

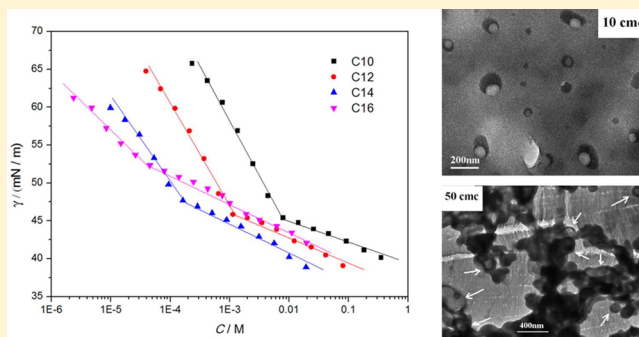
Surface Tension and Aggregation Properties of Novel Cationic Gemini Surfactants with Diethylammonium Headgroups and a Diamido Spacer

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S Supporting Information

ABSTRACT: A series of novel cationic gemini surfactants with diethylammonium headgroups and a diamido spacer were synthesized, and their surface and bulk properties were investigated by surface tension, electrical conductivity, fluorescence, viscosity, dynamic light scattering (DLS), and transmission electron microscopy (TEM) measurements. An interesting phenomenon, that is, the obvious decline in surface tension upon increasing concentration above the critical micelle concentration (cmc), was found in these gemini surfactant solutions, and two explanations were proposed. This surface tension behavior could be explained by the rapid increase in the counterion activity in the bulk phase or the continued filling of the interface with increasing surfactant concentration above the cmc. More interestingly, not only vesicles but also the surfactant-concentration-induced vesicle to larger aggregate (spongelike aggregate) transition and the salt-induced vesicle and spongelike aggregate to micelle transition were found in the aqueous solutions of these gemini surfactants. The spongelike aggregate that is first reported in the cationic gemini surfactant–water binary system is probably caused by the adhesion and fusion of vesicles at high surfactant concentration.



INTRODUCTION

Gemini surfactants that represent a new class of surfactants consisting of two amphiphilic moieties connected at the level of the headgroups or very close to the headgroups by a spacer have attracted increasing attention. Many studies have been carried out on gemini surfactants, focusing on their unique surface and bulk properties such as high surface activity, low critical micelle concentration, and abundant self-assembly morphologies.^{1–3} The most widely studied gemini surfactants are cationic alkanediyl- α,ω -bis(alkyldimethylammonium) dibromide, which are referred to as $C_mC_sC_m(\text{Me})$, where m and s stand for the carbon atom number in the tail alkyl chain and in the methylene spacer, respectively. Previous studies had shown that the variation of the spacer and the tail alkyl chain usually affects the aggregation behavior of $C_mC_sC_m(\text{Me})$,^{3,4} and the $C_mC_sC_m(\text{Me})$ series ($4 \leq s \leq 12$, $12 \leq m \leq 16$) tends to form higher-curvature aggregates in aqueous solutions, such as spherical or elongated micelles.^{2,5} Interestingly, when the dimethylammonium headgroups of $C_{12}C_sC_{12}(\text{Me})$ ($s = 4, 6, 8, 10, 12$) were converted to the diethylammonium headgroups ($C_{12}C_sC_{12}(\text{Et})$, $s = 4, 6, 8, 10, 12$), a large number of vesicles were observed in the aqueous solutions of the $C_{12}C_sC_{12}(\text{Et})$ series, and these vesicles are relatively stable over time and possess superior thermal stability,⁶ which means that the hydrocarbon parts of the polar headgroups of gemini surfactants also strongly affect the aggregation behavior. Vesicles composed of synthetic surfactants have attracted

more and more attention because they have many controllable factors that are very useful in understanding the nature of biomembranes and in developing new techniques by biomimetics.⁷ However, most work on synthetic vesicle formation involved mixed cationic–anionic surfactant systems,^{7–14} and the study of vesicle formation in the single cationic gemini surfactants is far from enough.^{6,15–17}

Huang and co-workers found that vesicle formation is a general phenomenon in the systems of the $C_{12}C_sC_{12}(\text{Et})$ series ($s = 4, 6, 8, 10, 12$), and they considered that with the increase in the hydrocarbon parts on the surfactant headgroup the hydrophobic effect of the whole amphiphile was also correspondingly increased. These structural effects will be more obvious for gemini surfactants because the stronger hydrophobic interaction and the resultant strong aggregation tendency allow the molecules to form aggregates larger than micelles.⁶ This idea interested us, and we were concerned about, besides the $C_{12}C_sC_{12}(\text{Et})$ series with a flexible methylene spacer, whether other gemini surfactants with diethylammonium headgroups that have different types of spacers (such as the diamido spacer that possesses rigidity and a hydrogen-bonding capability) also tend to form aggregates larger than micelles in aqueous solutions. On the basis of this question, we

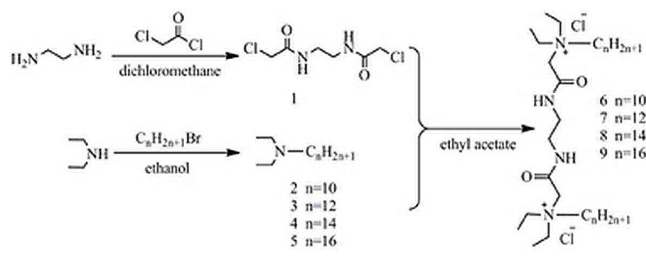
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designed and synthesized a series of novel cationic gemini surfactants with diethylammonium headgroups and a diamido spacer. Scheme 1 shows the molecular structure and synthesis

Scheme 1



route of these gemini surfactants. Their surface and bulk properties were investigated by surface tension, electrical conductivity, fluorescence, viscosity, dynamic light scattering (DLS), and transmission electron microscopy (TEM) measurements.

EXPERIMENTAL SECTION

Materials. Ethylenediamine (AP), diethylamine (AP), chloroacetyl chloride (CP), 1-bromodecane (CP), 1-bromododecane (CP), 1-bromotetradecane (CP), 1-bromohexadecane (CP), 1-bromooctadecane (CP), ethyl acetate (AP), dichloromethane (AP), and ethanol (AP) were purchased from Sinopharm Chemical Reagent Corporation. Pyrene (AP) was purchased from Sigma-Aldrich and used as received. Bidistilled water was used in all experiments (conductivity was less than $1.3 \mu\text{S}\cdot\text{cm}^{-1}$ at 298.15 K).

Synthesis. *N,N'*-(Ethane-1,2-diyl)bis(2-chloroacetamide) (**1**). Diethylamine (63.2 mmol, 3.8 g) in dichloromethane (20 mL) was added dropwise to a stirred solution of chloroacetyl chloride (132.8 mmol, 15 g) in dichloromethane (30 mL). The reaction mixture was stirred for 4 h at room temperature and then neutralized to a pH of ~ 9 with NaOH solution (6 M). The white precipitate was filtered out and recrystallized from bidistilled water and ethanol, respectively, to produce **1** as a white acerosc crystal (4.5 g, 33.4% yield). ^1H NMR (Varian Mercury-VX 300 MHz, $(\text{CD}_3)_2\text{SO}$): δ 3.16–3.17 (t, 4H), 4.05 (s, 4H), 8.29 (s, 4H). FTIR (Nicolet 5700 FT-IR, KBr): ν 3053, 3011, 2953, 1654, 1544, 1428, 1404, 1263, 1230, 752 cm^{-1} .

General Procedure for the Synthesis of 2–5. 1-Bromoalkane (0.15 mol) and diethylamine (0.45 mol, 3 equiv) were dissolved in ethanol (100 mL) and refluxed for 24 h. The solvent was evaporated, and the residue was poured in the NaOH solution (1 M, 200 mL) and stirred. The solution was extracted with ethyl acetate (3×70 mL), and the organic phase was dried over magnesium sulfate and filtered. The oily yellow liquid was isolated after evaporation of the solution as the crude product, which was distilled in vacuo to give the product as a colorless oil ($\sim 90\%$ yield).

N,N-Diethyldecan-1-amine (**2**). Yield, 90%. bp 110–111 $^\circ\text{C}/3$ mmHg. ^1H NMR (300 MHz, CD_3Cl): δ 0.85–0.90 (t, 3 H), 0.99–1.04 (t, 6 H), 1.26 (m, 14 H), 1.41–1.48 (m, 2 H), 2.37–2.42 (t, 2 H), 2.48–2.55 (q, 4 H).

N,N-Diethyldodecan-1-amine (**3**). Yield, 93%. bp 132–133 $^\circ\text{C}/3$ mmHg. ^1H NMR (300 MHz, CD_3Cl): δ 0.85–0.90 (t, 3 H), 0.99–1.04 (t, 6 H), 1.26 (m, 18 H), 1.41–1.46 (m, 2 H), 2.37–2.42 (t, 2 H), 2.48–2.55 (q, 4 H).

N,N-Diethyltetradecan-1-amine (**4**). Yield, 91%. bp 154–156 $^\circ\text{C}/3$ mmHg. ^1H NMR (300 MHz, CD_3Cl): δ 0.85–0.90 (t, 3 H), 0.99–1.04 (t, 6 H), 1.25 (m, 22 H), 1.41–1.45 (m, 2 H), 2.37–2.42 (t, 2 H), 2.48–2.55 (q, 4 H).

N,N-Diethylhexadecan-1-amine (**5**). Yield, 91%. bp 170–171 $^\circ\text{C}/3$ mmHg. ^1H NMR (300 MHz, CD_3Cl): δ 0.85–0.90 (t, 3 H), 0.99–1.04 (t, 6 H), 1.25 (m, 26 H), 1.41–1.44 (m, 2 H), 2.37–2.42 (t, 2 H), 2.48–2.55 (q, 4 H).

General Procedure for the Synthesis of 6–9. *N,N'*-(Ethane-1,2-diyl)bis(2-chloroacetamide) (20 mmol) and *N,N*-diethylalkane-1-amine (44 mmol, 2.2 equiv) were dissolved in ethyl acetate (60 mL) and refluxed for 72 h. After the reaction mixture cooled to room temperature, the white precipitate obtained was collected by filtration. The crude product was washed with ethyl acetate, and it was recrystallized from ethyl acetate/ethanol at least three times to produce the final product as a white solid ($\sim 60\%$ yield).

N,N'-((Ethane-1,2-diyl)bis(azanediyl))bis(2-oxoethane-2,1-diyl)-bis(*N,N*-diethyldecan-1-aminium) Dichloride (**6**, Abbreviated as C10). White powder crystals were obtained according to the general procedure. Yield, 53%. ^1H NMR (300 MHz, CD_3Cl): δ 0.85–0.90 (t, 6 H), 1.26–1.34 (m, 28 H), 1.46–1.51 (t, 12 H), 1.76 (m, 4 H), 3.36–3.39 (m, 4 H), 3.44 (s, 4 H), 3.51–3.67 (m, 8 H), 4.60 (s, 4 H), 9.90 (s, 2 H). ^{13}C NMR (300 MHz, CD_3Cl): 8.26, 14.03, 22.02, 22.56, 26.40, 28.96, 29.13, 29.29, 29.35, 31.74, 38.20, 55.42, 57.44, 59.27, 163.57. FTIR (KBr): ν 3179, 3041, 2952, 2919, 2851, 1680, 1560, 1452, 1247, 722 cm^{-1} . ESI-MS (P/ACE MDQ): m/z 284.4 ($(\text{M}-2\text{Cl})^{2+}/2$), 603.5 ($\text{M}-\text{Cl}^+$). Anal. Calcd for $\text{C}_{34}\text{H}_{72}\text{N}_4\text{O}_2\text{Cl}_2$: C, 63.82; H, 11.34; N, 8.76. Found (Vario EL III): C, 63.52; H, 11.13; N, 8.86.

N,N'-((Ethane-1,2-diyl)bis(azanediyl))bis(2-oxoethane-2,1-diyl)-bis(*N,N*-diethyldecan-1-aminium) Dichloride (**7**, Abbreviated as C12). White powder crystals were obtained according to the general procedure. Yield, 55%. ^1H NMR (300 MHz, CD_3Cl): δ 0.85–0.90 (t, 6 H), 1.25–1.34 (m, 36 H), 1.46–1.51 (t, 12 H), 1.76 (m, 4 H), 3.36–3.39 (m, 4 H), 3.43 (s, 4 H), 3.51–3.67 (m, 8 H), 4.59 (s, 4 H), 9.89 (s, 2 H). ^{13}C NMR (300 MHz, CD_3Cl): 8.26, 14.06, 22.03, 22.61, 26.40, 28.98, 29.24, 29.36, 29.51, 31.83, 38.17, 55.42, 57.47, 59.27, 163.58. FTIR (KBr): ν 3179, 3038, 2952, 2917, 2850, 1680, 1562, 1468, 1453, 1248, 721 cm^{-1} . ESI-MS: m/z 312.6 ($(\text{M}-2\text{Cl})^{2+}/2$), 659.5 ($\text{M}-\text{Cl}^+$). Anal. Calcd for $\text{C}_{38}\text{H}_{80}\text{N}_4\text{O}_2\text{Cl}_2$: C, 65.58; H, 11.59; N, 8.05. Found: C, 65.92; H, 11.99; N, 8.35.

N,N'-((Ethane-1,2-diyl)bis(azanediyl))bis(2-oxoethane-2,1-diyl)-bis(*N,N*-diethyltetradecan-1-aminium) Dichloride (**8**, Abbreviated as C14). White powder crystals were obtained according to the general procedure. Yield, 58%. ^1H NMR (300 MHz, CD_3Cl): δ 0.85–0.90 (t, 6 H), 1.25–1.34 (m, 44 H), 1.46–1.51 (t, 12 H), 1.76 (m, 4 H), 3.37 (m, 4 H), 3.44 (s, 4 H), 3.54–3.65 (m, 8 H), 4.60 (s, 4 H), 9.89 (s, 2 H). ^{13}C NMR (300 MHz, CD_3Cl): 8.23, 14.02, 22.01, 22.56, 26.36, 28.95, 29.22, 29.32, 29.46, 29.51, 31.78, 38.25, 55.41, 57.37, 59.26, 163.51. FTIR (KBr): ν 3178, 3039, 2917, 2850, 1681, 1561, 1468, 1453, 1247, 720 cm^{-1} . ESI-MS: m/z 340.6 ($(\text{M}-2\text{Cl})^{2+}/2$), 715.6 ($\text{M}-\text{Cl}^+$). Anal. Calcd for $\text{C}_{42}\text{H}_{88}\text{N}_4\text{O}_2\text{Cl}_2$: C, 67.07; H, 11.79; N, 7.45. Found: C, 67.02; H, 11.90; N, 7.55.

N,N'-((Ethane-1,2-diyl)bis(azanediyl))bis(2-oxoethane-2,1-diyl)-bis(*N,N*-diethylhexadecan-1-aminium) Dichloride (**9**, Abbreviated as C16). White powder crystals were obtained according to the general procedure. Yield, 64%. ^1H NMR (300 MHz, CD_3Cl): δ 0.85–0.90 (t, 6 H), 1.25–1.34 (m, 52 H), 1.46–1.50 (t, 12 H), 1.76 (m, 4 H), 3.37 (m, 4 H), 3.43 (s, 4 H), 3.55–3.65 (m, 8 H), 4.60 (s, 4 H), 9.86 (s, 2 H). ^{13}C NMR (300 MHz, CD_3Cl): 8.26, 14.03, 22.01, 22.58, 26.39, 28.96, 29.25, 29.35, 29.48, 29.55, 31.81, 38.23, 55.43, 57.41, 59.27, 163.51. FTIR (KBr): ν 3179, 3038, 2952, 2917, 2850, 1680, 1562, 1468, 1453, 1248, 721 cm^{-1} . ESI-MS: m/z 368.6 ($(\text{M}-2\text{Cl})^{2+}/2$), 771.6 ($\text{M}-\text{Cl}^+$). Anal. Calcd for $\text{C}_{46}\text{H}_{96}\text{N}_4\text{O}_2\text{Cl}_2$: C, 68.36; H, 11.97; N, 6.93. Found: C, 67.98; H, 11.90; N, 7.05.

Methods. **Surface Tension Measurement.** The surface tension was measured with a Fangrui tensiometer (type QBZY-2) using the ring method. Techniques were followed to ensure that the ring and glassware used in the measurements were scrupulously clean. To verify that the ring and glassware were clean, the surface tension of bidistilled water was measured regularly. Measurements were made in beakers thermostatted by means of a constant-temperature bath (Fangrui DC0506). Surface tensions from aged samples were obtained by allowing solutions to stand in covered beakers for 48 h at room temperature. Care was taken not to agitate the samples as they were uncovered and placed in the tensiometer.

Electrical Conductivity Measurement. The WTW conductivity meter (model inoLab Cond730) was used to perform the experiments. A 30 mL portion of bidistilled water was taken in a cell dipped in a

thermostatic water bath. A dip-type conductivity cell with a cell constant of 1.475 cm^{-1} was inserted into the water. A known volume of a concentrated solution of gemini surfactant ($200 \mu\text{L}$) was then added to the water with a microliter syringe (accuracy of $10 \mu\text{L}$) and thoroughly mixed, followed by the measurement of the conductance. In the course of conductivity testing, the temperature of the aqueous solution was maintained to within $\pm 0.1 \text{ K}$ of the desired temperature.

Fluorescence Measurement. The fluorescence emission spectra of pyrene were obtained using a Hitachi F-4600 spectrofluorophotometer. The intensity ratio of the first peak (I_1 near 373 nm) to the third peak (I_3 near 384 nm) was used as an index of the polarity of the pyrene-solubilizing medium.¹⁸ The excitation wavelength was 335 nm , and the emission spectra were scanned over the range of $350\text{--}450 \text{ nm}$. The slit widths of excitation and emission were all fixed at 1.5 nm . The solutions for fluorescence probing studied were prepared by injecting the appropriate amount (0.1% of the volume of the surfactant solution) of a probe stock solution ($1 \times 10^{-3} \text{ M}$ pyrene ethanolic solution) into the investigated surfactant solution, which was then treated by ultrasonication at room temperature for 1 h . We determined that this small amount of solvent had no effect on the measured properties. Measurements were performed at room temperature ($\sim 295 \text{ K}$).

Viscosity Measurement. The relative viscosities of the gemini surfactant solutions were measured in two Ubbelohde viscometers thermostatted at 298.15 K . The viscosities of all solutions were found to be independent of the capillary diameter and thus the flow rate.

Dynamic Light Scattering (DLS). DLS measurements were performed with Malvern Instruments Zetasizer Nano (ZEN 3600). Light of $\lambda = 632.8 \text{ nm}$ from a solid-state He–Ne laser was used as the incident beam. The measurement was conducted at a scattering angle of 173° . The measured autocorrelation function was analyzed by the CONTIN method. The effective hydrodynamic radius (R_h) was calculated according to the Einstein–Stokers equation $R_h = k_B T / (6\pi\eta D)$, where D is the diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity. The diffusion coefficient was measured three times for each sample, and all measurements were performed at $298.15 \pm 0.1 \text{ K}$.

Transmission Electron Microscopy (TEM). Micrographs were obtained with a JEOL JEM-2100 (HR) transmission electron microscope at a working voltage of 200 kV . The TEM samples were prepared by the negative-staining method. Phosphotungstic acid solution (2%) was used as the staining agent. A carbon Formvar-coated copper grid (200 mesh) was placed on one drop of the sample solution for 5 min , and the excess solution was wiped away with filter paper to form a thin liquid film on the copper grid. Next, the copper grid was placed onto one drop of phosphotungstic acid solution. The excess liquid was also wiped away with filter paper, and then the samples were dried in air.

RESULTS AND DISCUSSION

The surface tension measurement is a classical method of studying the critical micelle concentration (cmc) of surfactants. The variations of the surface tension γ with the surfactant concentration $C(\text{M})$ at 298.15 K are shown in Figure 1. The plots of γ versus C show a break at a concentration corresponding to the cmc of the gemini surfactant series (C10, C12, C14, and C16). From Figure 1, it can be found that the gemini surfactant with longer hydrophobic chains has a lower cmc value.

The packing densities of surfactants at the air–water interface are important to the interpretation of the surface activities of surfactants.¹⁹ The surface areas A_{min} occupied by the surfactant molecules should reflect their packing densities.²⁰ The surface excess concentration Γ and the surface area A_{min} at the air–water interface can be calculated using the Gibbs adsorption equation^{21,22}

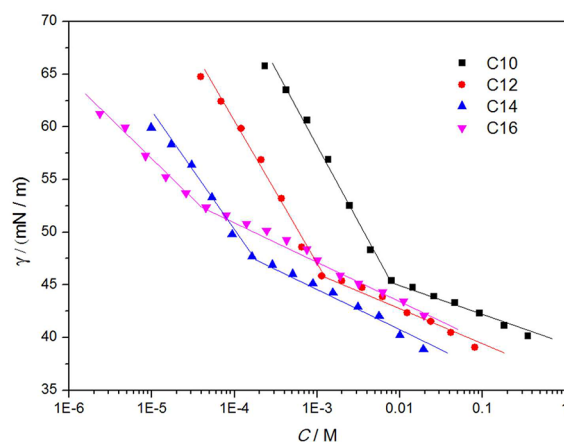


Figure 1. γ – C curves of the gemini surfactant series (C10, C12, C14, and C16) at 298.15 K .

$$\Gamma = \frac{-1}{2.03nRT} \left(\frac{d\gamma}{d \log C} \right)_T \quad (1)$$

and the equation

$$A_{\text{min}} = (N_A \Gamma)^{-1} \times 10^{16} \quad (2)$$

where $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $T = 298.15 \text{ K}$ with γ expressed in N/m , N_A is Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$), and n is a constant that depends on the number of species constituting the surfactant and adsorbed at the interface. For a uniivalent ionic surfactant, the value $n = 2$ is generally used,²¹ but for a gemini surfactant, the value of n could not be simply determined. The values $n = 2$ and 3 were used in calculating Γ .^{19,23,24} Nevertheless, if the value used for n affects the calculated values of Γ and A_{min} , then it has no bearing on the way in which Γ and A_{min} vary with the tail carbon number. Therefore, the use of a different value of n (2 or 3) does not affect the conclusion inferred from these variations.

The A_{min} value increases as the tail carbon number is increased from 10 to 16 (Table 1), suggesting that gemini surfactants with shorter hydrophobic tails have higher packing densities at the air–water interface. This rule is the same as that for other gemini surfactants, and a possible explanation is that the longer hydrophobic chains are more prone to curl and thus make the A_{min} value larger.¹⁹

In Figure 1, it is very noteworthy that the obvious decrease in γ upon increasing concentration at $C > \text{cmc}$ was found. For conventional surfactants, the surface tensions are constant with increasing concentration at $C > \text{cmc}$.²⁵ However, for some gemini surfactants, similar observations (the decrease in γ upon increasing concentration at $C > \text{cmc}$) were reported,^{6,21,26} especially for the gemini surfactants with diethylammonium headgroups. Unfortunately, those previous reports have given no explanation of this interesting phenomenon.

To explore the reason for this phenomenon, the Gibbs analysis that is now accepted theory in colloid/interface chemistry could be used. The Gibbs adsorption equation, in its most general form (eq 3), is fundamental to all adsorption processes where monolayers are formed.²⁷

$$d\gamma = - \sum_i \Gamma_i d\mu_i \quad (3)$$

where $d\gamma$ is the change in the surface tension of the solvent, Γ_i is the surface excess concentration of any component in the

Table 1. Parameters of Micellization and Adsorption at the Air/Water Interface of Gemini Surfactants

surfactant	cmc ^a (M)	cmc ^b (M)	γ_{cmc} (mN/m)	C ₂₀ (M)	10 ⁶ Γ (mol/m ²)		A _{min} (nm ²)		α^c
					n = 3	n = 2	n = 3	n = 2	
C10	6.72 × 10 ⁻³	7.07 × 10 ⁻³	45.62	2.52 × 10 ⁻³	0.90	1.35	1.85	1.23	0.40(0.33)
C12	1.05 × 10 ⁻³	1.03 × 10 ⁻³	46.13	4.00 × 10 ⁻⁴	0.84	1.26	1.98	1.32	0.45(0.41)
C14	1.90 × 10 ⁻⁴	2.15 × 10 ⁻⁴	47.21	6.73 × 10 ⁻⁵	0.63	0.95	2.62	1.75	0.55(0.48)
C16	3.80 × 10 ⁻⁵	4.75 × 10 ⁻⁵	52.22	4.42 × 10 ⁻⁵	0.47	0.71	3.53	2.35	0.60(0.50)

^aMeasured by tensiometry. ^bMeasured by conductometry. ^cThe values in parentheses are for $T = 278.15$ K.

system, and $d\mu_i$ is the change in chemical potential of any component in the system. At equilibrium between the interfacial and bulk phase concentrations, $d\mu_i = RT d \ln a_i$, where a_i is the activity of any component in the bulk phase, R is the gas constant, and T is the absolute temperature. Thus,

$$d\gamma = -RT \sum_i \Gamma_i d \ln a_i \quad (4)$$

When the surfactant concentration is higher than the cmc, the solution consisting of the solvent and only one ionic surfactant solute could be considered to contain four components: the solvent, the surfactant ion, the counterion, and the aggregate, $d\gamma = -RT(\Gamma_0 d \ln a_0 + \Gamma_1 d \ln a_1 + \Gamma_2 d \ln a_2 + \Gamma_3 d \ln a_3)$, where the subscript 0 refers to the solvent, the subscript 1 refers to the surfactant ion, the subscript 2 refers to the counterion, and the subscript 3 refers to the aggregate. In the surface (or Gibbs interface) phase, $\Gamma_0 = 0$, thus

$$d\gamma = -RT(\Gamma_1 d \ln a_1 + \Gamma_2 d \ln a_2 + \Gamma_3 d \ln a_3) \quad (5)$$

The surfactant ions characterized by surface activity tend to move to and be rich in the surface phase, so the surface excess concentration of surfactant ion is positive ($\Gamma_1 > 0$). Meanwhile, the surface excess concentration of counterions is also positive ($\Gamma_2 > 0$) because the surface phase as a whole is electrically neutral, containing equal numbers of positively charged ions and negatively charged ions. However, the surface excess concentration of aggregate is less than or equal to zero ($\Gamma_3 \leq 0$) on account of the fact that the aggregates could be regarded as a surface-inactive substance and they will not be enriched in the surface phase. For the conventional single-tail surfactant, the surfactant ion concentration above the cmc does not increase further as more surfactant is added to the solution.^{28,29} The micellization trend for gemini surfactant ions is greater than that for conventional surfactant ions, thus the gemini surfactant ion activity probably also stays constant or decreases with increasing concentration at $C > \text{cmc}$ ($d \ln a_1 \leq 0$). Moreover, as more surfactant is added above the cmc, the aggregate concentration increases ($d \ln a_3 > 0$) and the counterion concentration will also increase ($d \ln a_2 > 0$) because of the ionization of aggregates. Through the above analysis, it can be found that both the first and the third terms in parentheses in eq 5 are not greater than zero ($\Gamma_1 d \ln a_1 \leq 0$, $\Gamma_3 d \ln a_3 \leq 0$) and only the second term is positive ($\Gamma_2 d \ln a_2 > 0$), which means that as the surfactant concentration increases above the cmc, the activity variations of the surfactant ion and the aggregate will not lead to a reduction in γ except for the counterion. Provided that the decreased portion of γ caused by increasing the counterion activity is greater than the increased portions of γ caused by decreasing the surfactant ion and increasing the aggregate activity, the eventual decrease in γ upon increasing concentration at $C > \text{cmc}$ will be found. The greater the increase in the counterion activity, the greater the

decreased portion of γ . Thus, the eventual reduction of γ upon increasing these gemini surfactant concentrations at $C > \text{cmc}$ (as shown in Figure 1) could be due to the rapid increase in the counterion activity in the bulk phase. It should be pointed out that this inference is based on the assumption that the interface is considered to be saturated with surfactant below the cmc.²⁷ However, a recent report suggested that the interface may not in fact be saturated at the cmc.³⁰ Thus, the decrease in surface tension at $C > \text{cmc}$ may also be due to the continued filling of the interface above the cmc, which is a simpler explanation of the data.

The increase in the counter activity at a concentration above the cmc is related to the aggregate degree of ionization α . A higher α will give rise to a greater increase in the counter activity with increasing concentration above the cmc. According to this, these novel gemini surfactants should have a high α at 298.15 K, and the reduction of γ above the cmc will be smaller as the α is lowered. To validate this inference, the α values of these gemini surfactants at 298.15 K were examined by electrical conductivity measurements. (The experimental data were processed according to the method in ref 31.) In addition, because the aggregates' degree of ionization for ionic surfactants decreases with decreasing temperature,³¹ the variations in the electrical conductivity and the surface tension γ with the surfactant concentration C (M) at 278.15 K were also investigated. (The experimental data and the calculated results are included in the Supporting Information.)

As expected, these gemini surfactants do have high α values (0.4–0.6, Table 1) at 298.15 K, which are higher than those of conventional surfactant.³² Moreover, compared to the results of the surface tension measurement at 298.15 K (Figure 1), the results for 278.15 K show a smaller reduction of γ upon increasing concentration at $C > \text{cmc}$, especially for C14 and C16 (Figure 2), demonstrating that a lower α does lead to a smaller reduction of γ upon increasing the concentration above the cmc.

Besides the temperature, the ionic strength can also affect the variation in counterion activity in the bulk phase with increasing surfactant concentration. To determine if the postcmc decline in surface tension is due to the rapid increase in counterion activity in the bulk phase, we also measured the surface tension of these gemini surfactant solutions with 0.1 M NaCl. As expected, the surface tension of these gemini surfactant solutions remained almost constant with increasing concentration at $C > \text{cmc}$ when 0.1 M NaCl was added (especially C10 and C12 as shown in Figure 3). When 0.1 M NaCl was added, a high ionic strength and a large number of counterion (Cl^-) restrained the ionization of surfactant and aggregates, causing the counterion activity to remain almost constant in the bulk phase with increasing surfactant concentration. Thus, the surface tension remains almost constant at concentrations above the cmc.

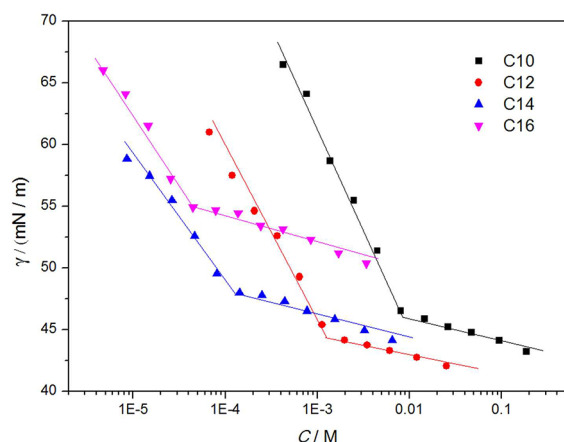


Figure 2. γ - C curves of gemini surfactant series C10, C12, C14, and C16 at 278.15 K.

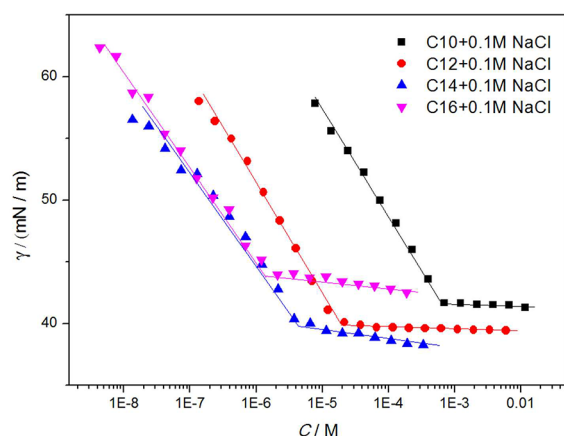


Figure 3. γ - C curves of gemini surfactant solutions with 0.1 M NaCl at 298.15 K.

It is known that a compact aggregate with a high charge density has a greater tendency to attract counterions than a loose one. The high α values of these gemini surfactants suggest that the gemini surfactants self-assemble into noncompact aggregates, which could be confirmed by steady-state fluorescence measurement.

Pyrene is often used as a probe to investigate surfactant aggregates in aqueous solution.^{3,10,19,32} The shape and intensity of the fluorescence emission of this probe is sensitive to its microenvironment at the site of solubilization of the fluorophore.^{3,19} When the surfactant concentration is above the cmc, the intensity ratio I_1/I_3 can be taken as a measure of the polarity of the microenvironment in aggregates, reflecting the compactness of aggregates, being high in polar media (loose aggregates) and low in hydrophobic environments (compact aggregates). For most surfactants, above the cmc, I_1/I_3 remains essentially constant because the aggregate structures are compact and the microenvironment does not change. However, in Figure 4 (the arrows mark I_1/I_3 at the cmc determined by electrical conductivity measurements) it can be seen that the values of I_1/I_3 at the cmc for these surfactants are higher than those of other surfactants,^{19,32,33} and when the concentrations exceed the cmc, the values of I_1/I_3 are still gradually decreased with increasing concentration, even at very high relative concentrations (50 times the cmc for C14 and C16), indicating that these surfactants form loosely bound aggregates in solution

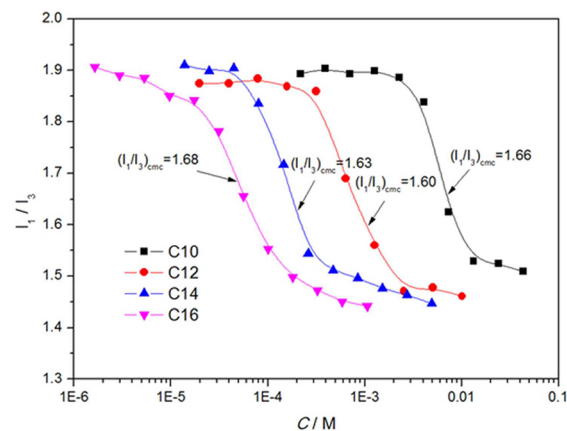


Figure 4. Pyrene fluorescence intensity ratio I_1/I_3 vs C for gemini surfactants.

within a wide concentration range.³⁴ The noncompact aggregate structures of these novel gemini surfactants can be related to the specific molecular structures. The large diethylammonium headgroups and the long diamido spacer that have a certain hydrophilicity and rigidity probably increase the steric hindrance of the self-assembly procedure, hindering the surfactant molecules from pack closely together.

The organized assemblies formed in these gemini surfactant aqueous solutions were investigated by dynamic light scattering (DLS) first. The size distributions of these gemini surfactants at 10 times the cmc by DLS are shown in Figure 5. There was one

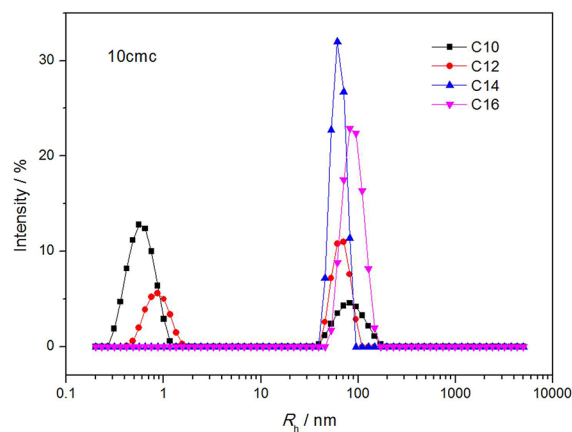


Figure 5. Hydrodynamic radius (R_h) distributions of the aggregates formed in the aqueous solutions of gemini surfactants at a concentration of 10 times the cmc at 298.15 K.

obvious peak with an average apparent hydrodynamic radius (R_h) of about 60–100 nm, reflecting the typical size of a large aggregate. It should be noted that the peaks centered at less than 1 nm (for C10 and C12) do not correspond to micelles, and they probably reflect some interaction in the unconventional surfactant systems with multipolar headgroups.⁶ By TEM observation, vesicles were observed in aqueous solutions of these novel cationic gemini surfactants as shown in Figure 6, indicating that the large aggregates in the DLS plot ($R_h = 60$ –100 nm) should be assigned to vesicles. In addition, we also tested the relative viscosities of these gemini surfactant solutions (10 cmc) and found that they were quite close to 1 (Figure S5 in Supporting Information). These testing results

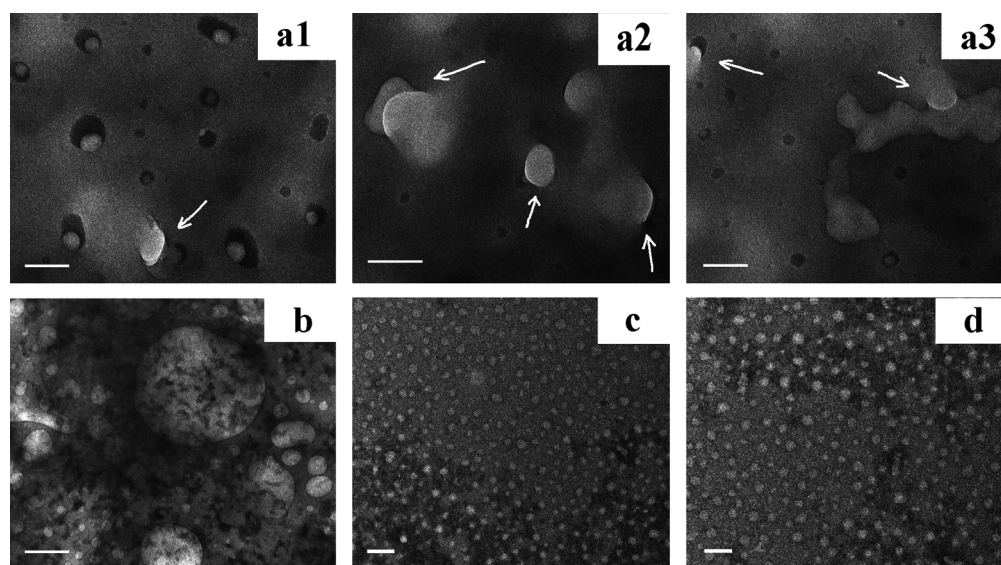


Figure 6. TEM micrographs of the gemini surfactants of aqueous solutions with 10 times the cmc: (a1–a3) C10, (b) C12, (c) C14, and (d) C16 (bar = 200 nm).

are analogous to that of $C_{12}C_8C_{12}(Et)$, and they further illustrate that vesicle formation is a general phenomenon in the systems of quaternary ammonium gemini surfactants with long hydrocarbon parts on the headgroups, whether they have the flexible methylene spacer or the diamido spacer, which has hydrophilicity and rigidity. Interestingly, some broken vesicles were observed in the solution of C10 (Figure 6a1,a2,a3, the arrows mark them), indicating that the vesicles formed in C10 are not very stable. In addition, an elongated vesicle was also observed in Figure 6a3.

The effect of salt on the formation of vesicles was also investigated. DLS results showed that the peaks assigned to vesicles with an average hydrodynamic radius (R_h) of 60–100 nm disappeared, leaving micelle peaks^{6,35} with R_h values of 1.8 nm (C10), 2.4 nm (C12), 2.7 nm (C14), and 2.8 nm (C16) (Figure 7). The TEM results also showed that the vesicles no longer existed in the gemini (C10, C12, C14, and C16) systems with the addition of 0.1 M NaCl (Figure S6 in Supporting Information). In combination with the DLS results, it can be

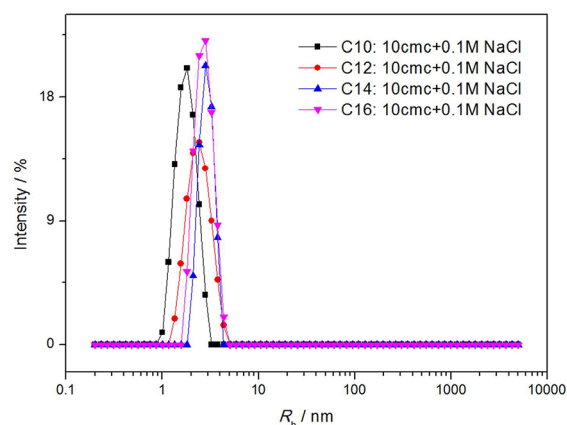


Figure 7. Hydrodynamic radius (R_h) distributions of the aggregates formed in the aqueous solutions of gemini surfactants at a concentrations of 10 times the cmc with 0.1 M NaCl addition at 298.15 K.

concluded that vesicles were destroyed and transformed into micelles in the aqueous solution of these gemini surfactants with 0.1 M NaCl addition.

Besides the addition of salt, the increase in surfactant concentration can also cause the transformation of the assembling structures.^{35,36} Upon increasing the gemini surfactant concentrations to 50 times the cmc, we also observed new size distributions (400–1000 nm, Figure 8).

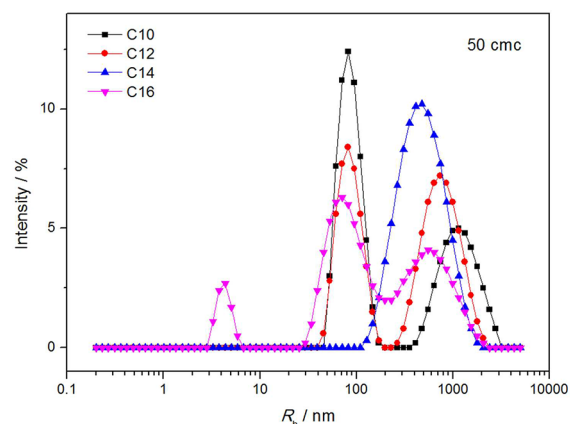


Figure 8. Hydrodynamic radius (R_h) distributions of the aggregates formed in aqueous solutions of gemini surfactants at a concentration of 50 times the cmc at 298.15 K.

The relative viscosity measurements showed that the viscosities of these gemini surfactant solutions (50 cmc) were significantly higher than the viscosity of water (Figure S5 in Supporting Information), indicating that the new size distributions (400–1000 nm) observed in DLS plots should not be assigned to large vesicles. To investigate these new aggregates further, a more intuitive transmission electron microscopy (TEM) technique was used.

By TEM observation, when the concentrations of gemini surfactants were increased to 50 times the cmc, spongelike aggregates with large sizes could be distinguished clearly as shown in Figure 9, which corresponded to the large size

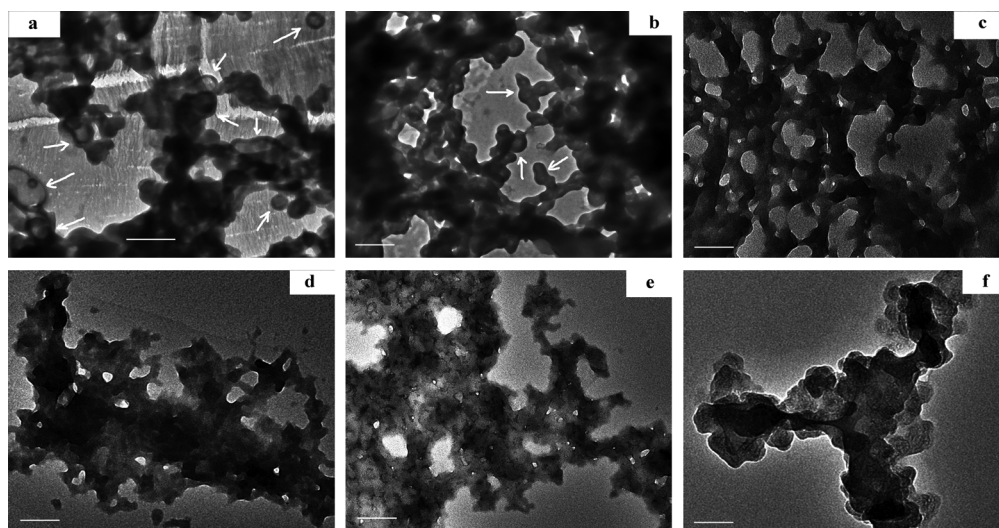


Figure 9. TEM micrographs of the gemini surfactants of aqueous solutions with 50 times the cmc: (a–c) C10, (d) C12, (e) C14, and (f) C16 (bar = 400 nm).

distributions (400–1000 nm) in the DLS plots. The previous studies of sponge morphology in coacervate basically involve complicated ternary (surfactant/alcohol/water) or quaternary (surfactant/alcohol/water/salt) systems,^{37,38} with the coacervate of the binary system (surfactant/water) having almost no reports besides that for only one binary system in which a zwitterionic gemini surfactant formed an elementary coacervate when added to water.^{39,40} Through careful observation, it can be found that vesicle-like structures existed in the large aggregates (Figure 9a,b, marked by arrows). Therefore, we speculated that the formation of spongelike aggregates is probably caused by the adhesion and fusion of vesicles at high concentration, and the adhesion between vesicles might be related to the hydrogen-bonding capability of the diamido spacer. (Further studies on the aggregates are ongoing in our laboratory.)

If these spongelike aggregates form by the adhesion and fusion of vesicles, then they probably have a poor salt tolerance, as do vesicles. DLS and TEM results showed that when 0.1 M NaCl is added to the gemini surfactant solutions (50 cmc) the large aggregates (vesicles and spongelike aggregates) indeed disappeared (Figures 10 and S7), leaving only micelles with R_h values of 2.0 (C10), 2.1 (C12), 2.4 (C14), and 2.8 nm (C16) (Figure 10). According to these results, it can be concluded that the large aggregates were destroyed and transformed into micelles in the aqueous solution of these gemini surfactants with 0.1 M NaCl addition. (Studies concerning the mechanism of the salt-induced vesicle or large aggregate to micelle transition in these novel cationic gemini surfactants systems are ongoing in our laboratory).

CONCLUSIONS

Novel cationic gemini surfactants with diethylammonium headgroups and diamido spacers were synthesized and investigated. An interesting phenomenon, that is, the obvious decrease in surface tension with increasing surfactant concentration above the cmc, was found by surface tension measurements. The large diethylammonium headgroups and the long diamido spacer probably hinder the gemini surfactant molecules from packing closely together, thus, the aggregates of these gemini surfactants possess incompact structures (as

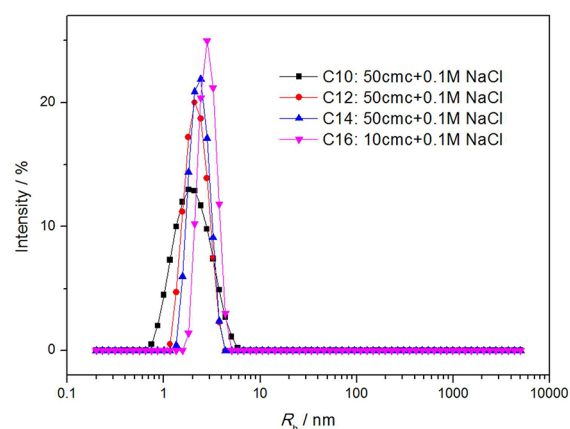


Figure 10. Hydrodynamic radius (R_h) distributions of the aggregates formed in the aqueous solutions of gemini surfactants at a concentrations of 50 times the cmc with the addition of 0.1 M NaCl at 298.15 K.

proven by the fluorescence measurement). Incompact aggregates with a low charge density bring about a high α (as proven by the electrical conductivity measurement), and the high α gives rise to the rapid increase in the counterion activity with increasing concentration above the cmc. Finally, on the basis of the Gibbs analysis, the rapid increase in the counterion activity could lead to the decrease in γ upon increasing concentration at $C > \text{cmc}$. In addition, if the interface is not saturated at the cmc and continues to fill up above the cmc, then there is a simpler explanation of the surface tension data; that is, the decrease in γ at $C > \text{cmc}$ may be due to the continued filling of the interface. The DLS and TEM experimental observations showed that, in the bulk phase, these novel gemini surfactants could form both vesicles and spongelike aggregates with a vesicle-to-spongelike aggregate transition with increasing concentration. The salt-induced vesicle and spongelike aggregate-to-micelle transitions were also found in these novel cationic gemini surfactants systems. The spongelike aggregate that is first reported in the cationic gemini surfactant–water binary system is probable caused by the adhesion and fusion of vesicles at high concentration, and further studies are ongoing in our laboratory.

■ ASSOCIATED CONTENT

● Supporting Information

Specific conductivity versus concentration and NMR spectra for C10, C12, C14, and C16. Parameters of micellization and adsorption at the air/water interface of gemini surfactants. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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