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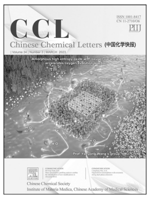

Surface activity of a series of fluoroether betaine amphoteric surfactants: Oxygen roles[☆]

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ABSTRACT

As PFOS, PFOA and their derivatives were banned according to the Stockholm Convention for their potential bioaccumulation and toxicity, people attempted to substitute the legacy fluorosurfactants with short-chain ones. Although short-chain alternatives can alleviate bioaccumulation, surface activity was compromised. Fluorine industry kept seeking for effective solution. In this work, we prepared and investigated a series of fluoroether betaine surfactants for their surface activity and spreading property. The role of oxygen on surface activity was discussed. We found that insertion of oxygen atoms into fluorinated chain could increase hydrophobicity and thus enhance surface activity. The contribution of one oxygen is approximately half of that of a difluoromethylene group by experience. Moreover, introducing oxygen diversified the structure to fill in the gap of surface activity between short and long fluorosurfactants. In summary, this work provided basic knowledge for molecular design.

Fluorinated surfactants are a unique class of surfactants different from their hydrocarbon counterparts [1]. They are applied in many different fields, such as fire-fighting, electronic equipment, cleaning products, textile and food packaging [1,2]. Fluorine is the most electron negative element, thus C-F bond is strong and the polarizability of fluorine atoms is extremely low [1,3]. Owing to that, interaction between fluorinated segments of per- and polyfluoroalkyl substances (PFASs) appears to be much weaker than hydrocarbons. Therefore, fluorosurfactant molecules are easy to aggregate on the surface and behave in a highly hydrophobic way. As a result, fluorosurfactants can reduce the surface tension of an aqueous solution to as low as 16 mN/m in a concentration of 0.1 wt% or less, which is hardly achieved by other types of surfactants [1]. In addition, the strong C-F bonds lead to excellent thermal and chemical stability of fluorosurfactants. Fluorosurfactants provide peculiar performance that are indispensable in many applications [4], for instance, aqueous film forming foam (AFFF) for oil-based liquid fire.

However, the extreme stability resulted from C-F bonds also causes potential environmental persistence and long-range mobility. Long-chain fluorosurfactants have been found to be bioaccumulative and toxic [5,6]. Perfluorooctanoic acid (PFOA, $C_7F_{15}CO_2H$), and perfluorooctane sulfonic acid (PFOS, $C_8F_{17}SO_3H$) and their derivatives are conventional fluorinated surfactants that have been widely used during last decades. They have been found to be ubiquitous in the environment, including meats, vegetables, surface water, sewage sludge, dust, wildlife and human serum [6–8]. Hence, PFOS, PFOA and their related substances were listed under Annex B (for global restriction) and Annex A (for global elimination) of the Stockholm Convention on Persistent Organic Pollutants, in 2009 and 2019, respectively [9]. After they were prohibited, many industrial processes and applications have been seriously affected. For example, without long-chain perfluorinated betaines, the efficiency of putting out oil-based fire has been reduced greatly and the cost has increased intensively [4]. Eventually, the effective alternatives are highly demanded.

Up to now, there are two alternative strategies to replace long-chain perfluoroalkyl substances [5,10]. One of the strategies utilizes compounds with short-chain fluorinated segments (*e.g.*, perfluorobutane sulfonyl moiety, $C_4F_9SO_2$-). The other strategy introduces heteroatoms into the fluorocarbon chain. Today, it is generally ac-

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[☆] This paper is dedicated to Professor Pei-Qiang Huang on the occasion of his 60th birthday.

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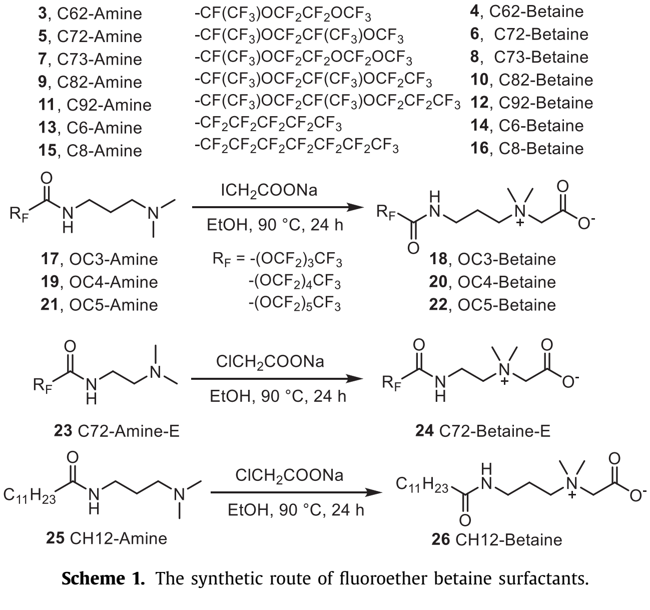
cepted that short-chain fluorinated alternatives are less bioaccumulative than long-chain homologs. However, short-chain PFAS tended to exhibit worse surface activity than long-chain PFAS did [5,11–13]. For example, Yoshimura *et al.* found that the surface tensions of perfluorohexyl (C6) and perfluorooctyl (C8) gemini surfactants were 19.8 mN/m and 13.7 mN/m at critical micelle concentration (cmc) [12]. Moreover, fluorosurfactants are generally prepared by electrochemical fluorination or telomerization of tetrafluoroethylene [1,2]. Both methods produced fluorinated chains with an even carbon number. Surface activity of C6 and C8 products differ greatly which makes broad space for oxygen-inserted fluorinated alternatives.

Currently, the role of oxygen atoms in fluorosurfactants is not quite clear. We wonder that 1) if oxygen atoms could enhance surface activity by reducing the surface tension and cmc? 2) if oxygen atoms could make fluorosurfactant molecules more diverse to fill in the gap of surface activity between C6 and C8? So far, only a few fluoroether surfactants have been reported [14]. Most of fluoroether surfactants derived from oligomers of hexafluoropropene oxide (HFPO). Starting from trimer of HFPO (HFPO-TA), Shen *et al.* [15] synthesized a long-chain fluoroether surfactant (**12**, C92-Betaine in Scheme 1), whose surface tension at cmc (γ_{cmc}) and cmc were about 16.9 mN/m and 0.07 mmol/L (0.05 g/L) respectively. The authors claimed C92-Betaine as an eco-friendly surfactant. However, Dai *et al.* investigated comprehensively the occurrence and toxicities of HFPO-TA which is the precursor and degradation product of C92-Betaine, and they found that HFPO-TA was detected ubiquitous, bioaccumulative and toxic [16–20]. HFPO-TA may not be a suitable alternative of PFOA. Wang *et al.* proposed a question whether the fluorinated alternatives to long-chain PFASs were safe for humans and the environment. They concluded that some alternatives cause a “lock-in” problem that is, “one chemical from a group of structurally similar chemicals was removed from the market and replaced by other chemicals from the same group, but the basic problem was not really solved” [10]. C92-Betaine may fall into this vicious “lock-in” circle. Finding an alternative for PFOA/PFOS is a huge challenge, and lack of the basic knowledge is an obstacle of searching for the alternative.

This article intends to explore the effect of the fluoroether segment in a series of betaine surfactants in order to inspire rational design of the alternatives in the future. Betaine surfactants have good synergistic effects when they are mixed with hydrocarbon surfactants and are widely used in practical applications [1]. We aim to diversify the molecular structure by inserting oxygen atoms, and interpret its function in surface activity from nature of chemistry. The following perspectives are studied: (1) the effect of fluorinated carbon number on surface tension with the same number of inserted oxygens; (2) the effect of oxygen number on surface tension and critical micelle concentration with the same carbon number; (3) mixtures of fluorosurfactants and hydrocarbon surfactants were prepared and their spreading properties were studied.



Scheme 1. The synthetic route of fluoroether betaine surfactants.

Betaine amphoteric surfactants have a wide isoelectric range and can be used in a wide range of pH. Therefore, they have excellent formulation property and can be mixed with almost any other type of surfactants to show superior performance. Previously, we found that the insertion of oxygen into perfluoroalkyl chain was an effective way to reduce the surface energy of gemini cationic and amino oxide fluorinated surfactants, and oxygen-rich hydrophobe could make surfactants highly flexible [21,22]. To the best of our knowledge, there is not similar work to study the effect of oxygen on perfluorinated hydrophobe. In this work, we introduced multiple fluoroether chains into betaine amphoteric surfactants. The synthetic route of fluoroether betaine surfactant was shown in Scheme 1. The hydrophobic fluoroether chains are composed of different carbon and oxygen atoms. We synthesized the surfactants containing with one oxygen atom (**2**), two oxygen atoms (**4**, **6**, **10**, **12** and **24**), three oxygen atoms (**8** and **18**), four oxygen atoms (**20**), and five oxygen atoms (**22**) in fluoroether segments. PFOA and PFHxA derivatives (**14** and **16**), as well as a hydrocarbon surfactant (**26**) were also synthesized for comparison.

The surface activity of different fluorinated surfactants is listed in Table 1, including critical micelle concentration (cmc), surface tension at cmc (γ_{cmc}) and limiting molecular areas (A_{min}) (also see Supporting information). As is depicted in Fig. 1, the γ_{cmc} of compounds was in an order as C82-Betaine (**10**) < C92-Betaine (**12**) < C72-Betaine (**6**) < C8-Betaine (**16**) < C62-Betaine (**4**) < C6-Betaine (**14**) and the cmc of these surfactants was in an order as C92-Betaine (**12**) < C82-Betaine (**10**) < C8-Betaine (**16**) < C72-Betaine (**6**) < C62-Betaine (**4**) ≈ C6-Betaine (**14**). When comparing C82-Betaine (**10**) with C8-Betaine (**16**), we noticed that γ_{cmc} decreased from 18.2 mN/m to 15.3 mN/m and cmc slightly changed from 7×10^{-4} mol/L (approximately 0.4 g/L) to 2×10^{-4} mol/L (approximately 0.1 g/L). A similar trend happened to the comparison between C62-Betaine (**4**) and C6-Betaine (**14**), indicating that two extra oxygens could improve surface tension reduction and decrease their cmc by increasing the length of the hydrophobic tail.

To explore the effect of the number of oxygen atoms on γ_{cmc} and cmc, we introduced more oxygen atoms in the fluoroether segment without altering number of fluorinated carbons, such as **8**

Table 1
The surface activity of carboxylic betaine.

Compound	γ_{cmc} (mN/m)	cmc ($\times 10^{-4}$ mol/L)	cmc (g/L)	A_{min} (nm^2)	T (°C)
C62-Betaine	19.0	106	5.2	0.51	23
C72-Betaine	16.5	26	1.4	0.58	28
C82-Betaine	15.3	2	0.1	0.58	24
C92-Betaine	15.5	0.8	0.05	0.62	29
C6-Betaine	22.3	113	5.2	0.44	26
C8-Betaine	18.2	7	0.4	0.46	23
C61-Betaine	21.3	207	9.8	0.56	24
C72-Betaine-E	16.9	19	1.0	0.52	25
C73-Betaine	16.9	12	0.7	0.59	23
OC3-Betaine	22.3	54	2.5	0.52	24
OC4-Betaine	19.1	21	1.1	0.46	22
OC5-Betaine	16.5	0.3	0.02	0.45	23
CH12-Betaine	35.8	11	0.4	0.64	23

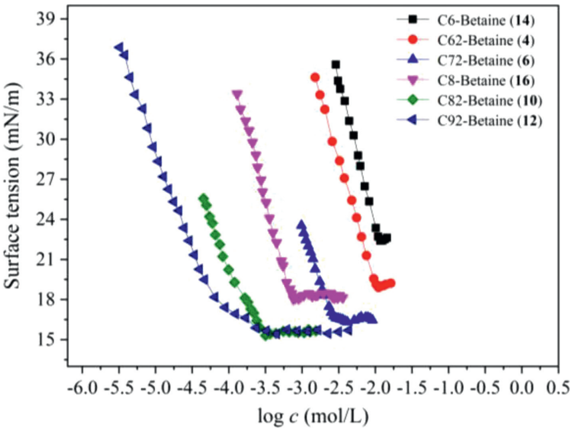


Fig. 1. The γ-log c curves for fluoroether betaine surfactants (**4**, **6**, **10**, **12**, **14** and **16**).

C73-Betaine (containing three oxygen atoms) and **22** OC5-Betaine (containing five oxygen atoms). Among them, the substituent of compound **22** OC5-Betaine is $CF_3(OCF_2)_5$ group. In Table 1 and Fig. 2, we compared fluorosurfactants which have seven fluorinated carbon atoms with different oxygen atoms in fluoroether chain. γ_{cmc} of these compounds were in an order as C72-Betaine (**6**) = OC5-Betaine (**22**) < C72-Betaine-E (**24**) = C73-Betaine (**8**). It seemed that betaine surfactants with the same number of fluorinated carbon atoms had similar γ_{cmc}. However, the cmc of these surfactants were in an order as OC5-Betaine (**22**) < C73-Betaine (**8**) < C72-Betaine-E (**24**) < C72-Betaine (**6**) which meant that the more oxygen atoms inserted, the lower cmc for fluoroether betaine surfactants. Oxygen atom in a hydrocarbon ether is usually considered hydrophilic. In contrast, the oxygen atoms inserted in the fluorinated segment are hydrophobic, which is consistent with our previous observation for fluoroether amine oxides [22]. In general, introducing oxygen atoms into fluorinated chains increased the hydrophobic properties of fluorosurfactants. Krafft and Riess argued that the ether oxygens are sterically sheltered and electron-depleted the bordering electron-withdrawing fluorinated chain, thus ether oxygens increase their resistance to harsh conditions [5]. Accordingly, we propose that there is hardly any hydrogen bond between water and oxygen atom in fluoroether chain [3]. Therefore, we could explain the increasing hydrophobicity with the addition of oxygen atoms.

We compared derivatives of PFHxA C6-Betaine (**14**) with other fluoroether betaine surfactants (**2**, **4** and **20**) which have six fluorinated carbons with different numbers of oxygen atoms inside. The substituent of compound OC3-Betaine (**18**) is $CF_3(OCF_2)_3$ group, which is one carbon less. In Table 1 and Fig. 3, the γ_{cmc} of compounds was in an order as C62-Betaine (**4**) < OC4-Betaine (**20**) < C61-Betaine (**2**) < OC3-Betaine (**18**) = C6-Betaine (**14**) and the cmc of these surfactants was in an order as OC4-Betaine (**20**) < OC3-Betaine (**18**) < C62-Betaine (**4**) < C6-Betaine (**14**) < C61-Betaine (**2**). We found that the number of oxygen atoms had little effect on γ_{cmc} but significant effect on cmc. Finally, we compared three sets of data separately: (1) The γ_{cmc} and cmc of **2** C61-Betaine and **14** C6-Betaine were 21.3 mN/m (9.8 g/L) and 22.3 mN/m (5.2 g/L), respectively. Embedding an oxygen atom in the hydrophobic segment of betaine fluorosurfactant reduced the surface tension of the compound, but the dosage was slightly larger. (2) The γ_{cmc} and cmc of **18** OC3-Betaine and **14** C6-Betaine were 22.3 mN/m (2.5 g/L) and 22.3 mN/m (5.2 g/L). **18** OC3-Betaine has three more oxygen atoms and one less -CF_2- than **14** C6-Betaine, but cmc was significantly lower, and γ_{cmc} was basically the same. (3) The γ_{cmc} and cmc of **2** C61-Betaine, **4** C62-Betaine and **20** OC4-Betaine were 21.3 mN/m (9.8 g/L), 19 mN/m (5.2 g/L) and 19.1 mN/m (1.1 g/L), respectively. It was found that with the same number of fluorinated carbon, the more oxygen atoms were added, the lower cmc was.

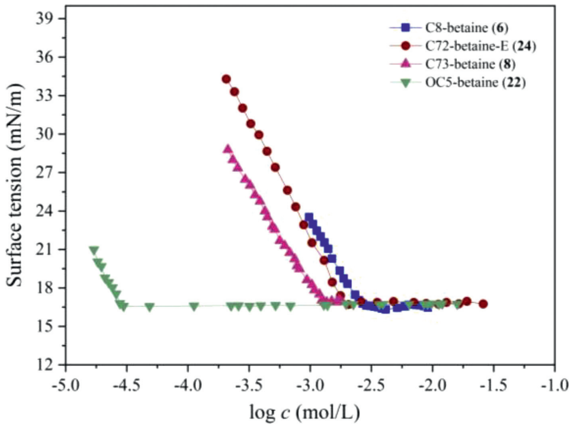


Fig. 2. The γ-log c curves for fluoroether betaine surfactants (**6**, **8**, **22** and **24**).

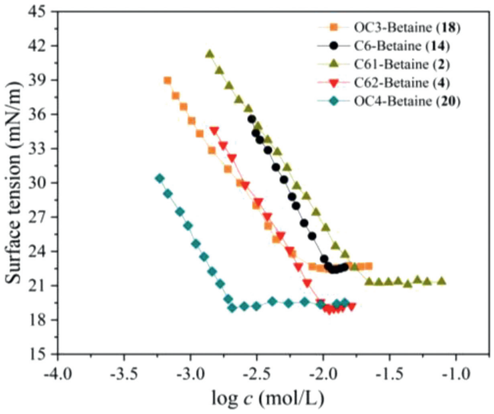


Fig. 3. The γ-log c curves for fluoroether betaine surfactants (**2**, **4**, **14**, **18** and **20**).

In Table 1 and Fig. 4, we compared betaine surfactants with ethylene and propylene linkage. The γ_{cmc} of compounds were in an order as C72-Betaine (**6**) < C72-Betaine-E (**24**) < C8-Betaine (**16**) < C6-Betaine (**14**). The cmc of these surfactants were in an order as C8-Betaine (**16**) < C72-Betaine-E (**24**) < C72-Betaine (**6**) < C6-Betaine (**14**). The γ_{cmc} and cmc of **6** C72-Betaine, **24** C72-Betaine-E and **16** C8-Betaine were 16.5 mN/m (1.4 g/L), 16.9 mN/m (1.0 g/L) and 18.2 mN/m (0.4 g/L), respectively. The difference in compound

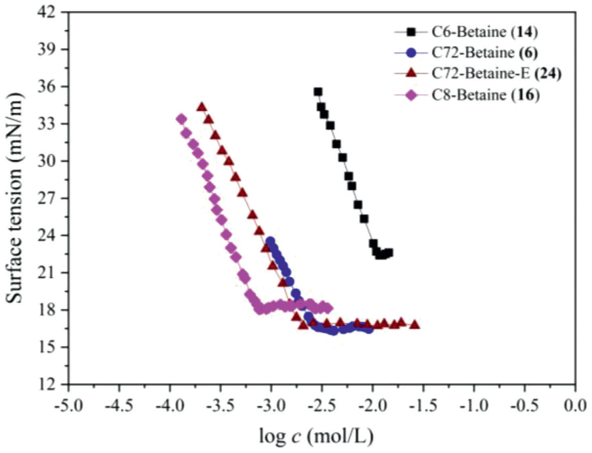


Fig. 4. The γ-log c curves for fluoroether betaine surfactants (**6**, **14**, **16** and **24**).

structure was that **16** had two more oxygen atoms and one less -CF_2- group compared with **6** while their surface activity of remained similar. Judging from experience, we can assume that two oxygen atoms in betaine fluorosurfactants are approximately equal to one -CF_2- fragment.

The surface excess $\Gamma_{\max}$ (also written as Γ_{cmc}) and the molecular limiting area $A_{\min}$ (also written as A_{cmc}) were used to characterize the behavior of surfactant molecules at air-water interface. $\Gamma_{\max}$ is defined as the concentration of surfactant molecules in a surface plane relative to that at a similar plane in the bulk at cmc. $A_{\min}$ corresponds to the area per surfactant molecule at air-water interface at cmc. We calculated $\Gamma_{\max}$ and $A_{\min}$ by using the Gibbs equation:

$$\Gamma_{\max} = -\frac{1}{2.303 \times nRT} \times \frac{d\gamma}{d \log c}$$

and the equation:

$$A_{\min} = \frac{10^{14}}{N_A \Gamma_{\max}}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T denotes the absolute temperature, γ is the surface tension of the surfactant aqueous solution, n was taken as 1 for betaine surfactants and c is the concentration of the surfactant aqueous solution. Here, N_A is Avogadro's constant (6.022×10^{23} mol^{-1}). The $A_{\min}$ of betaines is listed in Table 1.

In general, $A_{\min}$ is closely related to the adsorption of surfactant molecules at the air-liquid interface. As is illustrated in the Table 1, it seemed that $A_{\min}$ of fluoroether betaine with one or two branches in their hydrophobic tail is larger than that with no branch. For example, C61-Betaine, C62-Betaine all had larger $A_{\min}$ over 0.51 nm^2, while $A_{\min}$ of OC4-Betaine was 0.46 nm^2. C72-Betaine, C72-Betaine-E and C73-Betaine all had larger $A_{\min}$ over 0.52 nm^2, while $A_{\min}$ of OC5-Betaine is 0.45 nm^2. It might be explained that the branched CF_3 caused a larger cross-sectional area for the hydrophobic segment than linear one. C6-Betaine and C8-Betaine had a relatively small $A_{\min}$ probably owing to the same reason.

The application of fluorosurfactants in the field of firefighting has received an increasing attention, especially in aqueous film-forming foam (AFFF). However, two important properties in firefighting foams are surface tension and spreading volume. In order to make a water drop spread on an oil surface, its spreading coefficient ($S_{\mathrm{w/o}}$) must be greater than zero.

$$S_{\mathrm{w/o}} = \gamma_{\mathrm{o}} - (\gamma_{\mathrm{w}} + \gamma_{\mathrm{w/o}}) > 0$$

among them, γ_{o} is the surface tension of oil and the surface tension of cyclohexane in this experiment is 25.2 mN/m. γ_{w} is the surface tension of aqueous solution. $\gamma_{\mathrm{w/o}}$ is the oil-water interfacial tension. Theoretically, the aqueous solution of fluorosurfactant can spread on the oil surface only if $(\gamma_{\mathrm{w}} + \gamma_{\mathrm{w/o}})$ is less than γ_{o}. The irreplaceability of fluorosurfactants was illustrated for their excellent γ_{w} reduction. In actual application, after the fluorosurfactant was added to the aqueous solution ($\gamma = 72$ mN/m), the γ_{w} surface tension was reduced to 15–20 mN/m. However, $\gamma_{\mathrm{w/o}}$ can be reduced from 30–40 mN/m to 1–2 mN/m only when the synergistic mixture of fluorosurfactant and hydrocarbon surfactant is used. By adjusting the ratio of hydrocarbon surfactants, we studied the spreading properties of the compound.

The spreading experiment on different betaine fluorinated surfactants were carried out (see Supporting information for details). The results were listed as follows (Fig. 5): (1) The aqueous solution of fluorosurfactant with five fluorinated carbons (C6) (**2**, **4**, **14**, and **18**) did not spread on the cyclohexane. (2) The solution with only hydrocarbon surfactants (**26**) was unable to spread on the cyclohexane. (3) The spreading effect of fluorosurfactant with six fluorinated carbons (C7) (**24**, **6**, and **8**) mixed with 0.2% CAB is better than that with 0.6% CAB. This may be explained by $\gamma_{\mathrm{w/o}}$. (4) The spreading performance of long-chain fluoroether compounds (C82-Betaine and C92-Betaine) was not very good, which was comparable with C8-Betaine. Amazingly, C7 (C72-Betaine-E, C72-Betaine and C73-Betaine) are the best. In general, we assumed that when use of long chain compounds was not compulsory, and we could try out the slightly shorter "C7" series of fluoroether betaine surfactants.

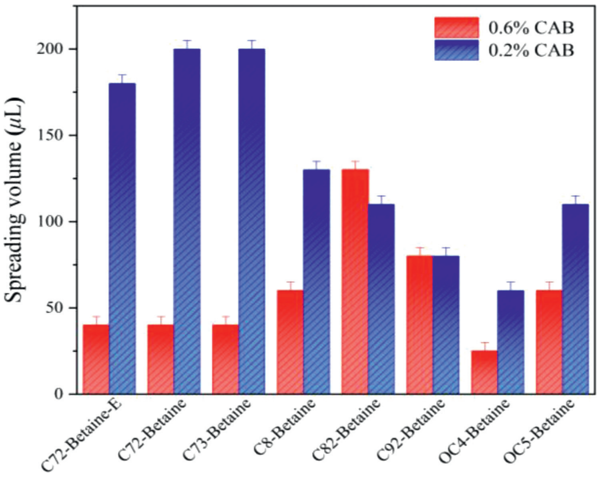


Fig. 5. Spreading volume of various aqueous fluorosurfactants on cyclohexane. The insets show its spreading volume, indicating the extinguishing ability of compounds on oil surface. Red indicates the addition of 0.6% CAB to the fluorosurfactant solution. Blue indicates the addition of 0.2% CAB to the fluorosurfactant.

Meanwhile, studies on the bioaccumulation and toxicity of short-chain fluoroether surfactants have been compared and they indicated a milder effect on creatures, especially on humans than long-chain analogues [16–20]. The bioaccumulation potential of these fluorinated surfactants appeared in the decreasing order of HFPO-TA ≈ PFOA > HFPO-DA in many biological indexes including BCF, IC_{50} and Log K_{ow} for animals or humans (see Supporting information for details). This may suggest that, similar to the case of perfluoroalkyl counterparts, the bioaccumulation of perfluoroether compounds decreases with the shortening of the chain length. However, C62-Betaine (**4**) has better surface activity than C61-Betaine (**2**), but less bioaccumulation in acid form ($CF_3OCF_2CF_2OCF(CF_3)COOH$) according the studies by Guo and his coauthors [23–26]. It might suggest the extra oxygen should give the fluorinated chain more tolerance to creatures and be more ecofriendly which nevertheless needs more evidence to confirm. In one word, the conflict of excellent performance and notorious bioaccumulation of perfluorinated surfactants can be alleviated in alternative oxygen-inserted fluoroether surfactants.

In this article, we found that the properties of C72-Betaine and C8-Betaine fluoroether betaine surfactants were essentially equivalent. Very recently, Yao and his colleagues detected C7 HFPO-TA (the corresponding carboxylic acid to C72-Betaine) in a fluorochemical industrial zone near Taihu Lake [27]. This indicated that C7 HFPO-TA and its derivatives had been applied as an alternative to PFOA and that C7 HFPO-TA might not easily be degraded in the environment. perfluoroalkyl carboxylic acids (PFCAs) and branched perfluoroalkyl ether carboxylic acids could be mineralized through a sodium hydroxide–mediated defluorination pathway in polar aprotic solvents [28]. It was worth to noting that carboxylic acids with the moiety as $OCF(CF_3)COOH$ degraded more rapidly than that with OCF_2CF_2COOH in DMSO [29,30]. Understanding the biodegradation of fluoroether surfactant in the nature is becoming urgent.

The oxygen atoms tend to play an important role in the hydrophobic segment of fluorosurfactants. First, oxygen atoms increase the length of the hydrophobic chain and make the molecules have a certain flexibility which is convenient for the rotation. Both of these two factors are beneficial for reducing surface tension. Work is required if fluorosurfactant molecules escape to the water surface from the bulk when a surfactant molecule is dissolved in water and its hydrophobic part is restricted by highly structured water. Molecules with long hydrophobic segments and flexibility are easy to go away from structured water to the surface, which means much work will be done and therefore the system with fluoroether surfactant is effective in reducing surface tension. According to our experiment, the contribution to reduction of surface tension for one oxygen among the fluoroether chain is approximately half of that for a difluoromethylene group (CF_2). Meanwhile, owing to sterically shield and electron-withdrawing influence from nearby fluorine, oxygens are unfavorable for forming hydrogen bonds so that inserted oxygens appear to be hydrophobic which facilitate the decrease of cmc. On the other hand, the insertion of oxygen atoms makes the hydrophobic segment structure of fluorosurfactants more diversified, providing more variety for alternatives. Finally, research on the perfluoroether is insufficient. The existence of a large amount of fluoroether acids in the environment suggest that oxygen atom is not a “weak point” in a fluorosurfactant molecule. Research on their degradation still needs to continue.

Solving PFOA/PFOS issue is a worldwide, urgent and formidable challenge and lack of basic knowledge is an obstacle to finding out alternatives. In this paper, we have synthesized a series of fluoroether betaine amphoteric surfactants with excellent performance, filling in the gap of surface activity between short and long-chain fluorosurfactants. The introduction of oxygen atoms not only increased the length of the hydrophobic chain and improved the surface activity of the compound, but also makes the compound more structurally diverse. However, HFPO-TA and HFPO-DA are ubiquitous in soil and surface water, and they also exhibit environmental persistence and long-range mobility. Our synthetic surfactants are acceptable as replacements only if they no longer cause "lock-in" problems. Therefore, our synthetic betaines still need to be investigated whether they can be degraded efficiently in the environment, and whether they have environmental persistence and long-distance mobility. In conclusion, the rule of these new fluoroether surfactants could provide a promising direction for future molecular design on PFOS and PFOA alternatives, and finally mediate the conflict between surface performance and environmental effects.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.107961.

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