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Equilibrium and dynamic surface tension properties of Gemini quaternary ammonium salt surfactants with hydroxyl

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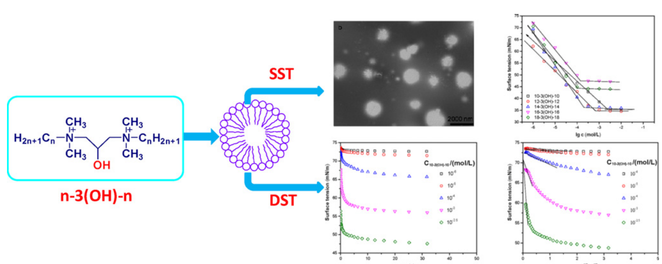
HIGHLIGHTS

- Five gemini surfactants *n*-3(OH)-n (n = 10, 12, 14, 16, 18) were synthesized.
- The cmc fell around by half with each additional 2 in n.
- Sizes of 18-3(OH)-18 vesicles were much larger than the conventional ones.
- D_S, D_L decrease with increased concentration with constant n.

GRAPHICAL ABSTRACT



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ABSTRACT

Five quaternary ammonium salt Gemini surfactants 2-hydroxyl-propanediyl-α,ω-bis (alkyldodecyl ammonium chloride) (*n*-3(OH)-n, where n represents hydrocarbon chain lengths of 10, 12, 14, 16, and 18) were synthesized and characterized by ^{1}H NMR. Surface activity, adsorption and aggregation behaviors of these cationic Gemini surfactants were investigated by methods of measuring equilibrium surface tension, dynamic surface tension and transmission electron microscope (TEM). The critical micelle concentration (CMC) decreased with an increase in hydrophobic chain length, while the surface tension at the CMC (γ_{CMC}) showed little change. With TEM measurements, formations of vesicles in *n*-3(OH)-n (n = 16, 18) solutions occurred and vesicles dimensions depended on their n values. Moreover, data obtained were analyzed in accordance with Word-Tordai equation, and the diffusion coefficients for ionic liquid molecular adsorption in the initial stage and final stage under different concentration were figured out respectively. The results indicated that the adsorption process was controlled by a diffusion step at low surfactant concentration while by a mixed kinetic-diffusion adsorption mechanism at high surfactant concentration.

1. Introduction

Gemini surfactants containing two hydrophobic chains and two hydrophilic groups in one molecule have attracted more and more attention. The spacer group is a unique component in Gemini surfactant molecule, which strongly tightens the connection and reduces the electrostatic repulsion between the hydrophilic groups. Thus it is more probably for the alkly chain to generate stronger hydrophobic force. Those combined is the root cause of spacer group's superior properties in comparision with traditional single-headgroup and single-alkyl chain surfactants. Given this, it is possible to obtain different functional Gemini surfactants through changing its component, hydrophobic chain, spacer

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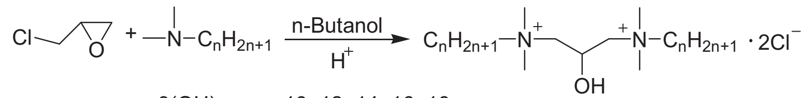

Scheme 1. Synthetic Routes of *n*-3(OH)-n (n = 10, 12, 14, 16 and 18).

group length, spacer group softness and introducing specific functional groups depending on factual need. Those changes of factors enrich structure of and add superior function to Gemini surfactants. Introducing hydroxyl into traditional Gemini surfactants could effectively enhance its aggregation ability, promote the viscoelastic wormlike micellar systems growth and enhance the system's viscoelasticity. Rosen and Liu, found that Geminis with a flexible, hydrophilic spacer appear to aggregate more readily than Geminis with a rigid, hydrophobic space. Their shorter homologs are also more surface active exhibited better surface active properties than those having a rigid, hydrophobic spacer [1,2]; Wei et al., researched the transforamtion performance of crystalline structure and mesomorphic properties of Gemini diammonium surfactants with a pendant hydroxyl group, the results showed that the unique crystal structure and mesomorphic properties could be attributed to the presence of a pendant hydroxyl group in the spacer, which may induce hydrogen bonding interactions and therefore promote the formation of the mesophase [3,4]; Pei et al., investigated the self-assembly of Gemini surfactants containing one hydroxyl substituted methylene spacer in aqueous solution. The study indicated that Gemini surfactant with a hydroxyl group could promote the growth of micelles compared with those without hydroxyl group [5]. Current research on Gemini surfactant containing hydroxyl concentrates on self-assembly and few covers the dynamic surface adsorption properties of the surfactant aqueous solution. Moreover, the research objects are mainly single structure sufactants a [6], which is against the research in the effect of hydrophobic chains and spacer group on properties and application.

Surfactants could change interface property significantly and adsorb onto the interface results in decreased surface tension, which is the foundation for its widespread application in commodity chemicals, agrochemicals, oil exploration and food processing [7]. The formation of fresh interface is a dynamic process, properties of equilibrium and dynamic adsorption in the process of Gemini surfactants' transfering to the interface influence the function of surfactants. The spreading of pesticides, the formation of foam, the formation of emulsion and other rapid adsorption processes have been completed before surfactants adsorption reached equilibrium. For example, research on dynamic surface tension of emulsifier is necessary in order to satisfy the pesticide's demand of spreading on the leaf surface speedily [8]. The oil displacement system with low dynamic interfacial tension in tertiary recovery could improve oil recovery because of the instantaneous contact between oil displacement system in capillary channel of the oil layer and crude oil [9]. In mineral extraction, the measure of froth flotation is also associated with the dynamic adsorption of surfactant [10]. Therefore, it can be predicted that further understanding of dynamic surface tension (DST) and the adsorption mechanism will contribute to the applications of surfactants in related frontiers.

In this article, a series of Gemini quaternary ammonium salt surfactant 2-hydroxyl-propanediyl-α,β-bis(alkyl dimethyl ammonium chloride)(abbreviated as *n*-3(OH)-n, where n represents hydrocarbon chain lengths of 10, 12, 14, 16, and 18) was synthesized according to the methods reported by Lu et al. [11] and their structure were characterized. Scheme 1 shows the synthesis route of Gemini surfactants *n*-3(OH)-n. Their properties were investigated by methods of measuring equilibrium surface tension, dynamic surface tension and transmission electron microscope (TEM).

2. Experimental

2.1. Materials

The chemicals *N*,*N*-dimethyldecylamine (93%, TCI, Japan), *N*,*N*-dimethyldodecylamine (97%, Sahn, China), *N*,*N*-dimethyltetradecylamine (90%, Sahn, China), and hexadecyldimethylamine (97%, Sahn, China), *N*,*N*-dimethyloctodecylamine (AR, Aladdin, China), epichlorohydrin. (AR, Aladdin, China), acetone (AR, Aladdin, China) and deuterochloroform (AR, Aladdin, China) were used as received. All other reagents and solvents uesd were of the analytical grade. Double distilled water was used throughout these studies.

2.2. Synthesis

Add hydrochloric acid to a stirred solution of *N*,*N*-(dimethylalkyl)amine($R(CH_3)_2N$, $R = C_nH_{2n+1}$, n = 10, 12, 14, 16, 18) (0.08 mol) in *n*-butanol (40 mL), wait until the white smoke disperses, add epichlorohydrin (0.04 mol) to the solution, heat the mixture to reflux and carry out the reaction for 8 h. After the solvent is evaporated under reduced pressure, the residue is recrystallized thrice from acetone and dried under reduced pressure. These Gemini surfactants with hydroxyl are finally obtained as white powder, the yield were 42, 39, 65, 74, and 77% for n = 10, 12, 14, 16, and 18, respectively.

2.3. ^{1}H NMR measurements

All the products are characterized using ^{1}H NMR spectra (Bruker ADVANCE 600 spectrometer) in $CDCl_3$, the final results of the analysis were listed in Table 1.

2.4. Surface tension measurements

The surface tension of the aqueous solution of the Gemini surfactant were measured with a Power Each JK99C tensiometer by the Wilhelmy plate technique. The dynamic surface tension was measured using a Kruss BP100 bubble-pressure tensiometer, necessary to blow a bubble in a liquid from the tip of a capillary. The measurements were conducted with effective surface ages ranging from 5 ms to 30 s.

2.5. Transmission electron microscopy measurements

Structures of surfactant aggregates in solutions were studied using JEOL JEM-1011 transmission electron microscopy. In addition, all of the surfactant solutions were freshly prepared in doubly distilled water, and all of the measurements were performed at 25 °C.

3. Results and discussion

3.1. Equilibrium surface tension

Static surface tension was measured to evaluate the surface activity of Gemini surfactants. In Fig. 1, surface tension was plotted against the concentration of *n*-3(OH)-n (n = 10, 12, 14, 16 and 18) aqueous solutions. The CMC and surface tension values at the