Surface Activities, Antibacterial Activity and Corrosion Inhibition Properties of Gemini Quaternary Ammonium Surfactants with Amido Group and Carboxylic Counterions

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Abstract: A series of gemini quaternary ammonium surfactants containing carboxylate counterion with the formula $C_{17}H_{35}CONH(CH_2)_2N^+(CH_3)_2(CH_2)_2N^+(CH_3)_2(CH_2)_2NHCO C_{17}H_{35}\cdot 2Y$ ($Y=HCOO^-$, CH_3COO^- , $CH_3CHOHCOO^-$) have been synthesized by a counterion conversion process and characterized by Fourier transform infrared spectroscopy and mass spectroscopy. It is found that these surfactants reduce the surface tension of water to a minimum value of $26.78 \text{ mN}\cdot\text{m}^{-1}$ at a concentration of $1.21 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$. TEM images reveal that aggregates with vesicles or tubular structure are spontaneously formed in these surfactants aqueous solution with the concentration of $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$. It is also found that they are effective corrosion inhibitors for A3 steel in acid solution and have superior antibacterial activity at a concentration of $0.1 \text{ g}\cdot\text{L}^{-1}$.

Key words: gemini quaternary ammonium surfactant, surface activity, antibacterial activity, corrosion inhibition

1 Introduction

Gemini surfactant has two lipophilic tail groups and hydrophilic head groups¹. Due to the unique chemical structure, gemini surfactant tends to form rather rich array of "self-assembled" structures in aqueous solution, including spherical micelle, ellipsoidal micelle, rodlike micelle, layered micelle, linear micelle, a membrane, vesicle, liquid crystals, sponge and other morphologies, and has better performance, such as low critical micelle concentration (CMC), high thermal stability, strong wettability, adhesion ability, and high surface reduction efficiency, etc²⁻⁶. In recent years, cationic gemini surfactants especially gemini quaternary ammonium surfactants, which have shown enormous potential applications in various fields, covering detergents, cosmetics, textile dyeing, biotechnology, the pharmaceutical industry, food industry and the petroleum industry, have attracted wide attention from researchers⁶⁻⁸.

Studies have shown that a gemini surfactant molecule with the requested properties to specific applications is possible to obtain by structure modification, such as changing its component, hydrophobic chain, counterion, spacer group length, spacer group softness and introducing specific functional groups⁹⁻¹³. At present, some studies

have reported the influence of positively charged counterions on surfactants, but the effect of negatively charged organic counterions on quaternary ammonium surfactants has rarely been reported^{14, 15}. In addition, numerous studies have confirmed that the water solubility, biodegradability and the aggregation tendency of the surfactant could be increased by insertion of an amide bond in the surfactant molecule^{16, 17}. Hoque *et al.* also demonstrated that surfactants with amido group had stronger surface activity than common hydrocarbon surfactants by small-angle neutron scattering and conductivity methods¹⁷. So, in this paper, a series of gemini quaternary ammonium surfactants were synthesized by introducing amide functional groups and carboxylic counterions into the molecular structure. The surface properties, corrosion inhibition properties and bacteriostatic activity of them as well as the effect of the counterion were studied. To date, the anions of general gemini quaternary ammonium surfactants are mostly inorganic halogen atoms, which affect their properties and limit their application to a certain extent. The quaternary ammonium gemini surfactant without halogen counterions synthesized by the green chemical reagent dimethyl carbonate in this study meets the requirements of green

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chemistry.

2 Experimental Procedures

2.1 Materials

Methyl stearate, triethylenetetramine and dimethyl carbonate were of analytical grade and purchased from J&K Scientific Ltd. Toluene, sodium hydroxide, formic acid, acetic acid, lactic acid, absolute ethanol, absolute methanol, absolute ethyl ether and acetonitrile were provided by Sinopharm chemical reagent Beijing Co., Ltd. Nutrient broth and benzalkonium chloride solution ($50 \text{ g} \cdot \text{L}^{-1}$) were supplied by Beijing OBO biotech Co., Ltd and Beijing Derun Pharmaceutical Co., Ltd, respectively. *Pseudomonas aeruginosa*, *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis* were obtained from environmental professional laboratory. The high-purity water ($\rho = 18.25 \text{ M}\Omega \cdot \text{cm}^{-1}$) was supplied by an ultrapure laboratory water purification system. N, N, N', N'-tetramethyl-N, N'-di-(2-stearyl-amideethyl)ethylenediamine methyl carbonate (purity > 98%) were prepared according to a green method reported in our previous paper.

2.2 Synthesis of Gemini Surfactants (17-2-17-2Y)

The 17-2-17-2Y gemini surfactants were synthesized according to the method reported in our previous paper^{13, 18}. The general formula and synthesis procedure for the 17-2-17-2Y surfactants were shown in Scheme 1. Their purity was great than 98% and the yield values were 90.5~92.4%. Owing to the carboxylic counterion of the surfactants, the pH values of the following experimental systems (measurement of surface tension, dynamic light scattering and antibacterial activity) are all about 6.

2.3 Confirmation of Structure

Mass spectroscopy (MS) and Fourier transform infrared (FTIR) analysis of the synthesized gemini surfactants were

performed using AB SCIEX API3200 LC/MS spectrometer and Thermo Fisher Nicolet ISLO FTIR spectrometer, respectively.

2.4 Measurement of Surface Tension

At 25°C , the static surface tension of these gemini surfactants aqueous solution within a concentration range of 1×10^{-7} – $1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ was measured on a Dataphysics tensiometer DCAT11 by the Wilhemy plate method.

2.5 Measurement of Dynamic Light Scattering (DLS)

The size distributions of self-assembled aggregate measurements were performed with Malvern Zetasizer Nano ZS instrument at 25°C with a solid state He-Ne laser (output power of 22 mW at $\lambda = 632.8 \text{ nm}$) as a light source. The scanning scattering angle was set as 173° . Each sample with the concentration of $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ equilibrated for 2 min before measurements, and then was measured at least three times. The distribution of diffusion coefficients (D) of the solutes was obtained by analyzing the correlation function of scattering data using CONTIN method. Then the apparent equivalent hydrodynamic radius (R_h) was calculated from Stokes-Einstein equation $R_h = kT/6\pi\eta D$, where k was the Boltzmann constant, T was the absolute temperature, and η was the solvent viscosity.

2.6 Transmission Electron Microscope (TEM)

The TEM sample was prepared as follows: (I) a drop of surfactant aqueous solution with the concentration of $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ was dropped onto the clean sealing film; (II) porous carbon support membrane (260 mesh) was put upside down on the surface of the droplet for 10 min; (III) excess of the droplet was sucked from the edge; (IV) the porous carbon support membrane was dried for at least 12 h in a vacuum dryer; (V) a drop of 1% dioxuranium acetate was added to another clean sealing film, then the adsorbed carbon support membrane was put upside down on it and dyed for 15 s; (VI) the porous carbon support

Scheme 1 Synthesis of 17-2-17-2Y.

membrane was dried for at least 12 h in a vacuum dryer. TEM measurements were made using the Oxford X-MAX JEM-2100 operating at an accelerating voltage of 120 kV by a negative-staining method.

2.7 Antibacterial Activity Measurement

Antibacterial activities of these surfactants were determined by monitoring the growth of Gram-negative bacteria (*Pseudomonas aeruginosa* and *Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus* and *Bacillus Subtilis*) using Finland Bioscreen automatic growth curve instrument. 200 μL bacteria was introduced to the fluid nutrient broth, which was prepared by mixing 1.8 g nutrient broth powder and 100 mL distilled water and was sterilized by autoclave. After cultivating for 12 h with oscillation at 37 $^{\circ}\text{C}$, 200 μL bacterial suspension was taken out and added to the other freshly prepared sterilized fluid nutrient broth, and oscillated continuously for 6 h to completely motivate the bacteria.

The baseline group consisted of 50 μL sterile water and 450 μL blank nutrient. 50 μL benzalkonium chloride solution with a concentration of $1.00\text{ g}\cdot\text{L}^{-1}$ was mixed with 450 μL bacterial solution to set as the control group. The blank group was prepared by mixing 50 μL sterile water with 450 μL bacterial solution. 50 μL surfactants solution with a concentration gradient of 0.50 and $1.00\text{ g}\cdot\text{L}^{-1}$ prepared by sterile water was mixed with 450 μL bacterial solution to prepare the experimental group. The prepared solution was separately placed into the middle part of the 100-well plates and monitored for 24 h with oscillation at 37 $^{\circ}\text{C}$, then the optical density (OD) value at 600 nm was measured every other hour.

2.8 Corrosion inhibition measurements

The corrosion inhibition of these surfactants for A3 steel ($\rho = 7.86\text{ g}\cdot\text{cm}^{-3}$) in 6.00 wt% HCl at 298.15 K was investigated using the weight loss method. A3 steel specimens ($50 \times 25 \times 2\text{ mm}$), which were first wiped clean with filter paper and then degreased by placed in petroleum ether, were soaked in anhydrous ethanol for 5 min and dried with cold wind, and were stored in a desiccator for 1 h. After that, the specimens were accurately weighted to 0.1 mg. Then 3 parallel specimens were immersed in the 6.00 wt% HCl solutions with and without addition of different concentrations of surfactants with stirring at 298.15 K. After 6 h, the specimens were removed, rinsed with water, further soaked in acid pickling liquid for 5 min, rinsed again with water, put into 5.66 wt% NaOH solution for 30 s, rinsed with distilled water, and immersed in ethanol for 5 min. After that, they were taken out, first placed on filter paper to dry in cold air, then in a desiccator to dry for 1 h, at last accurately weighted to 0.1 mg.

Fig. 1 Cationic scanning mass spectra of 17-2-17-2HCOO $^{-}$.

Fig. 2 Anion scanning mass spectra of 17-2-17-2HCOO $^{-}$.

3 Results and Discussion

3.1 Characterization of gemini quaternary ammonium surfactants

The detailed characterization of all the surfactants was done by mass spectroscopy and Fourier transform infrared spectroscopy. The Mass spectra and FTIR spectra of the representative compound 17-2-17-2HCOO $^{-}$ were shown in Figs. 1-3. Spectral characterizations results were as follows. In brief, their structures were confirmed.

17-2-17-2HCOO $^{-}$: Mass Spectra: Cationic scanning M/E : 369.0; Anion scanning M/E : 44.9; FTIR Spectra (KBr, ν , cm^{-1}): 3395.18, 3304.94 (N-H), 2917.89, 2849.85 (C-H), 1647.12 (C=O), 1558.60, 1260.05 (C-N, N-H coupling), 1470.89 (C-H), 1420.32 (COO), 720.97 (C-H).

17-2-17-2CH₃COO $^{-}$: Mass Spectra: Cationic scanning M/E : 369.0; Anion scanning M/E : 58.9; FTIR Spectra (KBr, ν ,

Fig. 3 FTIR spectra of 17-2-17-2HCOO⁻.

cm⁻¹): 3305.39 (N-H), 2919.32, 2850.68 (C-H), 1651.52 (C=O), 1558.54, 1264.12 (C-N, N-H coupling), 1467.92 (C-H), 1420.28 (COO), 721.77 (C-H).

17-2-17-2CH₃CHOHCOO⁻: Mass Spectra: Cationic scanning *M/E*: 369.0; Anion scanning *M/E*: 88.9; FTIR Spectra (KBr, v, cm⁻¹): 3339.03 (N-H), 2923.18, 2853.20 (C-H), 1654.32 (C=O), 1541.31, 1224.48 (C-N, N-H coupling), 1462.72 (C-H), 1373.18 (COO), 1130.42 (-OH), 1031.75 (C-OH).

3.2 Surface activity

In Fig. 4, surface tension (γ) is plotted against the concentration (c) of these surfactant aqueous solutions. The CMC values determined by the inflection point of the γ - c curve and the surface tension at the CMC (γ_{CMC}) acquired by analyzing the plateau region of the plots are summarized in Table 1. As is seen in Table 1, the γ_{CMC} values of these gemini quaternary ammonium surfactants are between 26.78 and 28.12 mN·m⁻¹, suggesting higher surface activities. Table 1 shows that the γ_{CMC} values are in the range of 1.21×10^{-5} to 2.54×10^{-5} mol·L⁻¹, which are lower than some of other gemini surfactants, indicating that these double-chain compounds aggregate more easily to form micelles. In addition, the CMC and γ_{CMC} values of these surfactants increase with the alkyl chain length of carboxylic counterions increase. It is because the hydrophilicity of counterions affects the micellization of the surfactants. The higher the hydrophilicity of counterions, the more unfavorable the micellization is, the higher the CMC will be¹⁹.

Fig. 4 Plots of γ against the concentration (c) of 17-2-17-2Y at 25°C, Y = HCOO⁻ (●), CH₃COO⁻ (▲), CH₃CHOHCOO⁻ (▼).

The maximum surface excess concentration (Γ_{max}) and the minimum area per surfactant molecule (A_{min}) adsorbed at the air-aqueous solution interface, which are listed in Table 1, are calculated according to the Gibbs adsorption equations²⁰:

$$\Gamma_{\text{max}} = \left(\frac{-1}{2.303nRT} \right) \left(\frac{d\gamma}{d \log c} \right) \quad (1)$$

$$A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}} \quad (2)$$

where R is the gas constant, N_A is Avogadro's number, T is the absolute temperature, and n is a constant. For gemini quaternary ammonium surfactants, the value of n , which has no effect on the variation trend of the values of Γ_{max} and A_{min} , is generally determined as 2 or 3^{21, 22}. However, some reports have suggested that it is more appropriate to use a value of 2 for n , because n is 3, the calculated A_{min} is unacceptably large²³. In this case, n is taken as 2. Table 1 shows that these three species of carboxylic counterions have little effect on the values of Γ_{max} and A_{min} . The reason may be that, these short alkyl chain counterions such as formic acid and acetate have strong hydrophilicity and weak hydrophobicity, will not or seldom insert into the surface adsorption layer, thus the surface adsorption parameters of these gemini quaternary ammonium surfactants have little change¹³.

Table 1 Characteristic Parameters of 17-2-17-2Y Aqueous Solutions at 298.15 K.

Gemini surfactant	CMC (mol·L ⁻¹)	γ_{CMC} (mN·m ⁻¹)	Γ_{max} ($\times 10^{-10}$ mol·cm ⁻²)	A_{min} (nm ²)
17-2-17-2HCOO ⁻	1.21×10^{-5}	26.78	2.13	0.78
17-2-17-2CH ₃ COO ⁻	1.44×10^{-5}	27.15	2.29	0.73
17-2-17-2CH ₃ CHOHCOO ⁻	2.54×10^{-5}	28.12	2.02	0.82

Fig. 5 R_h distribution of 17-2-17-2Y, Y = HCOO^- (●), CH_3COO^- (▲), and $\text{CH}_3\text{CHOHCOO}^-$ (▼) in aqueous solution with the concentration of $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

3.3 DLS and TEM measurements

The sizes and distributions of the aggregates formed in these surfactants aqueous solution with the concentration of $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ are investigated by DLS. Seen from Fig. 5, the R_h values of these surfactant solutions are distributed in the range of 40–2000 nm. In addition, at least two hydrated radius distribution peaks were observed in these surfactants solutions, although the first peak of 17-2-17-2 HCOO^- is not obvious. The peak near 100 nanometers may correspond to micro vesicles, and the peak of hun-

dreds of nanometers may be assigned to more complex aggregates, such as multilamellar vesicles, tubular micelle, lamellar micelle, etc. Correspondingly, the morphology of aggregates of these gemini surfactants in aqueous solution with the concentration of $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ have been studied by TEM measurement. The results are shown in Fig. 6.

Figure 6 shows that the size of these aggregates is practically consistent with the results of DLS. The mixed micelles of spheroidal vesicles and longish tubular structure are observed in aqueous solution of 17-2-17-2 HCOO^- (Fig. 6I), the mixture of single-room vesicles and multicenter vesicles (Fig. 6II) are formed in the case of 17-2-17-2 CH_3COO^- , and there mainly exists some longish tubular structure aggregates for 17-2-17-2 $\text{CH}_3\text{CH(OH)COO}^-$ (Fig. 6III). It can draw a conclusion that the counterions have little influence on the self-assembly behavior of these surfactants at a high concentration. The formation of various micelles is mainly due to the self-organization of quaternary ammonium cation driven by entropy. Hydrogen bonds between amide groups near the hydrophilic headgroups region can minimize the repulsive interactions among quaternary ammonium groups, which can further stable the micelles.

3.4 Measurements of antibacterial activity

The bacteriostatic efficiency is calculated according to the following formula:

$$X = \frac{(OD_0 - OD_1)}{OD_0} \times 100\% \quad (3)$$

Fig. 6 TEM micrographs of 17-2-17-2Y, I: Y = HCOO^- , II: CH_3COO^- , and III: $\text{CH}_3\text{CHOHCOO}^-$ in aqueous solution of the concentration of $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

where OD_0 and OD_1 refer to the OD values of the bacillus without surfactants and with surfactants at the same time, respectively. According to our previous work¹³⁾, the values at 15 h are used to evaluate the surfactant inhibition for *Pseudomonas aeruginosa* and *Staphylococcus aureus*, while the values at 10 h and 12 h are used to evaluate for *Escherichia coli* and *Bacillus subtilis*, respectively. The bacteriostatic efficiency of these gemini surfactants solution and 0.1 g·L⁻¹ benzalkonium chloride solution are listed in Table 2. The data presented in Table 2 shows that the antibacterial activities of most of these gemini surfactants with the concentration of 0.05 g·L⁻¹ is better than that of 0.1 g·L⁻¹ benzalkonium chloride solution. At the concentration of 0.1 g·L⁻¹, their bacteriostatic efficiency to Gram-positive and Gram-negative bacteria is more than 85%, indicting excellent bacteriostatic effect. Table 2 also shows that the variation trend of bacteriostatic effect to the same bacteria of ammonium formate, ammonium acetate, and ammonium lactate with the same concentration is gradually decreasing. Sterilization is due to the adsorption and penetration of surfactant molecules at the microbial surface. The counterions wrapped with the positive micelles are diffused manner, gemini surfactants with shorter alkyl chain length of counterions have larger diffusion region and can prevent the bacteria from exchanging substances with the nutrient medium better.

3.5 Corrosion inhibition

Surfactant molecules adsorb on the metals by electrostatic and chemical adsorption to form a protective layer blocking the active corrosion sites, thereby delaying the corrosion of the metal. The following equation is used to calculate the inhibition efficiency η of these gemini surfactants for the corrosion of A3 steel specimen:

$$\eta = \frac{\Delta m_0 - \Delta m_1}{\Delta m_0} \times 100\% \quad (4)$$

where Δm_0 and Δm_1 are the weight loss of the steel speci-

Fig. 7 Plots of inhibition efficiencies against the mass concentration of 17-2-17-2Y (Y = HCOO⁻, CH₃COO⁻, and CH₃CHOHCOO⁻) at 298.15 K.

mens after immersion in solutions without and with inhibitor, respectively. Figure 7 presents the variation of η versus the concentration. Figure 7 shows that η increases with the surfactants concentration increases, and a significant inflection point appears. After the inflection point, η increases slowly and tends to be stable, indicating the surfactant molecules have already formed a saturated adsorption in the steel surface. In addition, at the inflection point, η values of these three surfactants are more than 90%, suggesting they are effective.

Figure 7 also shows that there is a little change in inhibition efficiency of ammonium formate, ammonium acetate, and ammonium lactate. Moreover, their inhibition efficiency is higher than that of 17-2-17-2CH₃COO⁻. Yousefi *et al.* suggested that counterions can form an intermediate bond between the metal surface and the hydrophilic head group to increase the adsorption on the metal surface²⁴⁾. The stronger the hydrophilicity of the counterion is, the stron-

Table 2 The Bacteriostatic Efficiency of 17-2-17-2Y (Y = HCOO⁻, CH₃COO⁻, and CH₃CHOHCOO⁻) at different concentration (g·L⁻¹) at 37°C.

Bacteriostatic efficiency		Gemini surfactant			Benzalkonium chloride
		17-2-17-2HCOO ⁻	17-2-17-2CH ₃ COO ⁻	17-2-17-2CH ₃ CH(OH)COO ⁻	
<i>Pseudomonas aeruginosa</i> (%)	0.05	87.3%	80.8%	73.4%	/
	0.1	91.2%	88.6%	86.0%	76.0%
<i>Escherichia coli</i> (%)	0.05	82.3%	79.3%	81.0%	/
	0.1	92.8%	91.7%	89.7%	74.0%
<i>Staphylococcus aureus</i> (%)	0.05	83.4%	82.5%	80.2%	/
	0.1	94.0%	93.1%	91.8%	79.0%
<i>Bacillus subtilis</i> (%)	0.05	85.6%	81.2%	78.8%	/
	0.1	92.5%	90.9%	88.7%	74.0%

ger the binding force with the hydrophilic head group is, thus forming a better protection. In addition, these surfactants can also react with the corrosive medium to reduce the acidity of the corrosive medium, thereby increasing the corrosion inhibition efficiency.

4 Conclusion

In summary, three gemini quaternary ammonium surfactants with carboxylic counterions are synthesized. Studies have shown that the CMC values of these surfactants are $1.21 \times 10^{-5} \sim 2.54 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, and the γ_{CMC} values are $26.78 \sim 28.12 \text{ mN} \cdot \text{m}^{-1}$, suggesting their higher surface activities. With an increase of the alkyl chain length of the carboxylic counterions, the CMC and γ_{CMC} values of these surfactants increase, and the values of Γ_{max} and A_{min} have little difference. Meanwhile, the DLS and TEM results show that that aggregates with vesicles or tubular structure, the R_h values of which are distributed in the range of 40-2000 nm, are spontaneously formed in these surfactants aqueous solution with the concentration of $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. These gemini surfactants are also found to have superior antibacterial activity at a concentration of $0.1 \text{ g} \cdot \text{L}^{-1}$, and the variation trend of bacteriostatic effect to the same bacteria of ammonium formate, ammonium acetate, and ammonium lactate with the same concentration is gradually decreasing. Furthermore, they are also effective corrosion inhibitors for A3 steel in acid solution.

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