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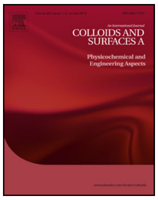

The self-assembly properties of a series of polymerizable cationic gemini surfactants: Effect of the acryloxyl group

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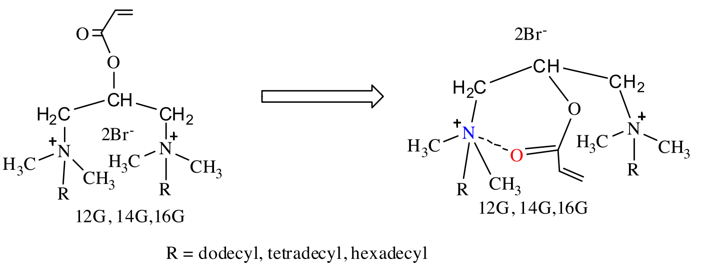
HIGHLIGHTS

- Three gemini surfactants with the acryloxyl group on the spacer were synthesized.
- The acryloxyl group on spacer results in a low critical micelle concentration.
- The aggregates in solution are characteristic of large size and high micropolarity.
- The intramolecular interaction exists in the polymerizable gemini surfactant.

GRAPHICAL ABSTRACT



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ABSTRACT

A new series of polymerizable cationic gemini surfactants bearing acryloxyl group in spacer and a variable alkyl chain length were synthesized and their surface active properties alongside with their self-assembly properties were investigated by surface tension measurement, electrical conductivity, fluorescence and dynamic light scattering (DLS) measurements. As compared to single-chain surfmer, this study shows that the gemini surfmers possess low critical micellar concentration (cmc) value and the surface tension value at cmc (γ_{cmc}). While compared to corresponding gemini surfactant without acryloxyl group, the introduction of the acryloxyl group into spacer results in a lower cmc value, higher degree of ionization and micropolarity of aggregate. The aggregates with large hydrodynamic*radius* (R_h) of 70–110 nm as the main component were observed in the surfmer solution, while the size of aggregate constructed by corresponding gemini surfactant without acryloxyl group is far smaller than the former. All the results can be attributed to the existence of intramolecular dipolar interaction between the carbonyl of acryloxyl group and the cationic nitrogen atom. This increases the hydrophobicity and the regularity of the molecule, which induces the formation of tighter and larger size aggregate in comparison with corresponding gemini without the acryloxyl group on the spacer.

1. Introduction

Polymerizable surfactants have drawn much attention because the polymerizable group in molecular structure results in novel properties distinct from conventional surfactants and various applications [1–4]. In general, the polymerizable groups are vinyl, allyl, or acrylic groups located at the tail of hydrophobic chain or head of hydrophilic group. The type and position of polymerizable groups on the surfactant can bring an effect on the properties. All kinds of polymerizable traditional surfactants, including cationic [5], anionic [6], and nonionic [7,8], have been synthesized to study the influence of the molecular structure on the properties and application.

Only in recent years, polymerizable gemini surfactants have attracted increasing attention for their novel physicochemical properties. The characterization of sodium di (undecenyl)

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tartarate, which was one of monomeric and polymeric gemini surfactants, was tested and found to be used as pseudostationary phases in micellar electrokinetic chromatography [9]. Bis(alkyl-1,3-diene) based phosphonium polymerizable gemini surfactant, as another polymeric gemini surfactant contain vinyl group, was applied to design nanostructures [10]. When the polymerization was occurred, in general, the vinylic groups in the gemini surfactant structure resulted in low conversions and oligomers. So gemini surfmers containing fairly reactive polymerizable groups such as acrylates, were investigated. *N*,*N*,*N*′,*N*′-tetramethyl-*N*,*N*′-bis(11-methacryloyloxyundecyl) ethylenediammonium dibromide, which have relatively high reactive polymeric groups, had been synthesized [11], and its aggregation properties in the condition of added electrolytes have been investigated [12]. The potential applications in stimulus-responsive material and nano-structural template were also reported [13]. Recently, semi-fluorinated gemini surfactants containing acrylic group located in the linkage between the two hydrophilic heads were synthesized to evaluate their surface active properties alongside with their antibacterial and antifungal properties [14]. The study showed that the introduction of a polymeric moiety into the spacer will build up advanced functional materials by polymerization. Our previous research also showed, the polymers built of polymeric gemini surfactant with acrylic group in the spacer exhibited novel self-association behavior and were expected to be functional materials [15]. It should be pointed out that the polymerization behavior and the properties of the polymer were related to the physico-chemical properties and the molecular structure of polymerizable gemini surfactant. However, detailed self-assembly properties of polymerizable gemini surfactant are rarely reported, although the kinds of surfmers with a single alkyl chain and a single polar head have been extensively studied [16,17].

To further understand the effect of the acryloxyl group on the self-assembly properties of polymerizable gemini surfactants, we synthesized a series of novel gemini surfactants with only one polymeric group in the spacer, 1,3-bis (*N*,*N*-dimethyl-*N*-dodecylammonium)-2-propylacrylate dibromide (12G), 1,3-bis(*N*,*N*-dimethyl-*N*-tetradecylammonium)-2-propylacrylate dibromide (14G), 1,3-bis(*N*,*N*-dimethyl-*N*-hexadecylammonium)-2-propylacrylate dibromide (16G). The self-assembly behaviors of the surfmers in aqueous solution were studied by surface tension method, electrical conductivity, dynamic light scattering measurements. For comparison, surface properties of corresponding surfmers with a single alkyl chain, acrylateoxyethyl alkyldimethylammonium bromide (alkyl = dodecyl, tetradecyl, hexadecyl, referred to as 12D, 14D, 16D, respectively) were also investigated. The chemical structures of surfmers and the reference gemini *n*–3–*n* are shown in Fig. 1.

2. Experiment section

2.1. Materials

N,*N*-dimethyldodecylamine, *N*,*N*-dimethyltetradecylamine, and *N*,*N*-dimethylhexadecylamine were purchased from Tokyo Chemical Industry Co., LTD (Japan). Epibromohydrin, acryloyl chloride and organic solvent were obtained from Beijing Chemical Co. and were of analytical grade. Acrylateoxyethyl alkyldimethylammonium bromide was prepared according to the procedure in the literature [18]. Triply distilled water was used in all experiments.

2.2. Synthesis of gemini type surfmers

The typical procedure for the synthesis of 1 3-bis (*N*,*N*-dimethyl-*N*-alkylammonium)-2-hydroxylpropane dibromide (HO-G) is according to the literature [19,20]. The synthesis procedure for the gemini surfmer is: acryloyl chloride (0.1 mol) was added dropwise to a mixture of anhydrous dichloromethane solution (50 mL) of HO-G (0.05 mol) and triethylamine (0.1 mol) under cooling with an ice water bath. The mixture was continuously stirred for 2 days at room temperature, after which it was filtered. The organic layer was subsequently washed with dilute HCl and 3 × 25 mL of 5 wt% $\mathrm{NaHCO_3}$ aq. solution. After dried by anhydrous magnesium sulfate and filtered, the solvent was removed under reduced pressure at room temperature, and the residue was repeatedly recrystallized from acetone/diethyl ether to afford surfmer. Structural confirmation of the surfmers was obtained by nuclear magnetic resonance (NMR). The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV 400 FT-NMR at 25.0 °C.

1,3-Bis(*N*,*N*-dimethyl-*N*-dodecylammonium)-2-proplylacrylate dibromide (12G, white solid, yield: 57.6%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, ppm): δ 0.87 (6*H*, t, –$\mathrm{CH_2}$–$\mathrm{CH_3}$), 1.25–1.34 (36*H*, m, –$\mathrm{(CH_2)_9}$–), 1.72–1.80 (4*H*, m, –N–$\mathrm{CH_2}$–$\mathrm{CH_2}$), 3.42–3.45 (12*H*, d, N–$\mathrm{(CH_3)_2}$), 3.55 (4*H*, m, N–$\mathrm{CH_2}$–), 4.59–4.65 (2*H*, m, N–$\mathrm{CH_2}$–CH), 4.86 (2*H*, d, N–$\mathrm{CH_2}$–CH), 6.17 (1*H*, d, $\mathrm{CH_2}$=CH–), 6.19–6.27(1*H*, d, $\mathrm{CH_2}$=CH–), 6.39 (1*H*, m, O–CH–), 6.89 (1*H*, d, $\mathrm{CH_2}$=CH–). ^{13}C NMR (400 MHz, $\mathrm{CDCl_3}$, ppm): δ 13.16, 22.18, 22.46, 25.74, 28.63, 28.82, 28.88, 28.93, 29.08, 31.40, 51.27, 63.93, 64.01, 67.02, 125.91, 136.39, 164.87.

1,3-Bis(*N*,*N*-dimethyl-*N*-tetradecylammonium)-2-proplylacrylate dibromide (14G, white solid, yield: 57.8%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, ppm): δ 0.87 (6*H*, t, –$\mathrm{CH_2}$–$\mathrm{CH_3}$), 1.24–1.33 (44*H*, m, –$\mathrm{(CH_2)_{11}}$–), 1.79–1.86 (4*H*, m, –N–$\mathrm{CH_2}$–$\mathrm{CH_2}$), 3.42–3.45 (12*H*, d, N–$\mathrm{(CH_3)_2}$), 3.55–3.57 (4*H*, m, N–$\mathrm{CH_2}$–), 4.57–4.66(2*H*, m, N–$\mathrm{CH_2}$–CH), 4.83 (2*H*, d, N–$\mathrm{CH_2}$–CH), 6.17 (1*H*, d, $\mathrm{CH_2}$=CH–), 6.19–6.26(1*H*, d, $\mathrm{CH_2}$=CH–), 6.35 (1*H*, m, O–CH–), 6.89 (1*H*, d, $\mathrm{CH_2}$=CH–). ^{13}C NMR (400 MHz, $\mathrm{CDCl_3}$, ppm): δ 13.22, 22.21, 22.53, 25.81, 28.61, 28.83, 28.88, 28.93, 29.07, 31.50, 51.31, 64.03, 65.07, 67.22, 125.96, 136.49, 164.89.

1,3-Bis(*N*,*N*-dimethyl-*N*-hexadecylammonium)-2-proplylacrylate dibromide (16G, white solid, yield: 55.3%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, ppm): δ 0.87 (6*H*, t, –$\mathrm{CH_2}$–$\mathrm{CH_3}$), 1.23–1.36 (52*H*, m, –$\mathrm{(CH_2)_{13}}$–), 1.74–1.83 (4*H*, m, –N–$\mathrm{CH_2}$–$\mathrm{CH_2}$), 3.42–3.45 (12*H*, d, N–$\mathrm{(CH_3)_2}$), 3.56 (4*H*, m, N–$\mathrm{CH_2}$–), 4.57–4.62(2*H*, m, N–$\mathrm{CH_2}$–CH), 4.84 (2*H*, d, N–$\mathrm{CH_2}$–CH), 6.16 (1*H*, d, $\mathrm{CH_2}$=CH–), 6.19–6.27(1*H*, d, $\mathrm{CH_2}$=CH–), 6.35 (1*H*, m, O–CH–), 6.85–6.90 (1*H*, d, $\mathrm{CH_2}$=CH–). ^{13}C NMR (400 MHz, $\mathrm{CDCl_3}$, ppm): δ 13.36, 22.38, 22.51, 25.77, 28.61, 28.75, 28.83, 28.89, 28.94, 29.11, 31.48, 51.29, 63.97, 64.02, 67.12, 125.92, 136.39, 164.88.

2.3. Surface tension measurement

Surface tension measurements were carried out using the drop volume method. To attain the surface adsorption equilibrium, the drop formation consisted of two steps: first, a pendant drop whose size was about 90 vol% of a falling drop was squeezed out rapidly. Then, it was permitted to stand for enough time until the whole drop was exposed and dropped automatically. Each surface tension value (γ) was determined from at least five measured values. The standard error of the surface tension data was 0.2 mN m^{-1}. The measurement temperature was controlled at 25.0 °C using a thermostat. The critical micelle concentration (cmc) and the surface tension at the cmc were determined from the breakpoint of the surface tension and the logarithm of the concentration curve.

2.4. Electrical conductivity

The conductivity of the surfactant solutions was measured as a function of concentration, using a JENWAY model 4320 conductivity meter. Measurements were performed in a temperature-controlled, double-walled glass container with a