

Synthesis and Properties of a Novel Fluorinated Surfactant via “Thiol-ene” Click Reaction

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Abstract: To meet the urgent requirement for the green fluorinated surfactants in practical applications, a novel fluorinated surfactant was synthesized in a facile two-step procedure. Firstly, (1,1,2-trifluoro-2-heptafluoropropoxy-ethylsulfanyl)-acetic acid (THEA), i.e. $\text{F}(\text{CF}_2)_3\text{OCFHCF}_2\text{SCH}_2\text{COOH}$, was prepared via “thiol-ene” click reaction between heptafluoropropyl trifluorovinyl ether (PPVE) and 2-mercaptoacetic acid (TGA), and then THEA was neutralized with sodium hydroxide to obtain the targeted surfactant (1,1,2-trifluoro-2-heptafluoropropoxy-ethylsulfanyl)-sodium acetate (THESA), i.e. $\text{F}(\text{CF}_2)_3\text{OCFHCF}_2\text{SCH}_2\text{COONa}$. The structure of this surfactant was characterized by ^1H NMR, ^{19}F NMR and FT-IR in detail. The surface properties of THESA were measured by the ring method, and the results demonstrated that the novel fluorinated surfactant exhibited lower surface tension ($15.86 \text{ mN}\cdot\text{m}^{-1}$) and critical micelle concentration (CMC, $20 \text{ mmol}\cdot\text{L}^{-1}$), compared with the conventional fluorocarbon surfactant, ammonium perfluorooctanoate (PFOA). The results presented in this work indicated that this novel fluorinated surfactant with excellent surface properties via versatile synthetic strategy, could be a promising candidate to overcome the limitations of the traditional fluorinated surfactant, such as PFOA.

1 INTRODUCTION

Fluorinated surfactants, a kind of the special surfactants with fluorocarbon chains as nonpolar groups, are partial or total substitution of hydrogen atoms with fluorine atoms on the hydrocarbon chains. Because of the unique properties of fluorocarbon bonds, the fluorinated surfactants exhibited excellent thermodynamic and chemical stability, exploring their applications for harsh industrial needs (Durga et al., 2006). Most importantly, the strong hydrophobicity and low molecular cohesion endowed the fluorinated surfactants with high surface activity, which could significantly reduce surface tension of water at lower dosage compared with the corresponding hydrogenated surfactants (Chen et al., 2011). Thus, they are often used as indispensable processing agents in the production of high-efficiency fluoropolymers that have aroused great interest in aviation technology, transportation, electronics, as well as household items such as kitchen appliances (Yukishige et al., 1998; Khaled et al., 2008).

Thereinto, perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and their derivatives are used most extensively, however, these fluorinated surfactants have been identified as persistent organic pollutants (POPs) and globally forbidden to use in related products (Blake et al., 1998; Völkel et al., 2008). Because they cannot be degraded under enzymatic or metabolic decomposition, resulting in water pollution, bioaccumulation and toxic hazard to environment and human body (Midasch et al., 2007). Therefore, the preparation of environmentally friendly and nontoxic alternative fluorinated surfactants has aroused wide attention with the increasing development of green chemistry. It is well known that the above environmental problems caused by PFOA and PFOS is mainly due to C8 perfluoroalkyl chain length. To address such problems, the widely-accepted idea is to reduce the number of fluorocarbon bonds. One of the effective methods is to introduce heteroatoms into the fluorocarbon chain. Due to the better flexibility of ether linkages, perfluoroether chains are more susceptible to degradation than fluorinated chains

(Sha et al., 2015; Alessandro and Bruno, 2012). Therefore, such surfactants could not only maintain the high surface activity, but also possess good degradation property.

Recently, Masahiko Abe (Masahiko, 1999) have successfully modified the fluorocarbon chain with ether bond, enhancing water solubility, and the introduction of hetero atoms endows the chain with flexibility. These fluorinated surfactants exhibited good surface ability to reduce surface tension. A non-bioaccumulable as novel alternative to PFOA, $\text{CF}_3\text{-X-(CH}_2\text{)}_n\text{-SO}_3\text{Na}$ (with X=O , $\text{C}_6\text{H}_4\text{O}$ or $\text{N(CF}_3\text{)}$ and $n=8\text{-}12$), was synthesized and characterized by Bruno Ameduri's group (Georgi et al., 2009), which keeps comparable surface tension with PFOA.

Besides, the reported methods of synthesizing the fluorinated surfactants are complicated, such as telomerization of fluoroolefins (Haszeldine, 1951), electrochemical fluorination (Lehmle, 2005), etc. Compared to these preparative techniques, "thiol-ene" click reaction is an effective chemistry in organic synthesis that it can simply combine two functional segments together with no residual by-products and had applied in many fields (Charles and Christopher, 2010).

Herein, it's necessary to design nontoxic and environmentally friendly fluorinated surfactants with facile synthetic process to meet urgent need for green chemistry and applications. In this work, a novel fluorinated surfactant, (1,1,2-trifluoro-2-heptafluoropropoxy-ethylsulfanyl)-sodium acetate (THESA, $\text{F(CF}_2\text{)}_3\text{OCFHCF}_2\text{SCH}_2\text{COONa}$), was rationally designed and prepared via "thiol-ene" click reaction. The structure and surface properties of the surfactant was analyzed in detail. This novel fluorinated surfactant is a promising candidate for the substitute of PFOA.

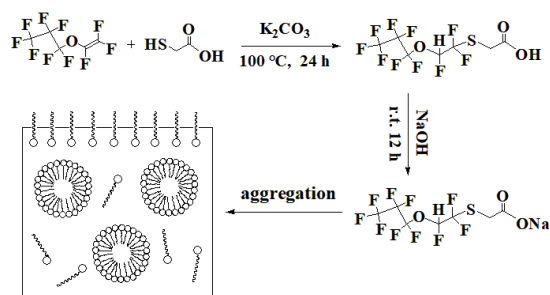


Figure 1: Synthesis of fluorinated surfactant THEAS.

2 EXPERIMENTAL SECTION

2.1 Materials

Heptafluoropropyl trifluorovinyl ether (PPVE, 99.8%) was purchased from Shandong Huaxia Shenzhou New Material Co., Ltd.. (China), 2-mercaptoacetic acid (TGA, >98%) and potassium carbonate (K_2CO_3) was obtained from Shanghai Macklin Biochemical Co., Ltd.. Ethyl acetate was purchased from Tianjin Fuyu Fine Chemical Co., Ltd.. (China) All reagents were used as received.

2.2 Synthesis of THESA

Firstly, (1,1,2-trifluoro-2-heptafluoropropoxy-ethylsulfanyl)- acetate was synthesized by the click reaction between the carbon-to-carbon double bond of PPVE and thiol group of TGA, with K_2CO_3 as catalyst system. Typically, PPVE (11.55 g, 0.04342 mol), TGA (8.0 g, 0.0868 mol), K_2CO_3 (1.955 g, 10 wt%) and ethyl acetate (20 mL) were accurately weighed and added into a 50 mL pressure reactor, respectively, and then the reaction was carried out for 24 h at 100 °C. Subsequently, the unreacted monomer and solvent were removed by the rotary evaporation. The row product was washed by deionized water for three times (3×100 mL), dissolved in ethyl acetate (30 mL) and extracted with saturated NaCl solution (3×80 mL), respectively. Afterward, the collected organic phase was dried over anhydrous MgSO_4 overnight and filtered off. Finally, the resulting organic phase was purified by rotary evaporation and a yellow liquid was obtained (11.1 g, 0.0328 mol, yield, 56.8%).

Then, the above yellow liquid was added slowly into sodium hydroxide aqueous solution (1.05 g, 0.026 mol; 40 mL) and stirred at room temperature for 12 h. The aqueous phase was extracted with ethyl acetate for three times (3×60 mL). Afterward, the aqueous phase was collected and dried at 100 °C, and powdery solid THESA was finally obtained.

2.3 Characterization

^1H and ^{19}F nuclear magnetic resonance (NMR) spectra were measured on Bruker Advance III 400 MHz NMR spectrometer in deuterium oxide (D_2O) with tetramethylsilane as the internal standard at room temperature. FT-IR spectra were recorded on a Nicolet iS10 FT-IR equipped with an attenuated total reflection (ATR) accessory with diamond crystal. Surface tension were measured by the ring method according to previously reported by zhang (Zhang et

al., 2013), and the critical micelle concentration (CMC) of the fluorinated surfactants was determined by the inflection point obtained by plotting c versus $\lg C$. Krafft point (K_p) was determined by the sudden increase of conductivity with temperature. In a thermostatic bath, the conductivity of a certain concentration of solution was measured using a DKK-TOA conductivity meter CM-60G while slowly heating (Shinoda et al., 1972).

3 RESULTS AND DISCUSSION

3.1 Chemical Structure of THESA

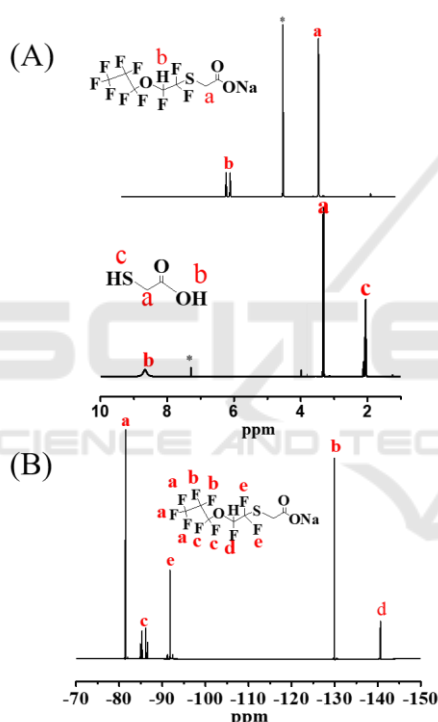


Figure 2: (A) ^1H NMR spectra of TGA (a), and THEAS (b), and (B) ^{19}F NMR spectra of THEAS.

A novel fluorinated surfactant THESA was synthesized in a double-step procedure in which PPVE and TGA was reacted via “thiol-ene” click reaction in the first step, and then sodium hydroxide was added to form the fluorinated surfactant, as elaborated in Figure 1. Figure 2(A) displays the representative structures of the raw TGA and THESA by ^1H NMR. The chemical shifts at 3.32 ppm (peak a), 2.08 ppm (peak b) and 8.82 ppm (peak c) are attributed to the methylene proton ($\text{S}-\text{CH}_2-$), the mercaptan proton ($-\text{SH}-$) and the carboxylic acid

proton ($-\text{COOH}$) of TGA, respectively. Beyond that, a new peak at 6.50-6.64 ppm (peaks b) belonging to the proton of the $\text{O}-\text{CFH}-\text{CF}_2-$ structure, has confirmed the successful click reaction between thiol group and $\text{C}=\text{C}$ double bond, resulting in the disappearance of the mercaptan proton. In addition, the chemical shift at $\delta=8.82$ ppm associated with the carboxylic acid proton was also disappeared, indicating that THESA was obtained via neutralization reaction with NaOH in the second step.

Besides, the structure of the THESA was also characterized by ^{19}F NMR spectra, as shown in Figure 2(B). The characteristic peaks of each F were clearly specified: the chemical shifts at -81.42 ppm (peak a), -85.59 ppm (peak c) and -129.82 ppm (peak b) are attributed to CF_3- , $-\text{CF}_2-\text{O}$ and $\text{R}_\text{F}-\text{CF}_2-$, respectively. The signals at -91.83 ppm and -140.59 ppm are due to the $-\text{CF}_2-\text{S}-$ and $-\text{O}-\text{CFH}-$ group, respectively.

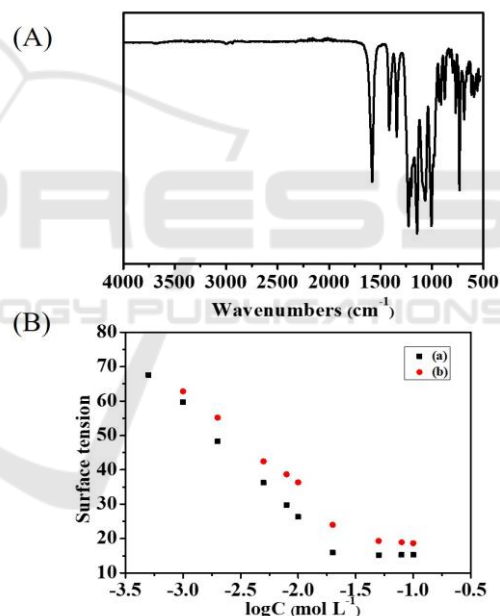


Figure 3: (A) FT-IR spectrum of THESA, and (B) surface tension plots of PFOA (a) and THESA (b) against concentration at 25 °C.

FT-IR was also determined the chemical structure of THESA as shown in Figure 3(A). The weak adsorption bands appeared at 2860-2940 cm^{-1} are mainly attributed to the stretching vibration of methylene group ($-\text{CH}_2-$), and the strong adsorption band appeared at 1582 cm^{-1} is due to the stretching vibration of the $\text{COO}-$ group. The characteristic peaks at 1444-1338 cm^{-1} are corresponded to the stretching vibration of CF, CF_2 and CF_3 . The above

results show that the targeted fluorinated surfactant THESA was successfully synthesized and whose purity is up to 98 % (by GC). It is worth noting that there is only one product exists, indicating that the “thiol-ene” click reaction is an effective chemistry in organic synthesis with no residual by-products, which is more suitable for the preparation of fluorinated surfactant.

Table 1: Summary of K_p , CMC and γ_{CMC} of THESA and PFOA at 25 °C.

	K_p (°C)	CMC (mmol·L ⁻¹)	γ_{CMC} (mN·m ⁻¹)
THESA	< 0	20.0	0.286
PFOA	< 0	33.3	0.067

3.2 Surface Properties of THESA

THESA and PFOA aqueous solution with different concentrations (10^{-4} , $10^{-3.3}$, 10^{-3} , $10^{-2.7}$, $10^{-2.3}$, 10^{-2} , $10^{-1.7}$, $10^{-1.3}$, $10^{-1.1}$, 10^{-1} mol·L⁻¹) were precisely prepared, and then the surface tension were measured by the ring method. As shown in Figure 3(B), in the first stage, the surface tension significantly decreased as the concentration of the surfactant increased, however, the surface tension would keep constant after the concentration rose to be a certain extent. A significant turning point was appeared, which was identified as the CMC of the surfactant. This novel fluorinated surfactant has lower surface tension ($15.86 \text{ mN}\cdot\text{m}^{-1}$) and CMC ($20 \text{ mmol}\cdot\text{L}^{-1}$) compared with PFOA, whose surface tension and CMC are $19.71 \text{ mN}\cdot\text{m}^{-1}$ and $33.3 \text{ mmol}\cdot\text{L}^{-1}$, respectively. The reason is the introduction of ether bond, C-O and C-S, which makes the surfactant more hydrophilic and therefore exhibits a lower CMC. Furthermore, as shown in Table 1, the Krafft point (K_p) of both THESA and PFOA were measured in a thermostatic bath, and the results showed that the values of K_p were all below 0 °C, also indicating THESA is hydrophilic compared with PFOA. On the basis of these results, this novel fluorinated surfactant THESA exhibited excellent surface properties and has the potential to be used as a substitute for PFOA in practical applications.

4 CONCLUSIONS

In this work, we have successfully synthesized a novel fluorinated surfactant THESA via “thiol-ene” click reaction, which has four-carbon perfluoroalkyl chain length and heteroatom (O) in the main chain.

Noticeably, this novel surfactant exhibited lower surface tension ($15.86 \text{ mN}\cdot\text{m}^{-1}$) and critical micelle concentration (CMC, $20 \text{ mmol}\cdot\text{L}^{-1}$), compared with the conventional fluorocarbon surfactant, ammonium perfluorooctanoate (PFOA), whose surface tension and CMC are $19.71 \text{ mN}\cdot\text{m}^{-1}$ and $33.3 \text{ mmol}\cdot\text{L}^{-1}$. The results presented in this work indicated that this novel fluorinated surfactant with excellent surface properties via simple synthetic strategy, could be a promising candidate to overcome the limitations of the traditional fluorinated surfactant, such as PFOA.

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