicites" and because they allow others to better plan their experiments. Table 1 shows a high chloroform solubility (i.e., 0.3 M or higher) for all PEs and DPEs investigated (even those with only six-carbon chains). Except for AD-6, the AD solubility in chloroform is in the mM range. Whether or not reverse micelles are formed in chloroform was not determined.

Water solubility at room temperature depends markedly upon chain length. Thus, PE-6, DPE-6, and AD-6 are all highly water-soluble (>0.5 M). In contrast, PE-12, DPE-12, and AD-12 are all rather water insoluble (<0.2 mM). This extreme sensitivity to chain length cannot be ascribed simply to "multiple chains" because the geminis all have one cationic charge per chain, which is no different from that in water-soluble conventional surfactants such as dodecyltrimethylammonium bromide. Clearly, geometry and connectivity are of the essence. We presume that our multiarmed geminis have difficulty self-assembling into aggregates where *each* chain can immerse itself in a hydrophobic environment (as occurs with conventional surfactants when they form spherical micelles). The point is clarified in Figure 1 in which it is

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[9] Bohon, R. L.; Claussen, W. F. *J. Am. Chem. Soc.* **1951**, *73*, 1571.

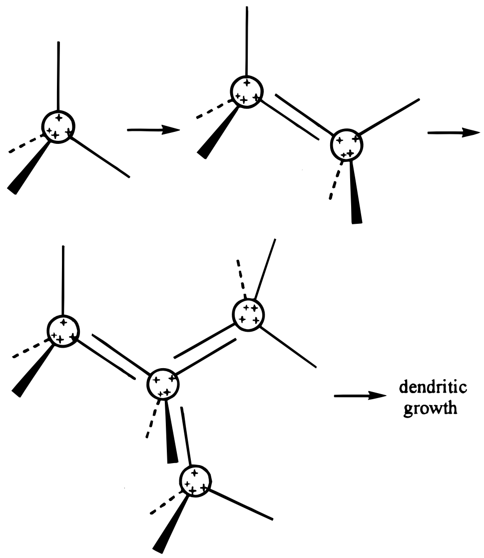

Figure 1. Schematic of the first steps in a possible "dendritic growth" of a multiarmed gemini.

seen that hydrophobic association between two ADs, each contributing one chain, leaves six exposed chains. If each of these six "loose ends" similarly associated with another gemini, then a "dendritic-like" aggregate with 18 exposed hydrocarbon chains would ensue. Further growth could, in principle, develop into a gelating network (a possibility that prompted, in part, this work). But, as will be shown, this did not occur. The geminis prefer to self-assemble into small aggregates or, alternatively, to resist dissolving in water altogether despite the multiple ionic charges.

In addition to the enforced dispositions of the hydrocarbon chains among the geminis, the surfactants have interconnected ionic groups. This too affects solubility adversely as one would not expect, for example, four interconnected cations to solubilize four 12-carbon substituents as effectively as four independent cations solubilize one 12-carbon chain each.

Gemini AD-10, whose modest water solubility of 3 mM increases 3-fold as the temperature is increased from 20 to 40 °C, shows no obvious Krafft point within this range. Solubility, of course, depends on solid-state forces as well as solution behavior. We are currently attempting to elucidate the solid-state properties of the geminis, including their tendency to form fibers, a topic upon that we will amplify at a later date.

Micelle Formation. Micelle formation is most commonly detected by plotting surface tension vs log [surfactant]. The surface tension will decrease until a point is reached where the plot abruptly levels off; this point is taken to be the CMC. The sharp bend in the plot results from surfactant joining micelles rather than adsorbing at the air/water interface.

Neither PE-6, DPE-6, nor AD-6 forms micelles according to surface tension data collected from 0.1 to 25 mM. For example, as seen in Figure 2, the surface tension of PE-6 diminishes from 73 to only 57 dynes/cm at 25 mM, and no break in the plot is evident. A lack of micelle formation is not surprising, perhaps, because a six-carbon chain is too short to induce aggregation of conventional surfactants below 1 M.

The situation is quite different with the three families of geminis having four or six eight-carbon chains. The behavior of DPE-8, for example, is portrayed in a surface

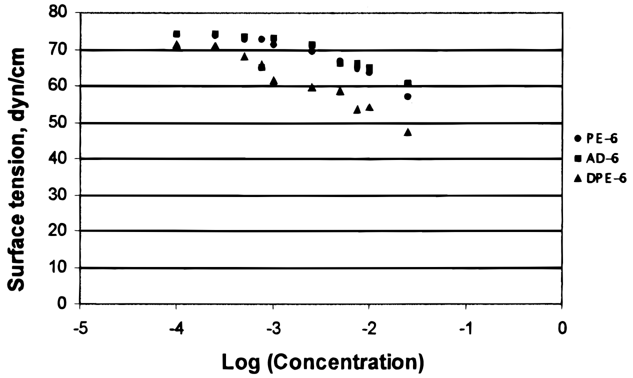

Figure 2. Surface tension of C_6-chained geminis.

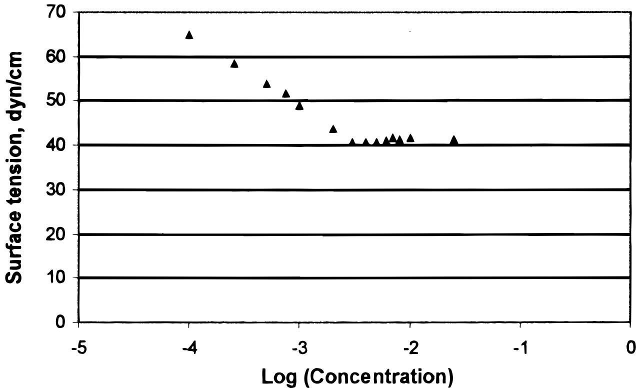

Figure 3. Surface tension of DPE-C8 water solutions.

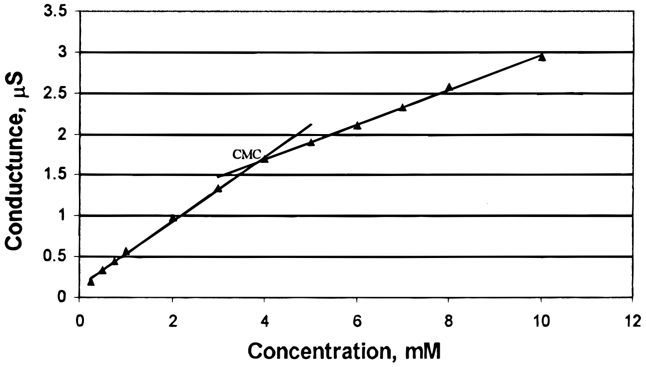

Figure 4. Specific conductance of DPE-C8 water solutions.

tension vs log [DPE-8] plot (Figure 3) where the surface tension falls steeply to 40 dynes/cm whereupon it levels off owing to micelle formation. The break point corresponds to a CMC of 3 mM. Surface tension-based CMC values for PE-8 and AD-8 are 5 and 6 mM, respectively. These numbers lie far below the CMC of 0.5 M for octyltrimethylammonium bromide.[10] A plot of specific conductance vs [DPE-8] in Figure 4 has a break at 3.9 mM, thereby confirming the presence of micelles as suggested by the surface tension data.

The multiarmed geminis with 12 carbons per chain are too insoluble (Table 1) to allow meaningful surface tension measurements. Moreover, it was not possible to make water-supported monomolecular films with them because their water solubility, low as it is, was sufficient to destabilize the films when compressed.

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[10] Zana, R. *J. Colloid Interface Sci.* **1980**, *78*, 330.

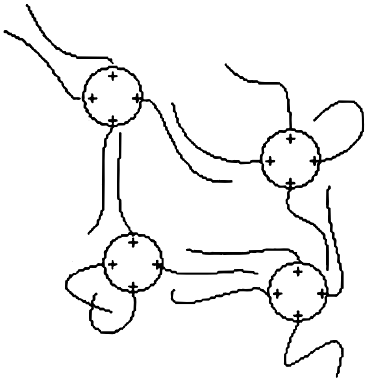

Figure 5. Highly schematic representation of a multiarmed gemini micelle showing ring formation, chain pairing, and chain coiling, all of which serve to diminish dendritic growth. (Light scattering data require only a few molecules per micelle.)

Dynamic light scattering experiments on PE-8, DPE-8, and AD-8, performed above their CMCs at 25 mM, provided information on the micelles' hydrodynamic diameters. In all three cases, the aggregates were small (<30 Å, the resolution limit of our instrumentation). We prefer to call the aggregates "micelles", but this is semantic matter. In any event, there is no evidence for dendritic growth of the surfactants.

In conclusion, the multiarmed geminis with eight-carbon chains have a high propensity to aggregate (i.e., to have a low CMC) relative to conventional surfactants of the same chain length. But the micellar aggregates are small, consisting of only a few molecules as opposed to the 50 or more that are commonly found in micelles of single-chain surfactants. And when the chains are moderately long (12 carbons), then water insolubility becomes an issue. The results point, therefore, to a family of surfactants that are inordinately hydrophobic considering that they all possess one cationic charge for each chain. No doubt this can be attributed to the geometric constraints imposed upon the chains. Rather than the chains being able to direct themselves inwardly into one central core, as with conventional micelles, the chains are projected outwardly into the water. Three factors diminish the likelihood of dendritic growth as pictured in Figure 1: (a) Molecular models suggest that, even in the adamantane series, two or three chains within a single molecule can lie, at least partially, side by side. This is true for eight-carbon chains; longer chains permit, of course, even greater van der Waals contact. Such an intramolecular chain−chain association is evident from molecular models assuming the preferred s-trans ester configuration and no more than two gauche linkages in the hydrocarbon chains. Thus, the geminis are less "multidentate" than might be presumed. (b) The hydrophobic chains can coil and curl, rather than project linearly into the water, thereby minimizing water−hydrocarbon contact. In this manner, dendritic growth would be impaired. (c) A third factor tending to diminish micellar growth is ring formation. Ring formation is portrayed in Figure 5 along with intramolecular chain−chain association and chain coiling, which, as just discussed, are also likely present in the assemblies. Since there exists, despite the three factors, a high degree of residual water−hydrocarbon contact in the gemini aggregates, relative to "normal" micelles, the geminis are particularly sensitive to chain length as indicated, for example, by the water insolubility of geminis with 12-carbon chains.

It seems clear that in order to achieve larger micelles, and possibly even a surfactant network, we must impart to the surfactants a more water-solubilizing functionality than a quaternary ammonium nitrogen. Work is this direction is underway.

Experimental Section

General Methods. Melting points are uncorrected. All reactions were carried out under a nitrogen atmosphere. Solvents were reagent grade and in most cases dried prior to use. All reagents were purchased from Aldrich. Amines were redistilled prior to use. Column chromatography was performed on silica gel 60 (Merk 230−400 mesh). ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz. Tensiometry was performed using 2 mL of freshly prepared solutions with a Kibron Microtrough S apparatus. Particle-sizing was accomplished utilizing a Coulter N4 Plus instrument. Conductivity measurements were carried out with the aid of a YSI model 35 digital conductance meter.

Pentaerythritol Tetratriflate. A stirred suspension of pentaerythritol (0.5 g, 3.68 mmol) in 2.5 mL of pyridine and 4 mL of CH_3CN was cooled to 0 °C. Triflic anhydride (5 g, 17.73 mmol) was added dropwise at this temperature over 1 h. The stirring was continued at rt for 3 h when 1 M HCl (20 mL) was added. The solution was cooled in an ice bath to complete the precipitation. The solid was filtered and washed with water. Recrystallization from CH_3CN/H_2O gave 2.3 g (94%) of white crystals: mp = 165−166 °C; ^{1}H NMR (acetone-d_6) δ 5.15 (s, 8H); ^{13}C NMR (acetone-d_6) δ 119.5 (q, J = 317.1 Hz), 72.46, 45.66. Anal. Calcd for $C_9H_8F_{12}O_{12}S_4$: C, 16.27; H, 1.21; S, 19.30. Found: C, 16.17; H, 1.12; S, 19.41.

Pentaerythritol Tetrakis(bromoacetate). A stirred suspension of pentaerythritol (0.43 g, 3.16 mmol) in 1.02 mL (12.6 mmol) of pyridine and 4 mL of CH_3CN was cooled to 0 °C. $BrCH_2COBr$ (1.37 mL, 15.7 mmol) was added dropwise at this temperature over 1 h. The ice bath was removed, and the stirring was continued at rt for 5 h. HCl (6 M, 2 mL) was then added to the reaction mixture together with 3 mL of CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL), and the combined organic layers were concentrated to give a yellow-orange oil. The oil was dissolved in 5 mL of CH_2Cl_2 and washed with brine and with 5 mL of aqueous 0.5 M Na_2CO_3, after which the organic layer turned cherry-black. This was concentrated and purified by filtering through a silica gel column. Elution with CH_2Cl_2 yielded 1.59 g (81%) of a yellow oily solid: ^{1}H NMR ($CDCl_3$) δ 4.28 (s, 8H), 3.86 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 166.8, 63.5, 42.9, 25.4. Anal. Calcd for $C_{13}H_{16}Br_4O_8$: C, 25.19; H, 2.60; Br, 51.56. Found: C, 25.45; H, 2.68; Br, 51.28.

Dipentaerythritol Hexakis(bromoacetate). A stirred suspension of dipentaerythritol (0.58 g, 2.3 mmol) in 1.13 mL (14 mmol) of pyridine and 5 mL of CH_3CN was cooled to 0 °C. $BrCH_2COBr$ (2 mL, 22.9 mmol) was added dropwise at this temperature over 1 h. The ice bath was removed, and stirring was continued at rt for 5 h. HCl (6 M, 3 mL) was then added to the reaction mixture together with 3 mL of CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL), and the combined organic layers were concentrated to give a yellow-orange oil. The oil was dissolved in 5 mL of CH_2Cl_2 and washed with brine and with 5 mL of aqueous 0.5 M Na_2CO_3, after which the organic layer turned cherry-black. This was concentrated and purified by filtering through a silica gel column. Elution with CH_2Cl_2 yielded 1.45 g (65%) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 4.22 (s, 12H), 3.86 (s, 12H), 3.46 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 166.8, 68.9, 63.6, 43.7, 25.6. Anal. Calcd for $C_{22}H_{28}Br_6O_{13}$: C, 26.97; H, 2.88; Br, 48.93. Found: C, 27.18; H, 2.90; Br, 48.80.

1,3,5,7-Tetrabromoadamantane. The tetrabromide was prepared by modification of a published procedure.[11] Adamantane (9.72 g, 71.5 mmol) was added in small portions over 30 min to a stirred mixture of bromine (45 mL) and anhydrous aluminum chloride (10 g, 75 mmol) at 0 °C. The mixture was then slowly heated to 70 °C and held at that temperature for 24 h. Hydrogen bromide evolved vigorously during the addition and heating. The reaction mixture was treated subsequently with aqueous sodium sulfite and hydrochloric acid. The resulting solid was filtered, dried in vacuo over P_2O_5, and recrystallized from CH_3CN to give 21.2 g (64%) of tan crystals: mp = 246−247 °C (lit.[11] mp = 245−247 °C); ^{1}H NMR ($CDCl_3$) δ 2.71 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 55.0, 54.8. Anal. Calcd for $C_{10}H_{12}Br_4$: C, 26.58; H, 2.68; Br, 70.74. Found: C, 26.62; H, 2.66; Br, 70.67.

1,3,5,7-Tetrahydroxyadamantane. The tetraalcohol was prepared by modification of a published procedure.[12] 1,3,5,7-Tetrabromoadamantane (4.17 g, 9.22 mmol) and Ag_2SO_4 (6.38 g, 20.45 mmol) were suspended in 10 mL of concentrated sulfuric acid. The mixture was slowly heated to 80 °C and stirred at this temperature for 5 h. After cooling, the AgBr precipitate was removed by filtration and washed with water. The filtrate was neutralized with KOH and evaporated. The resulting gray residue was dried over P_2O_5 and then extracted with 150 mL of ethanol in a Soxhlet apparatus for 12 h. After removal of ethanol, the residue was dissolved in methanol and filtered through a short Celite plug. Recrystallization from the MeOH/EtOH/acetone system afforded 1.5 g (81%) of a white solid: mp = 316−317 °C (lit.[12] mp = 317−320 °C); ^{1}H NMR (DMSO-d_6) δ 4.58 (s, 4H), 1.36 (s, 12H); ^{13}C NMR (DMSO-d_6) δ 68.9, 51.5. Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.85; H, 8.03.

1,3,5,7-Tetrakis(bromoacetoxy)adamantane. To a stirred suspension of 1,3,5,7-tetrahydroxyadamantane (0.59 g, 2.95 mmol) in 0.96 mL (11.8 mmol) of pyridine and 6 mL of CH_3CN was added a catalytic amount (10 mg) of 4-(dimethylamino)pyridine (DMAP). $BrCH_2COBr$ (2.06 mL, 23.6 mmol) was then added dropwise at 0 °C over 1 h. The ice bath was removed, and the stirring was continued at 50 °C for 5 h, after which time the solution became transparent and homogeneous. HCl (6 M, 3 mL) was then added to the reaction mixture together with 5 mL of CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (3 × 6 mL), and the combined organic layers were concentrated to give a light-brown solid residue. The solid was dissolved in 5 mL of CH_2Cl_2 and washed with brine and with 5 mL of aqueous 0.5 M Na_2CO_3, after which the organic layer turned brown-black. This was concentrated and purified by filtering through a silica gel column. Elution with CH_2Cl_2 gave the desired product as a yellow-white solid, which was recrystallized from CH_3CN/MeOH/H_2O yielding 1.45 g (82%) of white needles: mp = 170.5−171 °C; ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 8H), 2.58 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 166.0, 79.4, 42.8, 26.6. Anal. Calcd for $C_{18}H_{20}Br_4O_8$: C, 31.61; H, 2.95; Br, 46.73. Found: C, 31.89; H, 2.95; Br, 46.46.

General Procedure for the Preparation of the Gemini Surfactants Based on the Pentaerythritol Core. In a round-bottom flask, 0.54 g (0.87 mmol) of pentaerythritol tetrakis(bromoacetate) was dissolved in 10 mL of acetone ($CHCl_3$ was used as a solvent for the preparation of the C_8-chained surfactant). To the clear solution was added tertiary amine (5.2 mmol) in one portion, and the solution was refluxed for 3 h. During the reaction, a white precipitate formed gradually and was filtered and washed several times with acetone to give a white solid.

Pentaerythritol tetrakis(dimethylhexylammonioacetate), tetrabromide: yield 70%; mp = 152−153 °C; ^{1}H NMR ($CDCl_3$) δ 5.32 (s, 8H), 4.34 (s, 8H), 3.75 (t, 8H, J = 8.2 Hz), 3.48 (s, 24H), 1.76 (m, 8H), 1.35−1.25 (m, 24H), 0.84 (t, 12H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 164.7, 66.3, 64.9, 62.4, 51.0, 41.2, 31.3, 25.9, 22.8, 22.5, 14.0. Anal. Calcd for $C_{45}H_{92}Br_4N_4O_8$: C, 47.54; H, 8.16; N, 4.93; Br, 28.11. Found: C, 47.42; H, 8.04; N, 4.92; Br, 28.26.

Pentaerythritol tetrakis(dimethyldodecylammonioacetate), tetrabromide: yield 74%; mp = 154 °C dec; ^{1}H NMR ($CDCl_3$) δ 5.36 (s, 8H), 4.35 (s, 8H), 3.75 (t, 8H, J = 8.4 Hz), 3.50 (s, 24H), 1.78 (m, 8H), 1.38−1.23 (m, 72H), 0.87 (t, 12H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 164.7, 66.4, 64.9, 62.6, 51.0, 41.1, 32.0, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 26.4, 22.9, 22.8, 14.3. Anal. Calcd for $C_{69}H_{140}Br_4N_4O_8$: C, 56.24; H, 9.58; N, 3.80; Br, 21.69. Found: C, 56.25; H, 9.70; N, 3.76; Br, 21.81.

Pentaerythritol Tetrakis(dimethyloctylammonioacetate), Tetrabromide. In a round-bottom flask, 0.52 g (0.84 mmol) of pentaerythritol tetrakis(bromoacetate) was dissolved in 10 mL of $CHCl_3$. To the clear solution was added *N*,*N*-dimethyloctylamine (1.03 mL, 5 mmol) in one portion, and the solution was refluxed for 3 h. $CHCl_3$ was then evaporated, and the light-brown residue was washed with acetone yielding 0.53 g (51%) of white solid: mp = 104−105 °C; ^{1}H NMR ($CDCl_3$) δ 5.36 (s, 8H), 4.35 (s, 8H), 3.76 (t, 8H, J = 8.4 Hz), 3.50 (s, 24H), 1.78 (m, 8H), 1.35−1.25 (m, 40H), 0.86 (t, 12H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 164.7, 66.5, 65.0, 62.6, 51.0, 41.1, 31.8, 29.3, 29.2, 26.4, 22.9, 22.7, 14.2. Anal. Calcd for $C_{53}H_{108}Br_4N_4O_8$: C, 50.96; H, 8.72; N, 4.49; Br, 25.59. Found: C, 51.16; H, 8.62; N, 4.44; Br, 25.40.

General Procedure for the Preparation of the Gemini Surfactants Based on the Dipentaerythritol Core. In a round-bottom flask, 0.62 g (0.63 mmol) of dipentaerythritol hexakis(bromoacetate) was dissolved in 10 mL of acetone. To the clear solution was added tertiary amine (5.1 mmol) in one portion, and the solution was refluxed for 3 h. During the reaction, a white precipitate formed gradually and was filtered, washed several times with acetone, and recrystallized from CH_3CN/acetone to give a white solid.

Dipentaerythritol hexakis(dimethylhexylammonioacetate), hexabromide: yield 52%; mp = 161−162 °C; ^{1}H NMR ($CDCl_3$) δ 5.41 (s, 12H), 4.30 (s, 12H), 3.81 (t, 12H, J = 8.2 Hz), 3.64 (s, 4H), 3.49 (s, 36H), 1.77 (m, 12H), 1.39−1.27 (m, 36H), 0.84 (t, 18H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 165.0, 70.7, 66.0, 65.7, 62.6, 50.8, 42.4, 31.4, 26.0, 22.9, 22.6, 14.1. Anal. Calcd for $C_{70}H_{142}Br_6N_6O_{13}$: C, 47.90; H, 8.15; N, 4.79; Br, 27.31. Found: C, 47.69; H, 8.16; N, 4.73, Br, 27.53.

Dipentaerythritol hexakis(dimethyloctylammonioacetate), hexabromide: yield 60%; mp = 163−164 °C; ^{1}H NMR ($CDCl_3$) δ 5.38 (s, 12H), 4.25 (s, 12H), 3.77 (t, 12H, J = 8.2 Hz), 3.60 (s, 4H), 3.46 (s, 36H), 1.72 (m, 12H), 1.36−1.18 (m, 60H), 0.81 (t, 18H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 164.9, 70.3, 65.8, 65.5, 62.4, 50.6, 42.3, 31.7, 29.2, 29.1, 26.3, 22.8, 22.6, 14.1. Anal. Calcd for $C_{82}H_{166}Br_6N_6O_{13}$: C, 51.20; H, 8.70; N, 4.37; Br, 24.92. Found: C, 51.12; H, 8.75; N, 4.38; Br, 25.04.

Dipentaerythritol hexakis(dimethyldodecylammonioacetate); hexabromide: yield 62%; mp = 167 °C dec; ^{1}H NMR ($CDCl_3$) δ 5.43 (s, 12H), 4.28 (s, 12H), 3.80 (t, 12H, J = 8.2 Hz), 3.62 (s, 4H), 3.48 (s, 36H), 1.75 (m, 12H), 1.39−1.21 (m, 108H), 0.85 (t, 18H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 164.9, 70.5, 66.0, 65.7, 62.6, 50.7, 42.4, 32.1, 29.8, 29.7, 29.6, 29.6, 29.5, 29.5, 26.5, 23.0, 22.9, 14.4. Anal. Calcd for $C_{106}H_{214}Br_6N_6O_{13}$: C, 56.33; H, 9.54; N, 3.72; Br, 21.21. Found: C, 56.49; H, 9.39; N, 3.65; Br, 21.30.

General Procedure for the Preparation of the Gemini Surfactants Based on the Adamantane Core. In a round-bottom flask, 0.52 g (0.76 mmol) of 1,3,5,7-tetrakis(bromoacetoxy)adamantane was dissolved in 10 mL of acetone. To the clear solution was added tertiary amine (4.54 mmol) in one portion, and the solution was vigorously stirred for 3 h. During the reaction, a white precipitate formed gradually and was filtered and washed several times with acetone to give a white solid.

1,3,5,7-Tetrakis(dimethylhexylammonioacetoxy)adamantane, Tetrabromide. Recrystallized from CH_3CN: yield 78%; mp = 199 °C dec; ^{1}H NMR (DMSO-d_6) δ 4.50 (s, 8H), 3.48 (t, 8H, J = 8.0 Hz), 3.21 (s, 24H), 2.59 (s, 12H), 1.67 (m, 8H), 1.31−1.25 (m, 24H), 0.87 (t, 12H, J = 6.8 Hz); ^{13}C NMR (DMSO-d_6) δ 163.8, 79.5, 64.7, 60.8, 51.0, 42.1, 30.6, 25.3, 21.8, 21.8, 13.8. Anal. Calcd for $C_{50}H_{96}Br_4N_4O_8$: C, 50.01; H, 8.06; N, 4.67; Br, 26.61. Found: C, 49.78; H, 8.06; N, 4.63; Br, 26.49.

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1,3,5,7-Tetrakis(dimethyloctylammonioacetoxy)adamantane, Tetrabromide. Recrystallized from CH_3CN/acetone: yield 86%; mp = 201 °C dec; ^{1}H NMR (DMSO-d_6) δ 4.49 (s, 8H), 3.47 (t, 8H, J = 8.2 Hz), 3.21 (s, 24H), 2.59 (s, 12H), 1.68 (m, 8H), 1.33−1.23 (m, 40H), 0.87 (t, 12H, J = 6.6 Hz); ^{13}C NMR (DMSO-d_6) δ 163.8, 79.5, 64.8, 60.8, 50.9, 42.1, 31.2, 28.4, 28.4, 25.7, 22.1, 21.8, 13.8. Anal. Calcd for $C_{58}H_{112}Br_4N_4O_8$: C, 53.05; H, 8.60; N, 4.27; Br, 24.34. Found: C, 52.89; H, 8.63; N, 4.19; Br, 24.20.

1,3,5,7-Tetrakis(dimethyldecylammonioacetoxy)adamantane, Tetrabromide. Recrystallized from CH_3CN: yield 90%; mp = 193 °C dec; ^{1}H NMR (DMSO-d_6) δ 4.52 (s, 8H), 3.49 (t, 8H, J = 8.2 Hz), 3.22 (s, 24H), 2.59 (s, 12H), 1.67 (m, 8H), 1.32−1.21 (m, 56H), 0.85 (t, 12H, J = 6.8 Hz); ^{13}C NMR (DMSO-d_6) δ 163.8, 79.5, 64.8, 60.8, 50.9, 42.1, 31.3, 28.9, 28.8, 28.7, 28.5, 25.7, 22.1, 21.8, 14.0. Anal. Calcd for $C_{66}H_{128}Br_4N_4O_8$: C, 55.62; H, 9.05; N, 3.93; Br, 22.42. Found: C, 55.35; H, 9.16; N, 3.97; Br, 22.40.

1,3,5,7-Tetrakis(dimethyldodecylammonioacetoxy)adamantane, Tetrabromide. Recrystallized from CH_3CN: yield 87%; mp = 193 °C dec; ^{1}H NMR (DMSO-d_6) δ 4.50 (s, 8H), 3.48 (t, 8H, J = 8.2 Hz), 3.21 (s, 24H), 2.59 (s, 12H), 1.68 (m, 8H), 1.32−1.21 (m, 72H), 0.85 (t, 12H, J = 6.8 Hz); ^{13}C NMR (DMSO-d_6) δ 163.8, 79.5, 64.8, 60.8, 50.9, 42.1, 31.3, 29.0, 29.0, 28.9, 28.8, 28.7, 28.5, 25.7, 22.1, 21.8, 14.0. Anal. Calcd for $C_{74}H_{144}Br_4N_4O_8$: C, 57.81; H, 9.44; N, 3.64; Br, 20.79. Found: C, 57.59; H, 9.49; N, 3.49; Br, 20.60.

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