



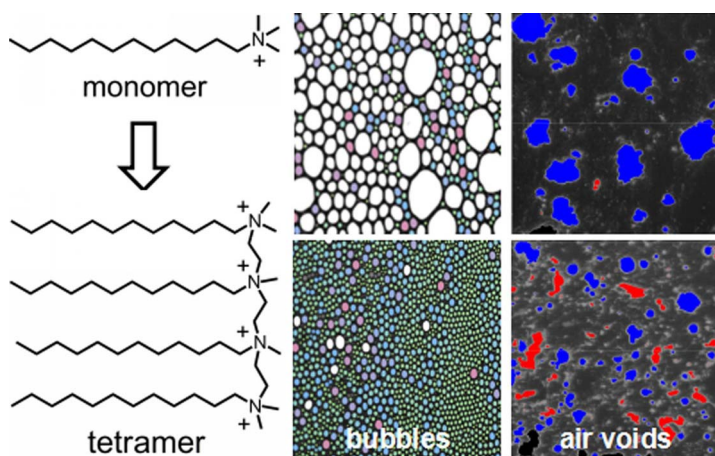
Cationic oligomeric surfactants as novel air entraining agents for concrete

Jian Chen^{a,1}, Min Qiao^{a,b,1}, Nanxiao Gao^a, Qianping Ran^{a,*}, Jingzhi Wu^a, Guangcheng Shan^a, Shuai Qi^a, Shishan Wu^{b,*}

^a State Key Laboratory of High Performance Civil Engineering Materials, Jiangsu Sobute New Materials Co. Ltd., Nanjing 211103, PR China

^b School of Chemistry and Chemical Engineering, Nanjing University, Xianlin Campus, 163 Xianlin Avenue, Qixia District, Nanjing 210023, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we report for the first time the applications of cationic oligomeric surfactants as novel air entraining agents for concrete. A series of oligomeric surfactants with the oligomerization degrees from 2 to 4 was synthesized. Using them as the air entraining agents, the surface activity and foaming properties were tested in both water and cement filtrate. The air contents and air-void parameters were also tested in both cement mortars and concretes. The results show that the oligomeric surfactants have higher performance compared with their monomeric analogue and traditional air entraining agents, and the surfactant with higher oligomerization degree has higher performance. The surfactants are also beneficial for the durability of concrete, and could only affect the strength of concrete slightly. Our studies indicate great potential of the oligomeric surfactants for practical applications.

1. Introduction

Surfactants are a unique class of surface active compounds which

have a tendency to concentrate at the water-air interface and lower the surface tension of water [1–4]. The surfactants with various structures have been developed because of their widespread importance in

* Corresponding authors.

E-mail addresses: qpran@cnjsjk.cn (Q. Ran), shishanwu@nju.edu.cn (S. Wu).

¹ These authors contributed equally to this work.

practical applications [5–7]. The traditional surfactants are mainly single-chained (monomeric) amphiphilic compounds consisting of one hydrophobic chain and one ionic group [8–10]. They can adsorb and assemble at the water–air interface via the hydrophobic interactions between the hydrophobic chains of the surfactant molecules [11–13]. However, the electrostatic repulsion between the ionic groups greatly diminish their tendency to assemble in a compact and order manner, which restrict their surface activity. Therefore, the development of a new class of surfactants with higher surface activity is highly desirable.

Gemini surfactants are newly developed compounds which have drawn more attention [14–17]. They can be seen as dimers of traditional monomeric surfactant fragments, which are linked by a spacer group near their ionic groups [18–24]. Since two ionic groups of surfactant molecules are covalently coupled, the electrostatic repulsion between two ionic groups is effectively neutralized, and the distance between two hydrophobic chains is greatly shortened. As a result, gemini surfactants assemble at the water–air interface more compactly and orderly, and some unique properties including lower critical micelle concentration (CMC), higher surface activity and higher foaming ability are observed [25–28]. Extending these observations, the analogues with higher oligomerization degrees (multiple hydrophobic chains and ionic groups), such as trimers and tetramers, have also been developed. They have become attractive as a new class of surfactants, which are all so-called “oligomeric surfactants” [29–37].

Since the air entrained concrete was developed in the mid-1930s, air entraining agents have been regarded to be highly beneficial for both workability and freeze–thaw durability of concrete [38–42]. It was observed that the effective size of the air voids in both fresh and hardened concrete may be smaller than 200 μm [41,43]. The development of high performance air entraining agents which can induce more small air voids in concrete is thus of great importance. A number of surfactants have been used as air entraining agents due to their good foaming ability. Some natural surfactants were selected in the early time, such as vinsol resin and saponin [44–46]. In recent years, more and more synthetic surfactants, such as sulfonated hydrocarbons and alkyl-aryl ethoxylate materials, have also been used [39,40,47]. Most of the chemicals used in the industry are anionic monomeric surfactants. Compared with them, cationic surfactants show higher saline-alkaline tolerance and oligomeric surfactants show higher foaming ability. However, the applications of cationic oligomeric surfactants as the air entraining agents for concrete have not been reported.

In our previous studies, we reported the applications of anionic gemini (dimeric) surfactants as the air entraining agents for concrete, which showed that the gemini surfactants had better air entraining performance compared with traditional monomeric surfactants [48,49]. In this work, cationic oligomeric surfactants were utilized as novel air entraining agents for the first time. A series of cationic oligomeric surfactants with different oligomerization degrees (dimer, trimer and tetramer) was synthesized and compared. The surface activity and foaming properties of them were tested in aqueous solutions. Using them as the air entraining agents, the air contents and air-void parameters were also tested in both cement mortars and concretes. The results clearly indicate that the oligomeric surfactants have higher surface activity, foaming ability, foam stability and air entraining performance compared with their monomeric analogue, and the surfactant with higher oligomerization degree has higher performance.

2. Experimental section

2.1. Instruments

Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker AVANCE 400 Fourier transform NMR spectrometer (400 MHz, Bruker, USA) with chemical shifts reported in parts per million (ppm) relative to tetramethylsilane, D_2O was used as the solvent. Elemental analysis results were obtained with a LECO 932 CHNS elemental

analyzer (LECO, USA). Surface tension results were obtained with a Krüss K100 surface tensionmeter (Krüss, Germany). Foam heights, bubble counts/areas, bubble images and bubble size distributions were obtained with a Krüss DFA100 dynamic foam analyzer (Krüss, Germany). Air contents of fresh cement mortars and concretes were obtained with a SANYO direct reading air content tester (SANYO, Japan). Air contents, air-void parameters, air-void images and air-void size distributions of hardened cement mortars and concretes were obtained with a MIC-840-01 hardened concrete pore structure analyzer (CHUO SEIKI, Japan). Relative dynamic elastic moduli and mass loss rates of hardened concretes were obtained with a CDR6-9 concrete rapid freeze–thaw test equipment (Yanke, China). Dielectric fluxes of hardened concretes were obtained with a NEL-PEU concrete dielectric flux test instrument (NELD, China). Compressive strengths of hardened concretes were obtained with a YAW-3000A pressure testing machine (SUNS, China). For each test, three same samples were prepared and measured, then the average value was calculated. All the tests showed good replicates.

2.2. Materials

N,N,N-trimethyl-1-dodecanaminium bromide (compound 1) was purchased from J&K Chemical Co. (China). All other chemicals were purchased from Aladdin, Energy, and TCI Chemical Co. (China) and used as received. Organic solvents were of analytical grade. PII52.5 Portland cement was purchased from Jiangnan-xiaoyetian Cement Co., Ltd., Nanjing, China. Cement filtrate was prepared from the mixture of cement and water with the weight ratio of 1:2, which was stirred for 30 min and then filtrated (the concentrations of Na^+ , K^+ and Ca^{2+} were tested to be 26, 1411 and 1334 mg/L). The fine aggregate in the tested samples was the river sand with a nominal grain size of 0.5–1.5 mm. Polycarboxylate superplasticizer was obtained from Jiangsu Sobute New Materials Co., Ltd., Nanjing, China.

2.3. Synthesis of the oligomeric surfactants [29,35,36]

Synthesis of compound 2: 1-Bromododecane (5.48 g, 22 mmol) and *N,N,N,N'*-tetramethylethylenediamine (1.16 g, 10 mmol) were dissolved in THF (30 mL). The mixture was stirred and refluxed for 2 days. After cooling to room temperature, the resulting precipitate was filtered and washed with acetone. After recrystallization with acetone and drying under vacuum, compound 2 was obtained as a white powder (4.81 g, 78.3%). ^1H NMR (400 MHz, D_2O): δ (ppm) = 3.48 (s, 4H), 3.15 (s, 12H), 2.93 (t, 4H), 1.68 (s, 4H), 1.23 (s, 36H), 0.81 (t, 6H). Elemental analysis: calculated for $\text{C}_{30}\text{H}_{66}\text{Br}_2\text{N}_2$ (%), C 58.62, H 10.82, N 4.56; found, C 58.44, H 10.98, S 4.79.

Synthesis of compound 3: 1-Bromododecane (8.22 g, 33 mmol) and 1,1,4,7,7-pentamethyldiethylenetriamine (1.70 g, 10 mmol) were dissolved in THF (40 mL). The mixture was stirred and refluxed for 3 days. After cooling to room temperature, the resulting precipitate was filtered and washed with acetone. After recrystallization with acetone and drying under vacuum, compound 3 was obtained as a white powder (6.47 g, 70.5%). ^1H NMR (400 MHz, D_2O): δ (ppm) = 3.47 (s, 8H), 3.12 (s, 15H), 2.92 (t, 6H), 1.69 (s, 6H), 1.21 (s, 54H), 0.80 (t, 9H). Elemental analysis: calculated for $\text{C}_{45}\text{H}_{98}\text{Br}_3\text{N}_3$ (%), C 58.68, H 10.73, N 4.56; found, C 58.63, H 10.69, S 4.63.

Synthesis of compound 4: 1-Bromododecane (10.97 g, 44 mmol) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (2.30 g, 10 mmol) were dissolved in THF (50 mL). The mixture was stirred and refluxed for 6 days. After cooling to room temperature, the resulting precipitate was filtered and washed with acetone. After recrystallization with acetone and drying under vacuum, compound 4 was obtained as a light yellow solid (7.76 g, 63.2%). ^1H NMR (400 MHz, D_2O): δ (ppm) = 3.45 (s, 12H), 3.12 (s, 18H), 2.91 (t, 8H), 1.69 (s, 8H), 1.22 (s, 72H), 0.82 (t, 12H). Elemental analysis: calculated for $\text{C}_{60}\text{H}_{130}\text{Br}_4\text{N}_4$ (%), C 58.72, H 10.68, N 4.56; found, C 58.79, H 10.63, S 4.53.

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