Preparation and Performance of A Novel Type of Concrete Air Entraining Agent

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Abstract. This article uses 1,4-dibromobutane, hexadecyl primary amine, sodium 3-chloro-2-hydroxypropionate, formaldehyde and formic acid as raw materials to synthesize a new type of concrete air entraining agent of (1,4)-bis(cetylmethyl hydroxy-propionic acid quaternary ammonium salt) butane through the reaction of ammonia alkylation and quaternization. The article characterizes the molecular architecture of the product, the surface activity of the aqueous solution, the bubble properties, the air entraining and air stabilizing properties of the fresh concrete, and the pore structure of the concrete after hardening. The research results show that the synthesized (1,4)-bis(cetylmethyl hydroxy-propionic acid quaternary ammonium salt) butane has good surface activity in aqueous solution, and its critical micelle concentration (cmc) is $5.3 \times 10^{-4}$ mmol/L, $\gamma_{\text{cmc}}$ is 28.86 mN/m; (1,4)-bis(cetylmethyl hydroxy-propionic acid quaternary ammonium salt) butane has better air-entraining performance and bubble stability in aqueous solution and concrete than SDS and AOS air entraining agents. The average chord length and spacing coefficient of bubbles in hardened concrete are smaller than that of SDS and AOS air entraining agent, giving rise to a better overall pore structure of the concrete. Compared with SDS and AOS, the concrete mixed with (1,4)-bis(cetylmethyl hydroxy-propionic acid quaternary ammonium salt) butane air entraining agent shows better mechanical property and durability.

1. Introduction

Freeze-thaw damages lead to premature cracking of concrete, a major factor that often seriously damage the service life of concrete and becomes one of the main reasons affects the durability of concrete. Addition of air entraining agent (AEA) to resist freeze-thaw is one of the most widely used technical approaches at present to improve the frost resistance and durability of concrete, where such practices are commonly performed in North America, Northern Europe, Japan and China. The mechanism is through the formation of large number of tiny pores in the hardened concrete, which act as "pressure relief tanks." When excess water freezes, the ice expands and enters the air spaces, avoiding damages to the concrete. In addition, the introduction of air bubbles into fresh concrete can also improve the initial state of fresh concrete, increasing the workability and reducing the risk of concrete segregation and bleeding. The air bubbles in concrete must remain stable in order to remain in fresh concrete for rheological benefits and to maintain the minimum amount of pores in solidified concrete. It has been reported that ensuring the appropriate number, spacing and distribution of micro bubbles in concrete has a significant impact on the mechanical properties of concrete, and is crucial to solve the problem of freeze-thaw cycle failure[1-2]. The essential reason why it is difficult for concrete to entrain air is due
to the incompatibility of AEAs in concrete, thus it is particularly important to choose the appropriate AEA.

AEA belongs to the class of surfactant. It is added to concrete and mortar to improve their workability, prevent bleeding, heat insulation, sound resistance and improve frost resistance [3-6]. One of the best classification method is to divide them by their charges, i.e. anionic, cationic and amphoteric type surfactants. The anionic AEA ionizes in the aqueous solution, dissociates the metal cation and forms anionic moiety in solution. In the field of concrete, anionic AEA has been widely used because of its relatively cheap price as this class constitutes largely fatty alcohol sulfonate based and pine soap based AEAs. However, the ionic groups of the anionic surfactant undergo electrostatic attraction with free calcium ions in the concrete, leading to a reduction in the air entraining efficiency. Cationic surfactant is primarily nitrogenous organic amine derivatives. Nitrogen atoms in the molecules contain lone pair of electrons that can undergo H-bonding with the acid, generating positively charged amino groups. In alkaline systems such as concrete with a pH value between 12 to 13, precipitation occurs resulting in a severe loss in surface activity of the surfactant, thus such cationic surfactants are rarely used in concrete as AEAs. Amphoteric AEAs contains both cationic and anionic groups, resulting in good acid and alkaline resistance, good wettability and foaming ability, and is known to produce synergistic effect with other surfactants [7-9]. While amphoteric AEAs can solve the sensitivity problem of anionic engrants, they have little effect on the stability of bubbles in the slurry.

This paper thus target to create a new type of AEA by exploiting the sweet spot. By using 1,4-dibromobutane, hexadecyl primary amine, sodium 3-chloro-2-hydroxypropane sulfonate, formaldehyde and formic acid as raw materials, (1,4)-bis(cetymethyl hydroxy-propionic acid quaternary ammonium salt) butane gemini type air entraining agent was synthezised. Its surface activity in aqueous solution and in the mortar and the effect of air bubbles in fresh and hardened concrete are investigated. Finally, the novel AEA is compared against different AEAs, and their effect on the mechanical properties and durability of concrete are analyzed.

2. Experimental section

2.1. Materials
1,4-dibromobutane (98%, Aladdin), 1-hexadecylamine (98%, Aladdin), sodium 3-chloro-2-hydroxypropane sulfonate (95%, Aladdin), ethyl alcohol (99.7%, Chron Chemicals), formaldehyde (37%, Chron Chemicals), formic acid (98%, Chron Chemicals), sodium hydroxide (98%, Chron Chemicals), sodium laurylsulfonate (98%, Aladdin) and AOS (Nanjing Qicheng New Material Co., Ltd.) were all purchased and used as supplied. Deionized water was used.

2.2. Synthetic method
(1) Synthesis of alkyl secondary amine: 60 g anhydrous ethanol and 86 g cetylamine are successively added into a 250 mL flask while stirring. Oil bath temperature is maintained at 35°C. 44 g 1,4-dibromobutane dissolved in 40 g anhydrous ethanol was added dropwise into the mixture over 30 min before maintaining reaction for a further 8 h. 30% NaOH solution further added to reach a constant pH value of 10±0.5. The proposed product obtained is as follows:
(2) Synthesis of tertiary alkyl amines: To the alkyl secondary amine, formic acid (88wt%) is added dropwise into the flask while rising temperature to 80℃ over a period of 1h. Formaldehyde solution (37wt%) is then added dropwise into the flask at a molar ratio of alkyl amine: formic acid: formaldehyde = 1:5.5:5 over 1h. The reaction is then continued for a further 6 h. NaOH (30wt%) is used to adjust the solution to pH 12. The synthesized solution is decanted by oscillating several times and the upper layer of yellowish oil liquid containing unreacted formaldehyde is removed by rotating evaporator. The remaining liquid is washed 2~3 times with 20wt% NaCl solution to achieve the alkyl tertiary amine (the yield is about 90%). The specific reaction formula is as follows:

![Reaction formula](image)

(3) A saturated solution of 3-chloride-2-hydroxyl-propylsulfonasites is placed in a three-necked, round-bottom flask and heated to 80℃. The alkyl tertiary amine ethanol solution is dropped into the flask slowly through the constant flow pump, adjusted pH to 8~9 with 30wt% NaOH solution before reacting for 24 h. The unreacted alkyl tertiary amine is removed by the cyclohexane extraction, while solvents by rotating distillation method. The white solid product is achieved by recrystallization of the product with anhydrous ethanol. Yield is about 70%.

![Reaction formula](image)

2.3. Infrared analysis of reaction products
The products in (3) are respectively ground with KBr and made into thin slices. Infrared test is carried out, and the structure is analyzed by VECTOR-22 Fourier infrared spectrum from Brock Company in Germany.

2.4. Surface activity test
The surface tension (γ) and critical micelle concentration (CMC) of the product in (3) are determined by hanging drop method using KRUSS DSA30s surface tensiometer at 25℃.

2.5. Bubble performance test
Waring-Blender method is used to test the initial bubble volume \(V_0\) and forming half-life \(T_{1/2}\) of the three air entraining agents.
2.6. Concrete test
The fluidity (slump, expansion) and air content of fresh concrete are tested in accordance with the Chinese national standard GB/T50080-2016 Standard “Testing Methods for Properties of Ordinary Concrete Mixes”. The dosage of SP employed in all concrete is 1% by weight of binder, while dosage of AEA added varied. In C30 concrete, the dosage of air-entraining agent AEA-1, AEA-2 and AEA-new is 0.02%, 0.01% and 0.008%, respectively. In C50 concrete, the dosage of air-entraining agent AEA-1, AEA-2 and AEA-new is 0.04%, 0.02% and 0.012%, respectively. The raw materials for concrete are shown in Table 1. C30 and C50 are both employed in fresh concrete measurements (Table 2), while only C30 mix proportion is engaged in determining the properties of hardened concrete. All concrete samples are prepared as 150 x 150 x 150 blocks, vibrated for 10s and stored under standard condition for 28 d before been cut along the horizontal, polished and analyzed. The air content of hardened concrete is controlled within 3.5-4.0%, while the nature of the air voids is measured according to the Chinese water conservancy industry standard SL 352-2006 "Hydraulic concrete test regulations" and ASTM C457 "Standard Test Method for Microscopical Determination of Parameters of the Air-void System in Hardened Concrete". The air content, the number of bubbles, the distribution of bubble aperture, the average chord length of bubbles, the specific surface area of bubbles and the coefficient of bubble spacing of hardened concrete are determined. GB/T50081-2019 "Concrete Physical and Mechanical Properties Test Method Standard" and GB/T50082-2009 "Ordinary Concrete Long Term Performance and Durability Test Method" are employed to determine the mechanical properties of hardened concrete test, and impermeability and frost resistance of hardened concrete. The HP-40 automatic digital display concrete impermeability tester and JW-28 concrete rapid freeze-thaw tester, both from Hebei Jingwei Test Instrument Co., Ltd. were used.

3. Results and discussion
3.1. Characterization of AEA-new
FTIR is first employed to characterize the newly synthesized AEA-new. Figure 1 displays the stretching vibration peak at 3488 cm⁻¹ is -OH, the stretching vibration peak at 2973 cm⁻¹, 2863 cm⁻¹, and the
The separation of -CH$_3$ and -CH$_2$-. The absorption peak at 1460 cm$^{-1}$ is the asymmetric stretching vibration of tertiary amine, and the absorption peak at 1123 cm$^{-1}$ is C-N. 1244 cm$^{-1}$ is the absorption peak of -SO$_3^-$ ion, so AEA-new was successfully synthesized.

![Infrared spectra of products](image)

**Figure 1** Infrared spectra of products

The surface activity of AEA-new is evaluated based on the critical micelle concentration (CMC) and surface tension ($\gamma$) of the AEA in aqueous solution[10-12]. Figure 2 shows the $\gamma$-LogC diagram of AEA-new. The lowest turning point of the surface tension curve is its critical micelle concentration (CMC), at which the surface tension corresponding to the surfactant is $\gamma_{\text{CMC}}$. A comparison of the properties of AEA-new to AEA-1 and AEA-2 are presented in Table 3. AEA-new induce the largest reduction in surface tension of water (28.62 mN/m), while SDS performed the worst (38.0 mN/m). The low surface tension, thus CMC can be attributed to the zwitterionic-amphiphilic distribution of this molecule, causing a weak electrostatic repulsion coupled with closely packed hydrophobic chains, enhancing the stability of the micelle formed[15]. It is of interest to note that the lower the CMC value, the more likely the surfactant is to self-assemble at low concentration [16]. AOS and SDS are both made up of mainly single chain anionic air-entraining agent molecules. AOS is a mixture, usually composed of sodium alpha-olefin sulfonate and sodium hydroxylalkyl sulfonate at a mass ratio of about 7:3. The length of hydrophobic carbon chain in its molecular structure is greater than 12, thus has a more hydrophobic characteristic than SDS. When AEA are more hydrophobic, their arrangements at the gas-liquid interface occurs in a folding and curling modules, decreasing the spatial spacing of the hydrophobic chain of the air entraining agents. In other words, the number of long hydrophobic chain surfactant molecules adsorbed at the gas-liquid interface decreases, thus CMC decreases as well.

![C-$\gamma$ curve of the product at 25°C](image)

**Figure 2** C-$\gamma$ curve of the product at 25°C
Table 3  CMC and $\gamma_{\text{CMC}}$ of the product. ($T=298.15\text{K}$)

| Surfactant | CMC (mol/L) | $\gamma_{\text{CMC}}$ (mN/m) |
|------------|-------------|-------------------------------|
| Product    | $5.3\times10^{-4}$ | 28.62                         |
| AOS[13]    | $6.0\times10^{-3}$ | 32.74                         |
| SDS[14]    | $9.8\times10^{-3}$ | 38.0                          |

For hydrocarbon based air entraining agents, the value of $\gamma_{\text{CMC}}$ depends on the density of the hydrophobic adsorption layer. The higher the density of the adsorption layer is, the more beneficial it is to reduce the surface tension. The adsorption layer density of (1,4)-bis(cetylmethyl hydroxy-propionic acid quaternary ammonium salt) butane air entraining agent molecules at the gas-liquid interface is the highest and $\gamma_{\text{CMC}}$ is the lowest. The hydrophobic chain of AOS is longer than that of SDS. After the hydrophobic chain folds, the adsorption layer density of the former is higher than that of the latter at the gas-liquid interface. Therefore, SDS has the largest $\gamma_{\text{CMC}}$ value.

3.2. Bubble properties in CPS

Air bubble is in itself a thermodynamic unstable system; transiting from stable bubble to bursting is a spontaneous process of energy reduction. The foaming and air stabilizing ability are indexes to evaluate the effectiveness of surfactants. At room temperature, foaming fluids with different mass percentages (0.1wt%, 0.2wt%, 0.3wt%, 0.4wt% and 0.5wt%) were prepared by the three kinds of air entraining agents. The relationship between the foaming volume $V_{\text{max}}$ of the three kinds of air entraining agents and the forming half-life $T_{1/2}$ with the solution concentration was studied respectively. The experimental results are shown in Figure 3 and Figure 4.

![Figure 3](image-url)  
Figure 3  The relationship between the foaming volume and concentration of the three kinds of air entraining agents

Figure 3 demonstrates that the foaming ability of the three air entraining agents greatly differs, whereby foaming is as follow: product > AOS > SDS. When an external force is applied, the inherent energy of the bubbling system, surface tension of the body fluid $\gamma$ and the area of the gas-liquid interface $A$ ($\gamma \times A$) all increases to maintain equilibrium. When external force is constant, a lower surface tension will then result in the development of larger air bubbles and greater ease in foaming and vice versa. Due to the presence of two hydrophobic chains in AEA-new, a stable directional array on the gas-liquid interface is exerted, thus excellent foaming capacity is observed (Fig 3), whereby AEA-new induces the largest reduction in water surface tension, followed by AOS and SDS respectively. Figure 3 also reveals that when a constant external force is exerted on the foaming liquid, the foam volume first increases and remains constant despite increasing concentration of the air entraining agent. The initial increment is
correlated to the decrease in surface tension as concentration of air entraining agent increases. When minimum surface tension is achieved i.e. no further adsorption of air entraining agent at the liquid-gas interface possible, the foam volume will then stay at its maximum.

Figure 4 The relationship between the forming half-life of the three air entraining agents and the concentration change

It is interesting to note that the half lives of air bubbles in concrete prepared with AOS and SDS are similar, while that with AEA-new differs greatly (Figure 4). It is speculated here that unlike absolute foaming capability (Figure 3) which is related to the amphiphilicity of the molecules, the similarity in half life is attributed to the molecular architecture of the AEAs. The stability of bubbles formed by SDS is more than a factor lower than AOS, attributing to the decrease in surface tension, whereby energy required to form the film at the gas-liquid interface decreases, increasing bubble thermodynamic stability [17]. When the concentration of AOS and SDS increased to 0.4wt%, the half-life of the air bubbles appeared to be reach a maximum, indicating that the surfactants at the gas-liquid interface may have reached saturation. In comparison, the half life of air bubbles produced in the presence of AEA-new continue to increase with dosage. The phenomenon correlated with the surface tension and CMC values of the air-entraining agents, indicating the importance of these values to achieve a stable porous concrete system.

3.3. Air entrainment investigation in fresh concrete

The air entrainment and resulting stability of the air bubbles produced in fresh concrete with the three AEAs in C30 and C50 each respectively is investigated (Table 4). In C30 concrete containing 0.02% AEA-1, the initial air content and at 60 min are 2.5% and 1.8% respectively. When 0.01% AEA-2 is added, the initial air content of C30 is 3.5%, which reduces to 3% at 60 min. In the case of AEA-new, the initial air content of C30 concrete is 4.5%, and maintaine above 4% after 60 minutes when a low dosage of 0.008% is employed. The differences can be attributed to the surface tension and hydrophilicity of the molecules, where (1) lower surface tension equates greater ease in air entrainment and (2) presence of two different hydrophilic groups in the structure of AEA-new weakens the electrostatic repulsion between them, reducing packing density of the overall molecule, thus allowing a denser arrangement at the gas-liquid interface, causing greater bubble stability.

To achieve similar air entrainment in C50 concrete, the amount of air-entraining agent increases. 0.012% of AEA-new, 50% higher than in C30 is needed to achieve an initial air content of 4.2%. Likewise, increasing AEA-1 and AEA-2 to more than 0.03% failed to increase the air concrete of
concrete (Table 4). This may be explained by the high viscosity of concrete; the viscosity of slurry acts as an energy barrier for the formation of bubbles [14]. However, it can be observed that AEA-new is more effective in producing entrained air in fresh concrete than the conventional AEAs.

### Table 4  Slump and air contents of fresh concrete

| Concrete grade | Type of air entraining agent | Initial slump/mm | Initial workability/mm | Initial air content/% | 60 min air content/% | Admixture/% |
|----------------|-------------------------------|------------------|------------------------|----------------------|----------------------|------------|
| C30            | AEA-1                         | 220              | 550                    | 2.5                  | 1.8                  | 0.02       |
|                | AEA-2                         | 220              | 560                    | 3.5                  | 3.0                  | 0.01       |
|                | AEA-new                       | 230              | 570                    | 4.5                  | 4.2                  | 0.008      |
| C50            | AEA-1                         | 225              | 580                    | 1.8                  | 1.3                  | 0.04       |
|                | AEA-2                         | 230              | 575                    | 2.4                  | 1.8                  | 0.02       |
|                | AEA-new                       | 235              | 590                    | 4.2                  | 4.0                  | 0.012      |

3.4. Investigation in hardened concrete

3.4.1. Porosity determination in hardened concrete

![Figure 5](image-url)

Figure 5 Influence of three kinds of air entraining agents on the air content contributed by bubbles of different sizes in concrete

Figure 5 displays the distribution of air bubbles in the hardened concrete. As observed, air bubbles with chord length of 0–200 μm are the most prevalent, whereby AEA-new produces the highest amount of air voids having chord length between 0–200 μm, similar in the range of 200-500 μm, and greater number of large air voids when AEA-1 and AEA-2 are employed. The variation in air voids can contribute greatly to the strength of concrete, frost resistance and permeability resistance, which will be discussed further.
3.4.2. **Corresponding bubble structure parameters in concrete with different air entraining agents**

| Type of air entraining agent | Air entraining agent dosage/% | Initial air content of fresh concrete/% | Air content of hardened concrete/% | Average chord length/μm | The bubble number | Bubble specific surface area/(mm²/mm³) | Bubble spacing coefficient/μm |
|-----------------------------|--------------------------------|--------------------------------------|----------------------------------|------------------------|------------------|--------------------------------------|-------------------------------|
| AEA-1                       | 0.035                          | 3.9                                  | 3.5                              | 268                    | 3252             | 26.4                                 | 286                           |
| AEA-2                       | 0.012                          | 3.8                                  | 3.6                              | 204                    | 3835             | 38.3                                 | 187                           |
| AEA-new                     | 0.006                          | 3.7                                  | 3.8                              | 102                    | 4316             | 52.7                                 | 115                           |

Table 5 presents the air voids in C30 concrete in the presence of different AEAs. By adjusting the amount of air entraining agent, the air content of freshly mixed concrete is close to 3.9%, 3.8% and 3.7%, respectively. The final air voids contents of concrete containing AEA-1, AEA-2 and AEA-new are 10.2%, 5.3% and 0% lower than that in fresh concrete respectively. As observed from Table 5, the overall bubbles in hardened concrete containing AEA-new is more than 10% higher than when the other two AEAs are employed, corresponding to the higher specific surface area: volume ratio and short average chord length of 102 μm. The stability of air bubbles is the lowest when AEA-1 is employed as demonstrated by the high loss in air content from fresh to hardened state (Figure 1 versus Table 5).

3.5. **Mechanical properties and durability of hardened concrete**

The 28-day compressive strength, impermeability and frost resistance of hardened concrete of the C30 concrete are tested (Table 6). Similar to previous observation, the 28-day compressive strength, impermeability and frost resistance of concrete are superior when AEA-new is employed. The compressive strength of the concrete is 10.7% higher than that of the concrete using the AEA-1, 8.2% higher than that of the concrete using the AEA-2, the impermeability grade and frost resistance grade are three grades higher than that of the AEA-1, two grades higher than that of the AEA-2. All of these are closely related to the concrete bubble structure in Table 5, and are consistent with the data in Table 5. Small bubble size and small bubble spacing coefficient mean that the mechanical properties (28-day compressive strength) and durability (impermeability and frost resistance) of concrete are better in the case of similar air content.

| Type of air entraining agent | Mechanical strength | Impermeability | Frost resistance |
|-----------------------------|---------------------|----------------|-----------------|
|                            | 28d compressive strength/MPa | Maximum Anti-seepage pressure value/MPa | Impermeability grade | Maximum number of freeze-thaw cycles | Frost resistance grade |
| AEA-1                       | 33.5                | 0.7            | P6              | 100                      | F100                |
| AEA-2                       | 34.3                | 1.1            | P10             | 225                      | F200                |
| AEA-new                     | 37.1                | 1.3            | P12             | 250                      | F250                |

4. **Conclusion**

In this paper, a new type of concrete air entraining agent (1,4)-bis(cetylmethyl hydroxy-propionic acid quaternary ammonium salt) butane (AEA-new) with CMC and γ_{CMC} values of 5.3×10^{-4} mmol/L and 28.86 mN/m respectively has been successfully synthesized. The effectiveness of this AEA in fresh and hardened concrete are compared with two conventional AEAs—SDS and AOS. It is confirmed that the air entraining performance, ease in producing smaller air bubbles and thus final air void system, and the
resulting stability of air bubbles produced by AEA-new are superior than those of SDS and AOS. This results in excellent mechanical properties and durability when AEA-new is used in concrete, whereby 28 d compressive strength is 10.7% and 8.2% higher than when SDS and AOS are employed respectively. The impermeability grade and frost resistance grade are three grades and two grades higher respectively.

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