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Synthesis, surface adsorption and micelle formation of a class of morpholinium gemini surfactants

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ABSTRACT

A series of novel gemini surfactants with morpholinium headgroup, 4, 4′-(alkane-4, n-4′)bis(4-decyl, dodecyl or tetradecyl morpholinium)bromide (M_m-n-M_m, m = 10, 12, 14, n = 3, 4), were synthesized and characterized using ^{1}H NMR. The surfactants were investigated for their adsorption and micellization in aqueous solutions through surface tension and conductivity methods It was found that the physicochemical properties, such as surface activity and thermodynamic property of the aqueous surfactant system, were dependent on the lengths of both hydrophobic tail chain and spacer. With the increase of the hydrophobic chain length or the decrease of spacer length, the *cmc* value of the surfactant decreases and the ability to reduce the surface tension is stronger. The calculation result of thermodynamic parameters indicated that the surfactants we synthesized are more inclined to aggregate in solution as compared with traditional *m-s-m* type gemini surfactants, and the micellization of M_m-n-M_m was an entropy-driven process.

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Introduction

Gemini surfactants, known as the "dimers" of identical amphiphilic moieties, are covalently connected by a rigid or flexible spacer group at the level of, or very close to the headgroups, and they have drawn wide attention recently [1–3]. Compared with conventional monomeric surfactants, gemini-type amphiphiles appear to possess more predominant physicochemical properties, such as higher surface activity, remarkably lower cmc and Krafft point, higher solubilization capacity, better wetting, detergency and emulsifying capacity [4,5]. Due to these unique properties, gemini surfactants have great application potential in various fields, such as washing, sterilization, emulsification, dispersion, cosmetics, antibacterial and antifungal preparations, tertiary oil recovery, synthesis of ordered mesoporous materials, etc [6,7].

The cationic gemini surfactants are one of the most widely studied gemini surfactants in recent years [8,9]. Among the cationic gemini surfactants, quaternary ammonium gemini surfactants are used extensively, due to the excellent surface activity and the ability to form complex with negatively charged groups [10]. The persistent endeavor to improve the performance of gemini surfactants has brought about the research upsurge of some novel gemini surfactants, such as heterocyclic gemini surfactants [11]. Heterocycles such as pyrrolidinium [12], imidazolium [13], piperidinium [14] and morpholinium [15], are commonly employed as the hydrophilic headgroups of quaternary ammonium gemini surfactants [16,17]. Compared with the traditional *m-s-m* type gemini surfactants, where *m* and *s* are the numbers of carbon atoms of the hydrophobic alkyl chain and spacer, respectively, gemini surfactants with heterocyclic headgroups have higher surface activities and more abundant aggregation behavior [18,19]. However, among the several categories of the quaternary ammonium gemini surfactants, systematic investigations concerning morpholinium gemini surfactants are less reported [20]. Due to the special ring structure and the existence of oxygen atom in morpholinium, the positive charge distribution of head groups can make a change, which can affect the interaction between the headgroups. On the other hand, the presence of oxygen atom can lead to some weak interactions such

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as hydrogen bonding between the surfactants and water molecules. Therefore, our study bases on the heterocyclic gemini surfactant with oxygen atom, namely morpholinium gemini surfactants [21,22].

As is known to all, the physicochemical properties of gemini surfactants are closely related to their molecular structures, such as the types of head groups, the length of hydrophobic chains and the nature of spacers [23,24]. When the chain length or spacer changes, the solution properties of gemini surfactants will present some differences as well [25,26]. Over the years, the influences of both the hydrophobic chain length and spacer on the properties of surface and bulk phase have been the focus of attention and research [27]. Generally, the influence of hydrophobic alkyl chain length on the surface activity of gemini surfactants resemble the corresponding single-tailed surfactants, while the effect of spacer is much more complicated [18]. Zana has proved that the cmc values of 12-s-12 and 16-s-16 go through a maximum at about $s = 5$ upon the increasing s [28,29], and when the spacer length is shorter than 10, the spacer can locate at the interface in both the lamellar and hexagonal lyotropic phases in solution, and the value of the occupied limiting area per molecule (A_{min}) at the air–water interface increases rapidly as the spacer length grows [30,31].

The micellar thermodynamics and interfacial properties of gemini surfactants are interrelated with the environment ingredients such as temperature, pH, pressure and additives, for instance, cosolvents, cosurfactants and added electrolyte, etc [32,33]. The change of thermodynamic parameter with temperature is one of the hot issues of research in recent years. The cmc value of a surfactant in aqueous solution obtained through the electrical conductivity measurement has been widely used to determine the free energy of micellization of the surfactant [34–36].

In the present work, gemini cationic surfactants with the headgroup of morpholinium were synthesized and characterized. With the objective to determine the different effects on the surface activities, we are motivated to make a simple comparison between the surfactants with different alkyl chain length or spacer length. Meanwhile, to illustrate the influence of the morpholinium headgroups, the physicochemical parameters of the surfactants we obtained were compared with those of the classic *m-s-m* type gemini surfactants. It is of great significance in helping to understand the structure-property relationship of gemini surfactants more comprehensively. This study is also intended to promote the deeper cognition of quaternary ammonium gemini surfactants, and with the constant effort, we noticed that the physicochemical properties of surfactant solution are not only sensitive to the variation of alkyl chain length, but also can be tuned by varying the nature of spacers.

Materials and methods

Materials

Morpholine, 1,3-dibromopropane, 1,4-dibromobutane, 1-bromodecane, 1-bromododecane and 1-bromotetradecane were all purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). All the solvent used in synthesis process, including ethyl acetate, methanol, dichloromethane, acetonitrile, diethyl ether, acetone, were analytical grade. Both the solvent and the reagents were used as received without further purification. Triply distilled deionized water was used in all experiments.

Synthesis

Synthesis of 12 MP (10 MP, 14 MP)

A mixture of morpholine (21.78 g, 0.25 mol) and 1-bromodecane (22.12 g, 0.1 mol), 1-bromododecane (24.92 g, 0.1 mol) or 1-bromotetradecane (27.73 g, 0.1 mol) in 2.5:1 ratio in 100 mL ethyl acetate solvent were added into 500 mL single-necked flask, and the reaction mixture was vigorous stirred for 24 h at the reflux temperature of 60 °C. The end of reaction was determined by thin layer chromatography. After the reaction finished, allowed it to cool to room temperature and the solvent was removed under reduced pressure by rotary evaporation. The crude reaction mixture was then washed twice with 200 mL of deionized water, followed by 100 mL of aqueous methanol (1:1 water: methanol). Thereafter it was extracted by dichloromethane and the solvent was removed under reduced pressure by a rotary flash evaporator to get the linear tertiary amine, 4-decylmorpholinium, 4-dodecylmorpholinium or 4-myristylmorpholinium (abbreviated as 10 MP, 12 MP and 14 MP, respectively) in 85–90% isolated yield.

Synthesis of M_{12}-3-M_{12} (M_{10}-4-M_{10}, M_{12}-4-M_{12}, M_{14}-4-M_{14})

A mixture of the intermediates 10 MP (20.68 g, 0.091 mol), 12 MP (22.99 g, 0.09 mol) or 14 MP (25.52 g, 0.095 mol) and 1,4-dibromobutane (8.64 g, 0.04 mol) or 1,3-dibromopropane (8.08 g, 0.04 mol) in 2.25:1 ratio in 100 mL acetonitrile solvent were added into 500 mL single-necked flask, then the reaction mixture was vigorous stirred for 24 h at the reflux temperature of 95 °C. The end of reaction was determined by thin layer chromatography. After the acetonitrile solvent was removed by rotary evaporation, the crude product obtained was subsequently washed twice with 100 mL of diethyl ether, and then purified by recrystallization in fresh acetone at least three times. The precipitates after removal of acetone through vacuum filtration were dried in vacuum drying oven for 48 h, which give pure corresponding gemini surfactants, 4,4′-(alkane-4, n-4′)bis(4-decyl, dodecyl or tetradecyl morpholinium)bromide (M_m-n-M_m, m = 10, 12, 14, n = 3, 4) in 45–50% isolated yield. The purity and accuracy of the final product was ascertained by the ^{1}H NMR spectrum in DMSO. Besides, the elemental analysis method was employed to determine the synthesis of M_{12}-3-M_{12} (As shown in Table S1).

^{1}H NMR measurement

^{1}H NMR spectra were recorded on a MP-400 nuclear magnetic resonance spectrometer (Varian Company, US) at a proton resonance frequency of 400.15 MHz. The spectra were determined in *deuterium oxide* and *deuterochloroform* (containing TMS as an internal reference).

Morpholinium gemini surfactants have been prepared through the methods mentioned in Scheme 1. The structure of the intermediate 12 MP and the desired products are determined through ^{1}H NMR measurement (As shown in Fig. S1).

Surface tension measurements

The surface tension was carried out on DCAT 21 surface tensiometer (dataphysics instruments GmbH, Germany) using the plate method in single-measurement way. Surfactant solutions were kept for 24 h at the temperature of 25 °C to equilibrate. All the subsequent measurements were performed at 25 °C and repeated at least three times until the results were reproducible.

Electric conductivity measurements

A low-frequency conductivity analyzer (model DDS-307, Shanghai Precision & Scientific Instrument Co., Ltd., accuracy ± 1%) was used to measure the electrical conductivities of the solutions at 25 °C, 30 °C, 35 °C, 40 °C, 45 °C. Surfactant solutions at different concentrations were measured at least three times until the errors were below 0.2 μs/cm, and all the surfactant solutions were kept for 48 h to equilibrate before the measurements. When