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LETTER TO THE EDITOR

A New Cationic Gemini Surfmer: Synthesis and Surface Activities

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Abstract A new cationic gemini surfmer (polymerizable surfactant or surface-active monomer) with an acrylic reactive group in its spacer group was synthesized and characterized, and its surface activity properties were examined in comparison with its intermediate surfactant 12-3OH-12·2Cl$^-$, a previously-reported gemini surfmer 12′-2-12′·2Br$^-$, as well as monomeric surfactant dodecyl trimethylammonium bromide. It was found that neither the incorporation of a double bond onto the gemini surfactant nor the change of location of the double bond will affect surface activities of the gemini surfactant.

Keywords Gemini surfactant · Surfmer · Cationic surfactant · Surface activity

Introduction

Gemini surfactants are a novel family of amphiphilic compounds made up of two amphiphilic moieties connected at the level of, or very close to the head groups by a spacer group [1], normally referred to as m-s-m·2X$^-$, where m, s are the carbon numbers in each alkyl chain and spacer, X$^-$ represents the counterion. These surfactants usually have superior surface-active behavior over their corresponding monomeric counterparts. Because of their unique properties [2, 3], gemini surfactants find many potential applications, such as catalysis and adsorption applications [4], new synthetic vectors for gene transfection [5], analytical separations [6], solubilization processes [7], biotechnology [8], enhanced oil recovery [9] and paint additives [10], etc.

Polymerizable surfactants or surface-active monomers (surfmers) are a class of vinyl amphiphilic compounds, which can function both as surfactants and monomers [11]. So surfmers could offer potential for developing hybrid nanometer-sized reaction and templating media [11], and have been used in a variety of applications including capturing the structure of spherical micelles and as a stabilizer in emulsion polymerization, miniemulsion polymerization, and microemulsion polymerization [12–14].

Nevertheless, few reports have focused on surfactants with both gemini architecture and a polymerizable group. To the best of our knowledge, only Abe et al. [15] have reported a cationic gemini surfmer 12′-2-12′·2Br$^-$ with the molecular structure $[CH_2=C(CH_3)COO(CH_2)_{11}N^+(CH_3)_2CH_2]_2\cdot 2Br^-$. It was found its surface activity is comparable to its corresponding conventional gemini surfactant 12-2-12·2Br$^-$ which does not have a reactive double bond. Unlike 12′-2-12′·2Br$^-$ whose double bonds are located at the terminal of the hydrophobic tails, a new cationic gemini surfmer with a polymerizable group in the spacer is first reported in this work.

As shown in Scheme 1, the preparation of gemini surfmer 12-3AG-12·2Cl$^-$ (AG denotes an acryloyl group) was followed a two-step procedure: In a three-necked flask, 41.2 g *N,N*-dimethyldodecan-1-amine was mixed with 10 ml hydrochloride (15%, v/v) for at least 0.5 h, and 5 g epoxy chloropropane was then added dropwise. The reaction solution was stirred continuously at 60 °C. After 12 h of reaction, the intermediate gemini surfactant

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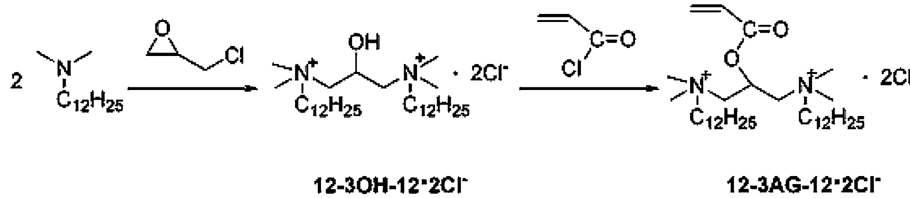
Scheme 1 The route towards synthesis of the cationic gemini surfmer



12-3OH-12·2Cl$^-$ (OH denotes a hydroxyl group) was obtained at an overall conversion of about 90%. ^{1}H NMR (Bruker AMX300 300 MHz, $CDCl_3$, TMS) for 12-3OH-12·2Cl$^-$: δ 0.875 [t, 6H, 2***CH*$_3$**CH_2], 1.178–1.257 [m, 36H, 2CH_3***(CH*$_2$*)*$_9$**CH_2], 2.021 [1H, $(CH_2)_2$CHO***H***], 3.224–3.321 [s, 12H, 4 N$^+$***CH*$_3$**], 3.541–3.622 [t, 4H, 2$CH_3(CH_2)_9$ CH_2***CH*$_2$**N$^+$], 3.754 [m, 4H, (CH_3N$^+$***CH*$_2$**)$_2$CHOH], 5.201 [m, 1H, $(CH_2)_2$***CH***OH]. The mixture of 8.3 g 12-3OH-12·2Cl$^-$, 0.05 g hydroquinone and 30 g chloroform was stirred at 45 °C for 2 h, and 1.5 g acryloyl chloride was then added dropwise to the mixture quickly. After 5 h of reaction, the solvent was evaporated off under reduced pressure. The residue obtained was purified by column chromatography on a silica gel column using chloroform/acetone (2:1, v/v) as a mobile phase. The gemini surfmer 12-3AG-12·2Cl$^-$, was obtained as a white solid (8.3 g, 85% yield, mp 125.7 °C) and ^{1}H NMR ($CDCl_3$, TMS) for 12-3AG-12·2Cl$^-$: δ 0.869 [t, 6H, 2***CH*$_3$**CH_2], 1.184–1.234 [m, 36H, 2CH_3***(CH*$_2$*)*$_9$**CH_2], 3.226–3.328 [s, 12H, 4 N$^+$***CH*$_3$**], 3.552-3.631 [t, 4H, 2$CH_3(CH_2)_9CH_2$***CH*$_2$**N$^+$], 3.774 [m, 4H, (CH_3N$^+$***CH*$_2$**)$_2$CHOCO], 5.011 [m, 1H, $(CH_2)_2$***CH***OCO], 6.102 [t, 1H, OCO***CH*** = CH_2], 6.203-6.311 [t, 2H, OCOCH = ***CH*$_2$**].

Surface tensions of the gemini intermediate 12-3OH-12·2Cl$^-$ and gemini surfmer 12-3AG-12·2Cl$^-$ were measured with the Wilhelmy plate technique using an automatic surface tensiometer (BZY-1, Shanghai Hengping Instrument, China) as described previously [16]. Measurements were taken at 25 ± 0.5 °C until a constant surface tension value was reached. The critical micelle concentration (CMC) values were taken at the intersection of the linear portions of the surface tension plots against the logarithm of the surfactant concentration. Stock solutions of 12-3OH-12·2Cl$^-$ and 12-3AG-12·2Cl$^-$ were diluted continuously with pure water, respectively, and the surface tension at each concentration was obtained by averaging three runs of measurement. For comparison, the surface activity of corresponding monomeric surfactant, dodecyl trimethylammonium bromide (DTAB), was measured under identical conditions. The amount of adsorbed surfactant Γ at the air–water interface was calculated using the Gibbs adsorption isotherm [17]

$$\Gamma = -\frac{1}{nRT} \times \frac{d\gamma}{d\ln C} \quad (1)$$

where R is the gas constant (8.31 J/mol·K), T is the absolute temperature (K), C is the surfactant concentration (mol/l), and dγ/dlnC is the slope below the CMC in the surface-tension plots. The value of n (the number of species at the interface whose concentration at the interface changed with a change in surfactant concentration) was taken as 3 for 12-3OH-12·2Cl$^-$ and 12-3AG-12·2Cl$^-$ because the gemini surfactants here are the divalent-monovalent type [18]. The area occupied by a surfactant molecule at the air/solution interface was obtained from the saturated adsorption as follows:

$$A_{\mathrm{CMC}} = \frac{1}{N\Gamma_{\mathrm{CMC}}} \quad (2)$$

where N is Avogadro's number, and Γ_{CMC} is the maximum surface excess concentration at CMC.

Shown in Fig. 1 are the variations in surface tension of 12-3OH-12·2Cl$^-$, 12-3AG-12·2Cl$^-$ and DTAB against their concentrations in pure water. The surface tension of all the three surfactants decreased with increasing surfactant concentrations and then reached clear break points, which were taken as their CMCs. The alteration in surface tension with surfactant concentration of 12-3AG-12·2Cl$^-$ was similar to that of 12-3OH-12·2Cl$^-$, indicating that the introduction of a double bond onto the skeleton of a gemini surfactant will not affect the surface activity significantly. This is in good agreement with the previous report on gemini surfmer 12′-2-12′·2Br$^-$ whose polymerizable

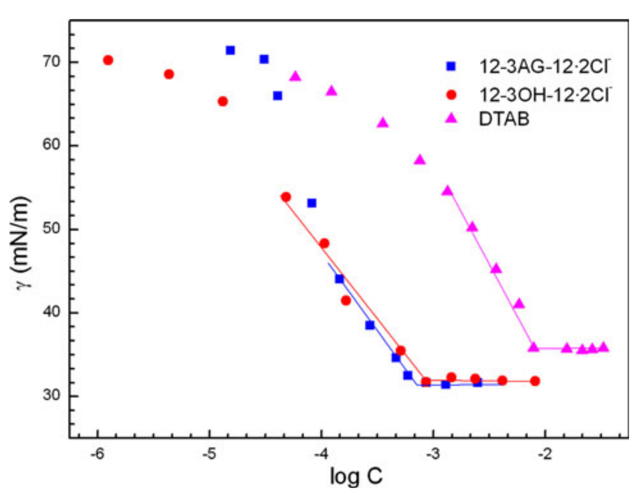


Fig. 1 Variation in surface tension with surfactant concentration for gemini intermediate 12-3OH-12·2Cl$^-$, gemini surfmer 12-3AG-12·2Cl$^-$ and DTAB at 25 °C

Table 1 Surface properties of gemini surfactant investigated 12-3OH-12·2Cl^{-} and other related surfactants at 25 °C

Surfactant	CMC (mol/l)	γ_{CMC} (mN/m)	A_{CMC} (nm^2/molecule)	$10^6\Gamma_{CMC}$ (mol/m^2)	CMC/C_{20}
12-3OH-12·2Cl^{-}	8.4×10^{-4}	32.0	0.364	4.22	24
12-3AG-12·2Cl^{-}	4.6×10^{-4}	31.6	0.451	3.38	25
12'-2-12'·2Br^{-}*	5.0×10^{-4}	32.1	0.22	7.01	30
12-3-12·2Cl^{-}**	1.0×10^{-4}	33.1	0.421	3.26	27
DTAB	2.1×10^{-2}	35.8	0.087	3.46	4.6

* Data reproduced from Ref. [15]

** Data reproduced from Ref. [19]

groups are located at the terminal of the hydrophobic tails, and corresponding gemini surfactant 12-2-12·2Br^{-} [15].

Table 1 compares surface activities in water for gemini surfmers 12-3AG-12·2Cl^{-}, 12′-2-12′·2Br^{-} [15], gemini surfactants 12-3OH-12·2Cl^{-}, 12-3-12·2Cl^{-} [19] and monomeric cationic surfactant DTAB. It is apparent that gemini surfmer 12-3AG-12·2Cl- has a CMC value 2 orders of magnitude smaller than that of DTAB. Moreover, the γ_{CMC} value in water, 31.6 mN/m, of 12-3AG-12·2Cl^{-} is smaller than that (33.8 mN/m) of DTAB. This is in line with previous work showing that the presence of two hydrophobic groups in the gemini molecule leads to greater surface activity [1, 20, 21]. On the other hand, the values of surface activity for the gemini surfactants 12-3OH-12·2Cl^{-}, 12-3AG-12·2Cl^{-}, 12-3-12·2Cl^{-} and 12′-2-12′·2Br^{-} are comparable and similar.

In summary, we successfully synthesized a cationic gemini surfmer 12-3AG-12·2Cl^{-} using *N,N*-dimethyldodecan-1-amine, epoxy chloropropane and acryloyl chloride. Comparing with the monomeric surfactant, 12-3AG-12·2Cl^{-} has the better efficiency and effectiveness in lowering the surface tension in water. Gemini surfmer 12-3AG-12·2Cl^{-} has a similar surface activity as other gemini surfactants. Polymerization of the gemini surfmer is under way.

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