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Synthesis and surface activity study of branched fluorinated cationic (FCS), gemini (FGS) and amphoteric (FAS) surfactants with $CF_3CF_2CF_2C(CF_3)_2$ group

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ABSTRACT

Fluorinated surfactants are usually composed of a perfluorinated chain and a hydrophilic group. Academic surveys have reported that straight chain fluorinated surfactants have the lowest surface tension in a relatively high concentration while the branched fluorinated surfactants show more efficient in a relatively low concentration. Introducing branch is one of effective strategies for synthesis of non-bioaccumulable fluorinated surfactants.

Three novel branched fluorinated surfactants were designed and prepared through a five-step route using perfluoro-2-methyl-2-pentene as starting material. The surface activities of them were investigated and found that they exhibited excellent surface activities. FCS can reduce the surface tension of water to below 20 mN/m, and the cmc value of FAS in water is about 1.04×10^{-4} mol/L at 298 K. All the values of surface properties of FCS, FGS and FAS are lower than that of sodium perfluorooctanoate.

1. Introduction

Fluorinated surfactants are more efficient than traditional surfactants since they display high surface activity at low critical micelle concentration (cmc). Besides, fluorinated surfactants usually have high thermal and chemical stability [1–3]. They are usually composed of a perfluorinated chain and a hydrophilic group [4–6]. The most known fluorinated surfactants are PFOA (perfluorooctanoic acid, $C_7F_{15}CO_2H$) and PFOS (perfluorooctane sulphonate, $C_8F_{17}SO_3X$, with X = K, Na, H). Up to now, fluorinated surfactants have been widely used in more than 200 applications [7] including clothing fabrics, electroplating, fire fighting foams, food packaging, petroleum, textile, etc.

However, compared with hydrocarbon surfactants, fluorinated surfactants are more difficult to synthesize. The methods reported are fluorination by electrolysis [8], telomerization of fluoroolefin [9–11], oligomerization of fluoroolefin [12], etc. Fluorination by electrolysis uses HF as a main raw material which is inexpensive, but the method has many by-products. Telomerization of fluoroolefin usually generates a mixture of products with different chainlength, therefore, strict control of the reaction conditions is required. The most commonly used fluoroolefin in oligomerization of fluoroolefin is hexafluoropropene.

With the forbidden of PFOA and PFOS for persistent, toxic and bioaccumulable pollutants [13–16], it is necessary to develop novel structural fluorinated surfactants. So far, basic research studies in this field revealed that straight chain fluorinated surfactants have the lowest surface tension at a relatively high concentration while the branched fluorinated surfactants show more efficient at a relatively low concentration. For example, Dmowski et al., prepared $CF_3CF_2CF_2C(CF_3)_2CH_2CH_2$–COONa and compared its surface activity with $CF_3(CF_2)_6COONa$ [17]. The result showed that $CF_3CF_2CF_2C(CF_3)_2CH_2CH_2COONa$ has better surface ability than $CF_3(CF_2)_6COONa$ to reduce the surface tension of water at the same concentration. So, introducing branched structure in fluorinated chain part is one of effective strategies for synthesis of non-bioaccumulable alternatives to PFOA [18]. Hexafluoropropylene oligomer is an important starting material which can be used to synthesize many branched fluorinated surfactants and most reported methods are based on hexafluoropropylene trimer. The

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methods for preparing branched fluorinated surfactants using hexafluoropropylene dimmer are extremely scanty [19–25]. Besides, hexafluoropropylene dimmer is easy to get and relatively inexpensive.

In view of these facts mentioned above, we designed an approach for preparation of the title compounds using perfluoro-2-methyl-2-pentene as starting material. In this paper, we would like to report the synthesis and characterization of these novel compounds. Furthermore, evaluation of their surface tension was also reported.

2. Results and discussion

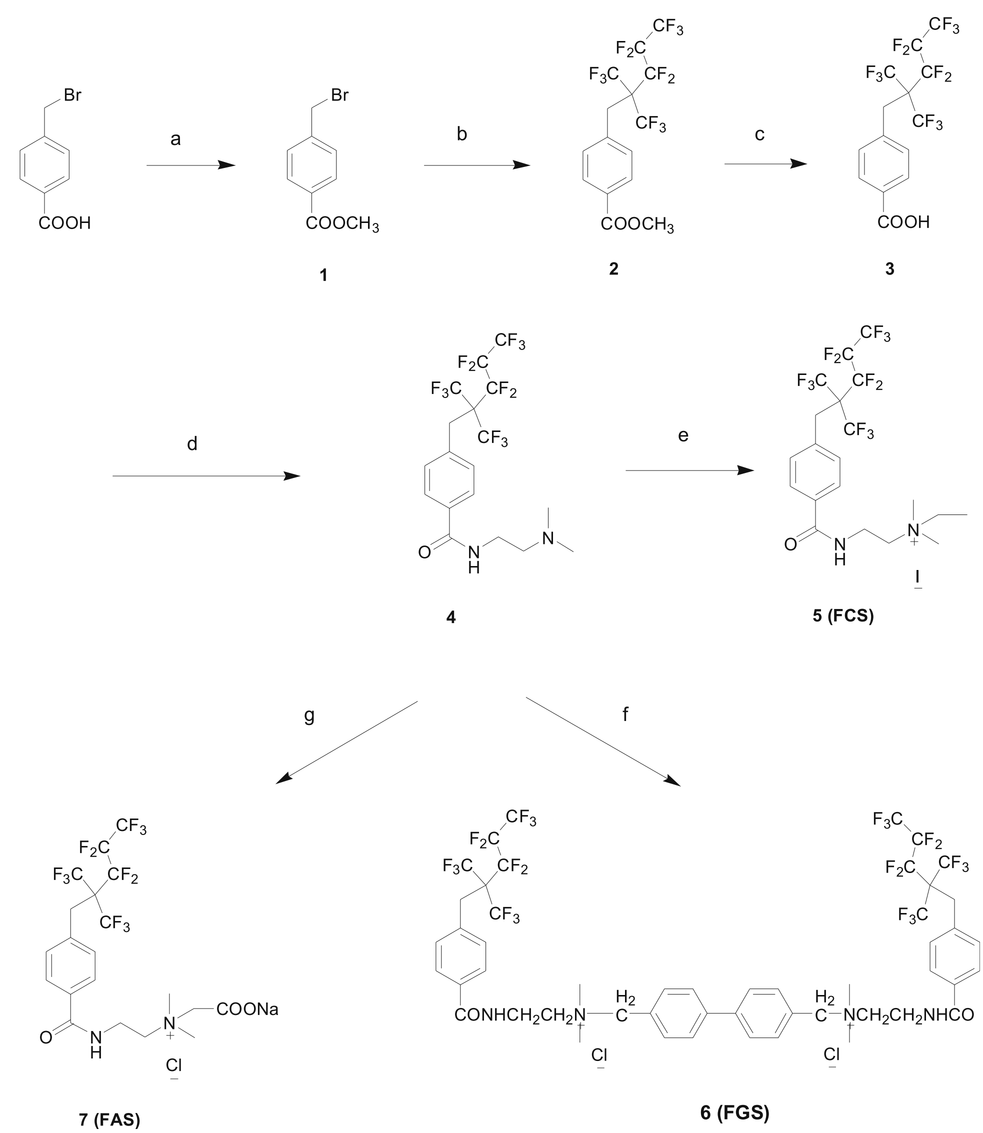
2.1. Synthesis

The synthesis pathway was shown in Scheme 1. Four steps led to the compound **4**. First, 4-(bromomethyl)benzoic acid was esterified with methanol to protect carboxyl. Second, compound **1** was changed to compound **2** by a nucleophilic substitution reaction. Third, saponification of the ester **2** followed by acidification led to the carboxylic acid **3**. Then, conversion of the acid **3** into the amide **4** was carried out by treating with EDCI and N,N-dimethylethylene diamine. Finally, the title branched fluorinated cationic (FCS), gemini (FGS) and amphoteric (FAS) surfactants were obtained in both high yields and high purity by the reactions of the tertiary amine intermediate **4** with appropriate alkyl halides in CH_3CN followed by filtration of the resultant precipitates. In each step, reaction proceeded under mild reaction conditions with high yield of the desired product and easy work-up procedures using low cost reagents. The structures of FCS, FGS, FAS and intermediates were characterized by ^1H NMR, ^{19}F NMR, ^{13}C NMR, FTIR and MS.

2.2. Surface tension

The surface tensions were tested at 25 °C by the Wilhemy plate method using a Kruss K100 tensiometer. A series of different concentrations of aqueous solution were prepared, average value of the surface tension at each concentration was obtained based on the data collection by three times measurement. The tensions were measured followed by concentrations from low to high. Results were shown in Fig. 1.

As is seen in Fig. 1, the cmc value of FCS in water is about 2.5×10^{-3} mol/L at 298 K and the surface tension of the aqueous solution is 19.678 mN/m at the cmc. The cmc value of FGS in water is about 3.4×10^{-4} mol/L at 298 K and the surface tension of the aqueous solution is 22.381 mN/m at the cmc. The cmc value of FAS



Scheme 1. Synthetic route to produce branched fluorinated surfactants.