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Research Paper

# Sulfonic gemini surfactants: Synthesis, properties and applications as novel air entraining agents for concrete

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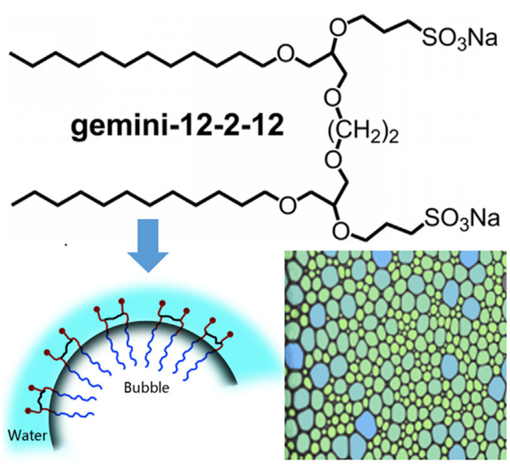
## HIGHLIGHTS

- Six sulfonic gemini surfactants with different structures were synthesized.
- They have higher surface activity, foamability and foam stability compared with their single-chained analogue.
- They were utilized as the air entraining agents for concrete for the first time.
- They show higher air entraining performance compared with their single-chained analogue.
- Our studies can help to explore ideal synthetic surfactants for the development of novel air entraining agents.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The development of high performance air entraining agents for concrete is of great importance. In this work, sulfonic gemini surfactants have been utilized as high performance air entraining agents for the first time. Six sulfonic gemini surfactants with different hydrophobic chains and spacer groups were designed and synthesized. The surface tensions and foam properties of their aqueous solutions were tested. Using them as the air entraining agents, the air contents and air-void parameters of the cement mortars were also tested. The properties of different geminis and their single-chained analogue were fully compared and discussed. The results show that the geminis have higher surface activity, foamability, foam stability and air entraining performance compared with their single-chained analogue, and the gemini with 12-carbon hydrophobic chains and 2-carbon alkyl spacer has highest performance.



## 1. Introduction

Surfactants are the compounds which can reduce the surface tension (or interfacial tension) of water by adsorbing at the water-air interface (or water-oil interface) [1–4]. They are usu-

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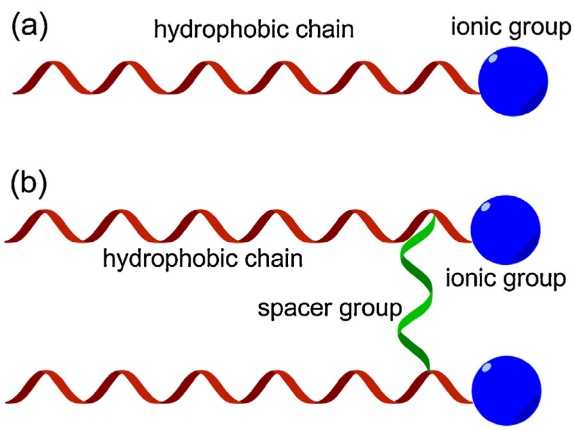



**Scheme 1.** Structures of (**a**) single-chained and (**b**) gemini surfactants.

ally organic amphiphilic compounds that contain both hydrophobic and hydrophilic groups [5–7]. In aqueous solutions, surfactants have a strong tendency to aggregate and arrange at the water-air interface (air bubble surface) via hydrophobic interactions, which could lower the surface tension then improve the foamability of the solution [8–12]. However, the traditional used surfactants are mainly single-chained compounds consisting of a hydrophobic chain and an ionic group. The electrostatic repulsion between the ionic groups of single-chained surfactants diminish their tendency to aggregate and arrange in a close and order manner, thus restrict their surface activity.

In recent years, gemini surfactants have drawn more and more attention due to their unique qualities, such as low critical micell concentration (CMC), high surface activity, and diverse aggregate structures [13–16]. From their molecular structure, gemini surfactants can be considered as dimers of classical single-chained surfactant fragments, which are coupled by a spacer group near their ionic groups (Scheme 1) [17–23]. Since two ionic groups of gemini sufactants are covalently linked, the electrostatic repulsion between the ionic groups is greatly neutralized, and the distance between two hydrophobic chains is significantly shortened. As a result, gemini sufactants can aggregate and arrange at the water-air interface (air bubble surface) more closely and orderly, and higher surface activity, foamablity and foam stability can be obtained [24–27].

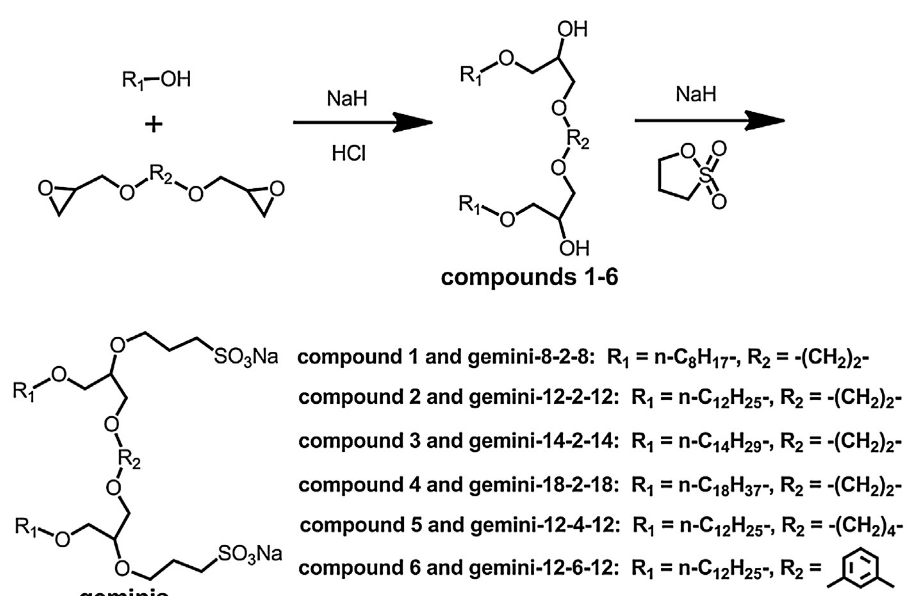
Air entrainment has been regarded to be highly desirable for concrete since the 1930s [28–30]. Entraining homogeneous, tiny and stable air voids in fresh concrete can effectively improve both workability and freeze-thaw durability of concrete [29,31,32]. Air entraining agents are important concrete admixtures that can help to intentionally create a number of air voids in concrete. Therefore, the development of high performance air entraining agents for concrete is of great importance. Some natural chemicals have been widely used as air entraining agents, such as vinsol resin and saponin [33–35]. In recent years, more and more synthetic single-chained surfactants, such as sulfonated hydrocarbons and alkyl-aryl ethoxylate compounds, have been introduced [29,30,36]. We envision that the synthetic surfacants having excellent surface activity, foamablity and foam stability may also have high air entraining performance for concrete, which could be potentially utilized as novel air entraining agents.

In this work, we report for the first time the applications of sulfonic gemini surfactants in the air entraining agents for concrete. Six sulfonic modified gemini surfactants with different structure (hydrophobic chains and spacer groups) were designed and successfully synthesized (Scheme 2). The surface tensions and foam properties of their aqueous solutions were tested. Using them as the air entraining agents, the air contents and air-void parameters of the cement mortars were also tested. The properties of different geminis and their single-chained analogue were fully compared and discussed. The results clearly show that the gemini surfactants have higher surface activity, foamability, foam stability and air entraining performance compared with their single-chained analogue, and the gemini with 12-carbon hydrophobic chains and 2-carbon alkyl spacer has highest performance.

## 2. Experimental section

### 2.1. Instruments

$^1$H NMR spectra were obtained with a Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer with chemical shifts reported in parts per million (ppm) relative to tetramethylsilane. Elemental analysis results were carried out on a LECO 932




**Scheme 2.** Synthetic routes for the sulfonic gemini surfactants.