Surface, Interfacial and Aggregation Properties of Sulfonic Acid-Containing Gemini Surfactants with Different Spacer Lengths

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Four sulfonic acid-containing gemini surfactants 9BA-m-9BA (m = 2, 3, 4, 6), 6,6′-(ethane-1,2-diylbis(oxy)) bis (3-nonylbenzenesulfonic acid) (9BA-2-9BA), 6,6′-(propane-1,3-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid) (9BA-3-9BA), 6,6′-(butane-1,4-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid) (9BA-4-9BA), and 6,6′-(hexane-1,6-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid) (9BA-6-9BA), were synthesized and characterized by Fourier transform infrared (FTIR), ^{1}H NMR, elemental analysis, and melting temperature measurements. Their ability to lower the water surface tension and hexadecane/water interfacial tension was measured and correlated with the hydrophobicity and length of their alkyl spacer chain. Their aggregates in aqueous solutions were investigated using dynamic light scattering and transmission electron microscopy. Spherical vesicles could be found in aqueous solutions of four gemini surfactants with an apparent hydrodynamic radius (R_h) of ∼100 nm. The critical micelle concentration (cmc) of four gemini surfactants evaluated by surface tension measurements was 1 order of magnitude smaller than that of conventional single-chain surfactant sodium dodecylsulfonate (SDS). And their C_{20}, the gemini surfactant concentration required for lowering the surface tension of water by 20 mN/m, was about 2 orders of magnitude smaller than that of SDS, showing excellent efficiency at reducing the surface tension of water. In addition, the hexadecane/water interfacial tension could be less than 1.0 mN/m after using pure 9BA-m-9BA in water. Using 9BA-6-9BA the hexadecane/water interfacial tension was reduced to 0.21 mN/m.

Introduction

Gemini surfactants are generally made up of two hydrocarbon chains and two hydrophilic head groups covalently connected by a spacer chain at the level of, or near to hydrophilic head groups.[1−4] These surfactants possess more predominant surface active properties than corresponding traditional single-chain surfactants: a lower critical micelle concentration (cmc), a higher efficiency in reducing air/water surface tension and oil/water interfacial tension, unusual aggregation morphologies, and better wetting and solubilizing properties. Therefore, they have attracted great interest in both scientific and industrial aspects.[3−5]

Much attention has been paid to cationic gemini surfactants since 1991.[6−12] Anionic gemini surfactants including carboxylate,[13−17] sulfate and sulfonate,[18−24] and phosphate[25,26] have been prepared, and their cmc, surface tension, and wetting ability have been examined. However, not much is known on the properties of gemini surfactants in acid form, such as sulfonic acid. Moreover, very few papers have been issued on the investigation of liquid−liquid interfacial properties influenced by gemini surfactants;[27,28] although, a large number of studies on aqueous solutions of gemini surfactants has been reported.

In our previous work, an anionic gemini surfactant containing two sodium sulfonates as hydrophilic head groups, i.e., 6,6'-(butane-1,4-diylbis(oxy)) bis(sodium 3-nonylbenzenesulfonate) (9B-4-9B), was synthesized and used as a micelle stabilizer in the preparation of conducting polyaniline (PAni) for the first time. The stable PAni dispersions were obtained, and the resulting PAni particles had fine granular morphology and high doping

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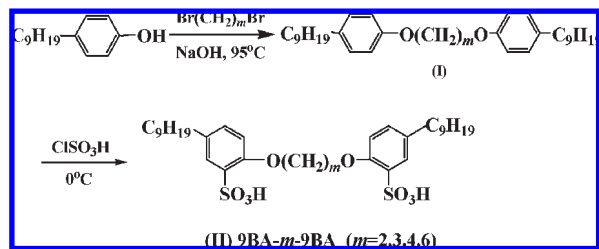

Figure 1. The synthesis pathway of four sulfonic acid-containing gemini surfactants 9BA-*m*-9BA. 9BA-2-9BA: 6,6′-(ethane-1,2-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid); 9BA-3-9BA: 6,6′-(propane-1,3-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid); 9BA-4-9BA: 6,6′-(butane-1,4-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid); 9BA-6-9BA: 6,6′-(hexane-1,6-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid).

levels. The drawback of using 9B-4-9B was that the extra inorganic acid, hydrochloric acid, needed to be added into the emulsion system to induce the polymerization of aniline and to give conducting PAni.[29]

On the basis of this consideration, we prepared a sulfonic acid-containing gemini surfactant, 6,6′-(butane-1,4-diylbis(oxy)) bis (3-nonylbenzenesulfonic acid) (9BA-4-9BA) in a facile two-step reaction using nonylphenol (NP) as the starting material (Figure 1). This surfactant with two sulfonic acids as the hydrophilic head groups is expected to be used in the polymerization of aniline as micelle stabilizer and the dopant of resulting PAni, simultaneously.[30]

To better understand the properties of this kind of gemini surfactants, a series of sulfonic acid-containing gemini surfactants 9BA-*m*-9BA (*m* = 2, 3, 6) with different spacer lengths as shown in Figure 1 was synthesized, and their surface properties were compared with those of 9BA-4-9BA in this contribution. Furthermore, the aggregation behavior of four surfactants 9BA-*m*-9BA (*m* = 2, 3, 4, 6) in aqueous solutions and the hexadecane/water interfacial properties influenced by 9BA-*m*-9BA in water were studied. Among these surfactants, using 9BA-6-9BA with a longer spacer length in water could result in a quite low interfacial tension of 0.21 mN/m between hexadecane (oil phase) and water. To the best of our knowledge, there is only limited information on the interfacial tensions between long chain hydrocarbon compounds and aqueous solutions of highly purified anionic gemini surfactants. For a pure gemini surfactant solution, the oil/water interfacial tension of less than 1.0 mN/m is quite difficult to reach.

Experimental Section

Materials. NP and chlorosulfonic acid (Beijing Chemical Industry Corporation, China) were stored at low temperature prior to use. 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane (Shanghai Chemical Reagent Company, China), 1,6-dibromohexane (Alfa Aesar, USA), and other chemicals were used as received without further purification. Distilled water was used in all experiments. Hexadecane (Aldrich, USA) was more than 99% pure.

Synthesis and Characterization of Gemini Surfactants. Four gemini surfactants 9BA-*m*-9BA were synthesized by a two-step reaction as shown in Figure 1, basically according to a procedure reported in the literature with modified post-treatments.[29,30]

In detail, phase transfer catalyst tetra-*n*-butylammonium bromide was mixed with NP in 20% (wt%) sodium hydroxide (NaOH). A 2.5-fold molar excess of alkyl dibromide (1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane,

1,6-dibromohexane, respectively) was added into the mixture at 70 °C under stirring. Then the reaction system was heated to 95 °C and stirred for 4 h. The mixture of reaction was extracted three times using ether. The ether phase was washed by using 3% glacial acetic acid and distilled water to give the diethers (I) after evaporating the solvent, in which the diether with *m* = 2 or *m* = 3 was separated from NP by liquid chromatography. The structure of the diether (I) was characterized by Fourier transform infrared (FTIR, Nicolet NEXUS-470) with the KBr pellet technique and ¹H NMR (JEOL, AL-300) using CDCl₃ as solvent.

A 2.1-fold molar excess of chlorosulfonic acid was added dropwise into the diether (I) solution in anhydrous dichloromethane (CH_2Cl_2) for 1 h at 0 °C and stirring. After reaction for 5 h, the solution was purged with nitrogen for 1 h to remove the evolved hydrochloric acid and remaining chlorosulfonic acid. Petroleum ether was added to the reaction solution to give the crude precipitate. Pure sulfonic acid-containing gemini surfactant was obtained after crude product was dissolved in dichloromethane and recrystallized three times from petroleum ether. The yield was 57.7%, 59.4%, 69.0%, and 37.3% for 9BA-2-9BA, 9BA-3-9BA, 9BA-4-9BA, and 9BA-6-9BA, respectively.

The FTIR spectra of 9BA-*m*-9BA were measured with the KBr pellet technique (spectra are given in the Supporting Information). FTIR band assignments: 3400 cm^{-1} (v_{O-H}); 2960, 2932, and 2870 cm^{-1} ($v_{C-H\,in\,alkyl\,chain}$); 1600 and 1500 cm^{-1} ($v_{C-H\,in\,benzene\,ring}$); 1170 and 1030 cm^{-1} (v_{S-O}); 829 cm^{-1} ($v_{1,2,4-substituted\,benzene\,C-H\,out-plane\,bending}$).

The structure and purity of 9BA-*m*-9BA were confirmed by ¹H NMR (JEOL, AL-300) with D₂O as solvent at the surfactant concentration of 0.1 mmol/L. The four surfactants synthesized gave spectra (shown in Supporting Information), indicating that they were purified well. The detailed ¹H NMR data of 9BA-*m*-9BA are listed in Table 1.

The purity of 9BA-*m*-9BA was also checked by elemental analysis (Vario EL III analyzer, Germany) and melting temperature measurements with XSP-9F optical microscope. 9BA-2-9BA calcd. for $C_{32}H_{50}O_8S_2$: C, 61.31%; H, 8.04%; found: C, 59.49%; H, 7.69%. 9BA-3-9BA calcd. for $C_{33}H_{52}O_8S_2$: C, 61.84%; H, 8.18%; found: C, 60.52%; H, 7.92%. 9BA-4-9BA calcd. for $C_{34}H_{54}O_8S_2$: C, 62.35%; H, 8.31%; found: C, 61.46%; H, 8.17%. 9BA-6-9BA calcd. for $C_{36}H_{58}O_8S_2$: C, 63.31%; H, 8.56%; found: C, 61.70%; H, 8.09%. The measured melting temperature was 99.1−99.3 °C, 101.3−101.5 °C, 149.4−149.5 °C and 80.1−80.3 °C for 9BA-2-9BA, 9BA-3-9BA, 9BA-4-9BA and 9BA-6-9BA, respectively. The impurity content in 9BA-*m*-9BA was estimated to be below 2%.

Surface Tension Measurements. The equilibrium surface tensions of the 9BA-*m*-9BA aqueous solutions were examined using the Wilhemy plate method on a tensiometer (Data physics DCAT21, Germany) at 25.00 ± 0.05 °C. Equilibrium surface tension data were reproducible within 0.02 mN/m. The cmc was determined from the plot of the surface tension versus the logarithmic molar surfactant concentration of 9BA-*m*-9BA in water. The surface tension of the distilled water used was 71.8 mN/m.

Dynamic Light Scattering (DLS). DLS measurements were performed with a laser light scattering spectrometer (ALV/DSL/SSL-5022F) and a 22mW HeNe-laser (λ = 632.8 nm) at 25.0 °C. The scattering angle was 90°, and the intensity autocorrelation function was analyzed using the Contin method. The 9BA-*m*-9BA aqueous solution at a concentration of 10 mmol/L was filtered directly into a 7 mL quartz cell using a Millipore membrane filter (0.45 *μ*m pore size). The quartz cell was rinsed several times with filtered water and filled with the filtered sample solution. The DLS measurements began 10 min after the sample cell was placed in the DLS optical system. The data obtained in each case were the average of 10 runs, each run of 300 s duration.

Transmission Electron Microscopy (TEM). TEM samples were prepared from 9BA-*m*-9BA aqueous solutions at a

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Table 1. The ^{1}H NMR Data of Gemini Surfactants 9BA-m-9BA

9BA-m-9BA	^{1}H NMR data	Chemical groups in 9BA-m-9BA					
		$C_9\underline{H}_{19}$-	-O-CH$_2$-C$\underline{H}_2$-	-O-C$\underline{H}_2$-	(a);	(b);	(c)
m=2	^{1}H number*	38.96	N/A	3.96	2.00;	2.00;	1.94
	δ (ppm)	0.2-1.6	N/A	4.29	6.56;	6.95;	7.62
m=3	^{1}H number	38.60	1.92	4.04	2.03;	1.97;	2.00
	δ (ppm)	0.2-1.8	2.00	4.08	6.52;	6.85;	7.58
m=4	^{1}H number	38.47	4.04	4.00	1.99;	2.00;	2.01
	δ (ppm)	0.2-1.5	1.64	3.75	6.44;	6.90;	7.56
m=6	^{1}H number	46.59		4.07	2.00;	2.01;	2.05
	δ (ppm)	0.2-1.6		3.68	6.43;	6.92;	7.56

* The number of hydrogen nuclei (^{1}H number) is proportional to the integration of NMR signals.
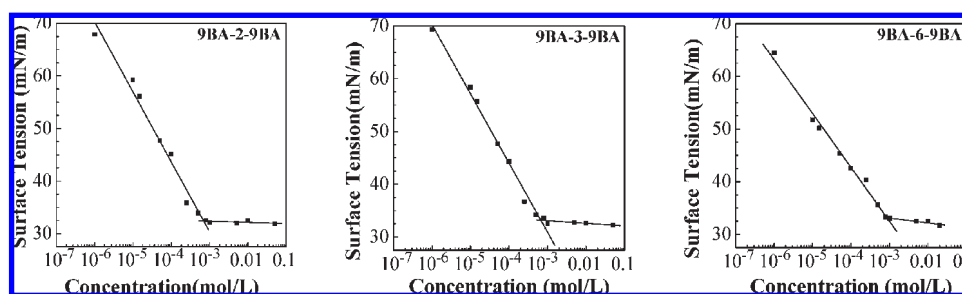
Figure 2. Plots of equilibrium surface tensions versus the logarithmic molar surfactant concentrations of 9BA-m-9BA (m = 2, 3, 6) in water.

concentration of 10 mmol/L using a negative-staining method. A drop of the solution was placed onto a carbon Formvar-coated copper grid (300 mesh), and the excess liquid was wiped away with filter paper. Then one drop of uranyl acetate solution (1%) as staining agent was placed onto the copper grid. The excess liquid was also wiped away with filter paper. After drying, the samples were imaged under a JEM-2100F electron microscope at a working voltage of 200 kV.[12,23]

Interfacial Tension Measurements. Interfacial tension between hexadecane and 9BA-m-9BA aqueous solution was measured by a spinning-drop tensiometer (TX-550A, American Bowing Industry Corp.) at 25.0 ± 0.1 °C. The interfacial tension values were recorded until equilibrium was reached, which was considered to be obtained when successive values agreed to within 0.1 mN/m.

Results and Discussion

Surface Properties of Gemini Surfactants 9BA-m-9BA. The equilibrium surface tensions of gemini surfactant 9BA-m-9BA (m = 2, 3, 6) aqueous solutions at different surfactant concentrations were measured and shown in Figure 2. Clearly, the surface tension of 9BA-m-9BA aqueous solution decreased with increasing the surfactant concentration until the cmc. Above the cmc, the surface tension became steady.

Generally, the contribution of one benzene ring to the surface properties is similar to that of 3.5 −CH$_2$−.[20] In other words, the contribution of one nonyl benzene is basically equal to that of 12.5 −CH$_2$−. Therefore, the comparison of the surface properties of 9BA-m-9BA with conventional single-chain surfactant sodium dodecylsulfonate (SDS) is shown in Table 2 because these surfactants have identical hydrophilic head groups and similar hydrophobic tails.

It could be found that the synthesized gemini surfactants 9BA-m-9BA in water gave smaller cmc and greater efficiency in

Table 2. The Surface Properties of Gemini Surfactants 9BA-m-9BA and Single-Chain Surfactant SDS in Aqueous Solutions

surfactant	cmc (mmol/L)	γ_{cmc} (mN/m)	C_{20} (mmol/L)	cmc/C_{20}
9BA-2-9BA	0.69	32.4	0.025	27.6
9BA-3-9BA	0.66	33.2	0.024	27.5
9BA-4-9BA^a	0.65	32.8	0.018	36.1
9BA-6-9BA	0.86	33.2	0.013	66.2
SDS^b	12.0	33.0	4.4	2.7

^{a} From ref 30. ^{b} From ref 31.

lowering the surface tension than the single-chain surfactant SDS. The surface tensions of the gemini surfactant 9BA-m-9BA aqueous solutions at cmc (γ_{cmc}) were similar with that of SDS. However, the cmc of 9BA-m-9BA in water was 1 order of magnitude smaller than that of SDS, suggesting an excellent micelle forming ability of gemini surfactants in water.

Furthermore, the C_{20} of 9BA-m-9BA, the surfactant concentration required for lowering the surface tension of water by 20 mN/m, was 2 orders of magnitude smaller than that of SDS, showing remarkable efficiency at decreasing the surface tension of water. In addition, cmc/C_{20} value of 9BA-m-9BA was 1 order of magnitude greater than that of SDS. The cmc/C_{20} value presents the relationship between the surfactant micellization in water and the adsorption at the surface. The surfactant with a higher cmc/C_{20} value indicates that its micellization in water is inhibited more than adsorption at the surface of aqueous media, or adsorption is facilitated more than micellization.[18,32,33] The

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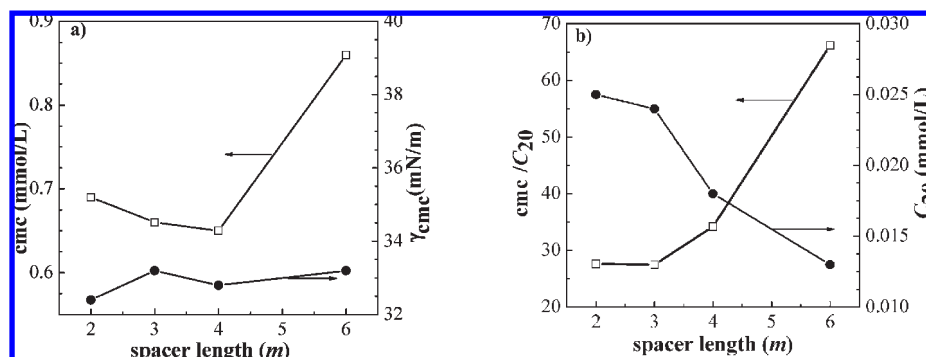
Figure 3. The influence of spacer length (*m*) on the surface properties of gemini surfactant 9BA-*m*-9BA aqueous solutions.

Table 3. The Γ_{max} and a_{min} of Gemini Surfactants 9BA-*m*-9BA

	air/water interface		hexadecane/water interface	
surfactant	$\Gamma_{max/air}$ (10^6 mol/m^2)	$a_{min/air}$ (nm^2)	$\Gamma_{max/oil}$ (10^6 mol/m^2)	$a_{min/oil}$ (nm^2)
9BA-2-9BA	1.152	1.44	0.531	3.12
9BA-3-9BA	1.150	1.45	0.526	3.16
9BA-4-9BA	1.093	1.52	0.545	3.05
9BA-6-9BA	0.895	1.86	0.388	4.28

gemini surfactants 9BA-*m*-9BA with higher cmc/C_{20} suggest they adsorb more readily to the air/water interface than the single-chain surfactant, therefore they possess higher efficiencies at reducing surface tension, which is consistent with the C_{20} results above. The sole molecule of gemini surfactant is equal to two single-chain surfactants linked by one spacer at the level of or close to the head groups; therefore, the repulsive force between two charged head groups is screened by a hydrophobic spacer making a positive contribution to adsorption at the interface.

The influence of spacer length (*m*) on the surface properties of gemini surfactant 9BA-*m*-9BA solutions is depicted in Figure 3. The cmc goes through a minimum of small amplitude for *m* = 4 and then increases with increasing spacer length. Zana et al. also found that cmc increased with increasing spacer chain length in gemini surfactants 12-*s*-12 when *s* < 6. [4,6] We suppose the surfactant 9BA-6-9BA with the highest cmc is partly due to the contribution of the hydrophobicity and length of its spacer chain. ^{1}H NMR data of 9BA-*m*-9BA provided useful information (Table 1 and Supporting Information). [1]H chemical shift of the methylene groups close to the oxymethylene groups in the spacer chain of 9BA-6-9BA overlapped with that of methylene groups in the nonyl chain, implying that they were located in the same chemical environment. That means the methylene groups in the longer spacer chain of 9BA-6-9BA are more hydrophobic than those of other three surfactants, resulting in a 9BA-6-9BA molecule being more easily adsorbed to the air/water interface. Therefore, a higher concentration of 9BA-6-9BA is needed to form micelles in water. That is to say, 9BA-6-9BA with longer hydrophobic methylene groups shows a slightly higher cmc.

On the other hand, the C_{20} value of 9BA-*m*-9BA decreased with increasing spacer chain length, indicating that the surfactant 9BA-6-9BA with the longest spacer chain has the highest surface efficiency in lowering surface tension.

The maximum surface excess concentration at the air/water interface, $\Gamma_{max/air}$, is calculated by applying the Gibbs adsorption isotherm equation: [23,32]

$$\Gamma_{max/air} = -\frac{1}{2.303nRT}\left(\frac{d\gamma}{d\log c}\right)_T \tag{1}$$
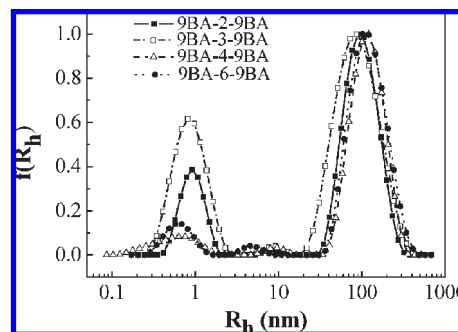

Figure 4. Apparent hydrodynamic radius (R_h) distributions of aggregates formed in 9BA-*m*-9BA aqueous solutions at a concentration of 10 mmol/L.

where *n* represents the number of solute species whose concentration at the interface changes with change of surfactant concentration *c*, *R* is the gas constant (R = 8.314 J/mol·K), and dγ/d log *c* is the slope of the surface tension γ vs log *c* dependence below the cmc at a constant absolute temperature *T* in Kelvin.

The minimum area occupied by a surfactant molecule at the air/water interface, $a_{min/air}$, can be estimated from the relation

$$a_{min/air} = \frac{1}{N_A\Gamma_{max}} \tag{2}$$

where N_A is Avogadro's number.

The correct value of *n* for a gemini surfactant was discussed by Zana[4] who pointed out that *n* varied between 2 and 3 according to the spacer length and concentration of the surfactant in solution. Also, *n* can take the value 2 for an ionic surfactant where the surfactant ion and the counterion are univalent. [4,23,32] Therefore we choose to use *n* = 2 with the understanding that we are mainly comparing the $\Gamma_{max/air}$ values within a series of compounds. The calculated values of $\Gamma_{max/air}$ using *n* = 2 in eq 1 and $a_{min/air}$ from eq 2 are given in Table 3.

The $\Gamma_{max/air}$ values decreased, while the $a_{min/air}$ values increased with increasing spacer chain length of gemini surfactants 9BA-*m*-9BA. This is in agreement with the trends of 12-*s*-12 and
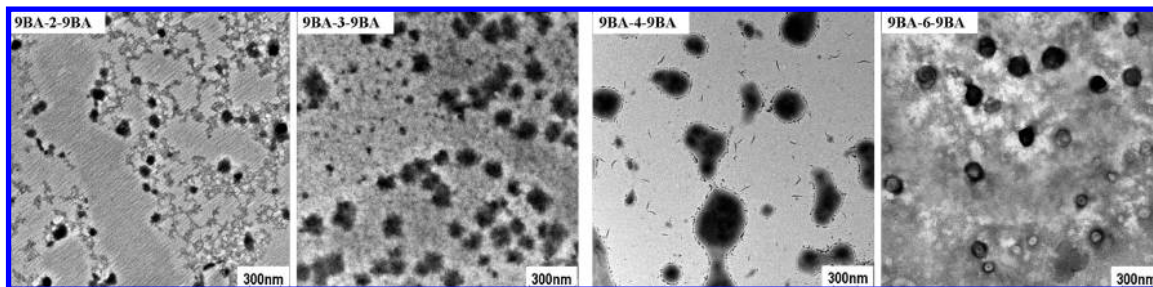
Figure 5. TEM images of 9BA-*m*-9BA aqueous solutions at a concentration of 10 mmol/L by the negative-staining method.
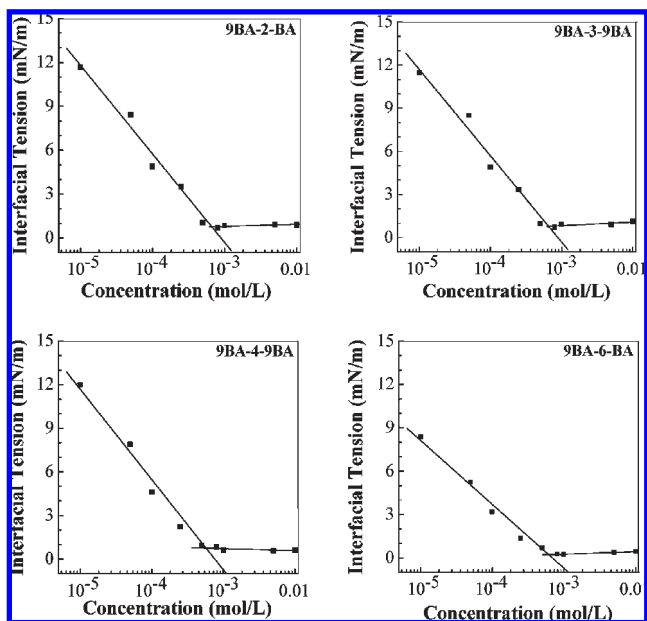

Figure 6. Plots of hexadecane/water interfacial tensions versus the logarithmic molar surfactant concentrations of 9BA-*m*-9BA in water.

12-EO$_Z$-12 surfactants, which are bisquaternary ammonium bromide gemini surfactants possessing spacer chain $-(CH_2)s-$ or $-(OCH_2CH_2)_Z-$.[4,34] Khurana et al. reported the results of fully atomistic molecular dynamics simulations of the gemini surfactants 12-*s*-12 series at the air/water interface with *s* = 3, 4, 6, 12, 14, 16, and found the same tendency when spacer chain length was less than 12.[35]

$\Gamma_{max/air}$ measures how much the air/water interface has been changed by surfactant absorption, which is related to the molecular structures of gemini surfactants, including the spacer chain structure and length. The head groups in conventional single-chain surfactants are randomly distributed on the surface, and the minimum occupied area per molecule at the air/water interface is the cross section area of the aliphatic chain (~0.205 nm^2). With gemini surfactants 9BA-*m*-9BA, particularly those with short spacer length (*m* ≤ 6), the hydrophobic spacer chain and the hydrophilic head groups would be tightly arranged at the air/water interface because of the electrostatic repulsions between the charged surfactant head groups and the influence of the rigid benzene ring. This would result in the spacer chain being rather rigid and lying flat with a fairly linear conformation at the air/water interface.[4,34,35] Therefore, the gemini surfactant

9BA-*m*-9BA molecule with longer spacer chain (*m* ≤ 6) certainly occupies a greater interfacial area.

Aggregates of Gemini Surfactant 9BA-*m*-9BA in Aqueous Solutions. It was found that the aqueous solutions of gemini surfactants 9BA-*m*-9BA were clear and transparent in the concentration range of 10^{-6}–0.1 mol/L. Figure 4 shows the apparent hydrodynamic radius (R_h) distributions ($f(R_h)$) of aggregates formed in four gemini surfactant aqueous solutions at a concentration of 10 mmol/L and 25 °C measured by DLS. There are three distributions around 1, 10, and 100 nm, which agrees with the results of Wang et al.[12] The gemini surfactants with spacer length *m* = 2, 3, 4, 6 had comparable aggregate sizes in water. The distribution centered at R_h of about 1 nm did not correspond to micelles, whereas the distribution with R_h of around 6–10 nm could be associated with micelle formation.[12] On the other hand, the larger aggregates with $R_h \approx 100$ nm could be assigned to vesicles confirmed by TEM investigations pictured in Figure 5. Spherical vesicles with diameters of 50–300 nm were observed in four gemini surfactant solutions at a concentration of 10 mmol/L and 25 °C. The influence of spacer length in 9BA-*m*-9BA on the aggregate sizes was not very remarkable except that the aggregation distribution of 9BA-4-9BA was a little bit bigger than that of the other three gemini surfactants, as shown in Figure 5.

Hexadecane/Water Interfacial Properties Influenced by Gemini Surfactants 9BA-*m*-9BA. The equilibrium interfacial tensions between hexadecane oil phase and gemini surfactant 9BA-*m*-9BA aqueous solutions at different surfactant concentrations were measured and shown in Figure 6. The hexadecane/water interfacial tension decreased with increasing surfactant concentration in water to a limiting concentration. Above this concentration, hexadecane/water interfacial tension reached a constant. This relationship between interfacial tensions and gemini surfactant 9BA-*m*-9BA concentration in water is similar to the surface tension isotherm of 9BA-*m*-9BA in aqueous solutions. Two curves intersect at the concentration corresponding to the micelle formation, allowing identification of the cmc for surfactants in the hexadecane/water system (cmc$_{oil}$). δ_{cmc} is hexadecane/water interfacial tension at cmc$_{oil}$.

As shown in Figure 6, there was no obvious premicellar minimum value of interfacial tension near the cmc$_{oil}$ of 9BA-*m*-9BA, implying that four gemini surfactants 9BA-*m*-9BA were synthesized with high purity in this research.[28]

Furthermore, the hexadecane/water interfacial tension at the cmc$_{oil}$ (δ_{cmc}) of 9BA-*m*-9BA was quite low. δ_{cmc} was smaller than 1.0 mN/m, that is, 0.75, 0.79, 0.75, and 0.21 mN/m by using 9BA-*m*-9BA in water with *m* = 2, 3, 4, 6, respectively, showing excellent efficiency in reducing hexadecane/water interfacial tension, and could provide potential applications in emulsification and liquid–liquid extraction. As far as we know, it is not easy to reduce interfacial tension between a long chain hydrocarbon compound and water below 1.0 mN/m using a pure

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(35) Khurana, E.; Nielsen, S. O.; Klein, M. L. *J. Phys. Chem. B* **2006**, *110*, 22136.

surfactant. We suppose that the lowest hexadecane/water interfacial tension of 0.21 mN/m by using 9BA-6-9BA in water is related to its longer hydrophobic alkyl spacer chain, which is more compatible with hexadecane. Therefore 9BA-6-9BA has a higher capability to lower the hexadecane/water interfacial tension.

It is worth noting that the minimum area occupied by a surfactant molecule at the hexadecane/water interface, $a_{min/oil}$, is much larger than the minimum area occupied by a surfactant molecule at the air/water interface, $a_{min/air}$, as illustrated in Table 3. The $a_{min/oil}$ of 9BA-*m*-9BA was about 2 times larger than $a_{min/air}$ for the same surfactant. This suggests that the gemini surfactants 9BA-*m*-9BA have good compatibility with hexadecane so that long alkyl tails ($C_9H_{19}-$) in surfactant could arrange and partly lie flat in the hexadecane/water interface, resulting in larger $a_{min/oil}$ occupied by one surfactant molecule.

Conclusions

In summary, a simple two-step reaction pathway to prepare sulfonic acid-containing gemini surfactants in high purity was proposed in this research. Four gemini surfactants 9BA-*m*-9BA (*m* = 2, 3, 4, 6), that is, 6,6′-(ethane-1,2-diylbis(oxy)) bis (3-nonylbenzenesulfonic acid) (9BA-2-9BA), 6,6′-(propane-1, 3-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid) (9BA-3-9BA), 6,6′-(butane-1,4-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid) (9BA-4-9BA), and 6,6′-(hexane-1,6-diylbis(oxy)) bis(3-nonylbenzenesulfonic acid) (9BA-6-9BA), were successfully synthesized and characterized by FTIR, ^{1}H NMR spectroscopy, elemental analysis, and melting temperature measurement. Aggregates of four surfactants formed in aqueous solutions with an apparent hydrodynamic radius (R_h) of ∼100 nm could be assigned as spherical vesicles, while the aggregates with $R_h \approx$10 nm might be

micelles measured by DLS and TEM. The cmc of four surfactants in water evaluated by surface tension measurements was 1 order of magnitude smaller than that of conventional single-chain surfactant SDS. The C_{20} value was 2 orders of magnitude smaller than that of SDS. These results indicate that surfactants 9BA-*m*-9BA have excellent efficiencies of micelle formation and reduced surface tension, which is related to the hydrophobicity and spacer chain length in gemini surfactants.

Furthermore, the surfactants 9BA-*m*-9BA show striking efficiencies in reducing the hexadecane/water interfacial tensions. The hexadecane/water interfacial tension at cmc$_{oil}$ (δ_{cmc}) could be less than 1.0 mN/m after using pure 9BA-*m*-9BA in water. Using 9BA-6-9BA in water, the hexadecane/water interfacial tension was reduced to 0.21 mN/m. In addition, gemini surfactants 9BA-*m*-9BA had good compatibility with hexadecane so that the minimum area occupied by a surfactant molecule at hexadecane/water interface ($a_{min/oil}$) was larger than the minimum area occupied at the air/water interface ($a_{min/air}$) for the same surfactant.

Supporting Information Available: FTIR and ^{1}H NMR spectra of 9BA-*m*-9BA in D$_2$O. This material is available free of charge via the Internet at http://pubs.acs.org.