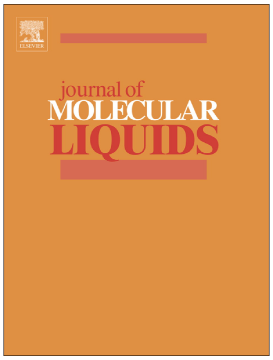

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Synthesis and Structure–Activity Relationships of Nonionic Surfactants with Short Fluorocarbon Chains

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ABSTRACT

The biodegradability of fluorinated surfactants can be improved by reducing the length of the fluorocarbon chain. In this study, ten new nonionic fluorinated surfactants with various hydrophilic and hydrophobic chain lengths were synthesized by means of substitution and ring-opening reactions using methoxypolyethylene glycols (mPEGs) or 2-methoxyethanol, epibromohydrin, and perfluoroalkyl alcohols as raw materials. We measured the static and dynamic surface tension of the synthesized surfactants and used the resulting data to develop structure–activity relationships. We found that mPEG molecular weight was the main determinant of minimum surface tension, and the number of fluorocarbon atoms was the main determinant of critical micelle concentration. Diffusivity decreased with increasing number of fluorocarbon atoms but increased with increasing mPEG molecular weight. Surfactant **5i** showed the best performance, lowering the surface tension of water to 17.89 mN/m.

KEYWORDS

Nonionic fluorinated surfactant, Static surface tension, Dynamic surface tension, Diffusivity coefficient, Structure-activity relationships

1. INTRODUCTION

Compared with traditional hydrocarbon surfactants, fluorinated surfactants have outstanding physico-chemical properties determined by the very special properties of fluorine. Fluorinated surfactants have high heat stability and chemical stability because the C-F bond is very strong and chemically stable. Fluorine has a larger size than hydrogen and is more electronegative, but its polarizability is smaller. Due to the low polarizability, the interaction between the fluorinated chains is weak, resulting in low cohesive energy of fluorocarbons and consequently low surface tension and low critical micelle concentration (CMC) [1]. Fluorinated surfactants can be divided into two categories, ionic and nonionic, depending on the polarity of their hydrophilic groups. Many syntheses of ionic fluorinated surfactants have been reported [2–6]. Nonionic fluorinated surfactants, which have different properties than ionic fluorinated surfactants. They can act as antifogging agents for glass, metal, and plastic surfaces [7]. When used in hard-surface-cleaning formulations, they impart better wetting, emulsifying, dispersing, and solubilizing properties [8], and they are also used to lower the surface tension of stimulating fluids for petroleum recovery [9].

Nonionic fluorinated surfactants are divided into two main types on the basis of their hydrophilic polar groups: polyol types and polyethylene glycol types. Polyol surfactants are generally obtained by reactions of organic compounds containing multiple hydroxyl groups (e.g., glycerin, glycerol pentaerythritol, sorbitan, and sucrose) with fluorinated compounds [10–16]. Polyethylene glycol, a nontoxic and harmless hydrophilic compound, has been widely used for the synthesis of nonfluorinated surfactants [17–20]. Modified polyethylene glycols are also used for the synthesis of nonionic fluorinated surfactants [21–25] by means of reactions with fluoroalkyl alcohols, which are readily available hydrophobic raw materials [26]. The Zaggia group [27] investigated the effect of polyethylene glycol molecular weight (up to approximately 1000 g/mol) on the critical micelle concentration and surface tension of aqueous solutions of surfactants synthesized by reactions of the polyethylene glycols with 2-(perfluorooctylmethyl)oxirane, which has eight fluorocarbon atoms. They found that the CMC depended on the number of EO groups. The increase in the value of n (the number of ethylene oxide units) from 1 to 20 induces an increase of CMC from 9.3×10^{-5} mol/L to 188×10^{-5} mol/L. The Hedhli group [28] prepared surfactants by means of reactions between polyethylene glycols with molecular weights up to 500 g/mol and fluorinated mercaptans with six or eight fluorocarbon atoms. They found that the CMC was more sensitive to the number of ethylene oxide units than the numbers of fluorocarbon atoms.

Although there have been important advances in design of polyethylene glycol nonionic fluorinated surfactants, most of them are concentrated in long fluorocarbon chains (>6). However, such surfactants are particularly difficult to degrade; not only are they persistent and bioaccumulative but they also can be transported over long distances in the environment [27, 29]. Therefore, the need for new, environmentally friendly fluorinated surfactants is urgent. One way to facilitate biodegradation is to shorten the fluorocarbon chain [22, 26], and this strategy has potential utility for the development of biodegradable fluorine-containing surfactants.

In this study, we used environmentally friendly methoxypolyethylene glycols (mPEGs) or 2-methoxyethanol, epibromohydrin, and short-fluorocarbon-chain (≤6) perfluoroalkyl alcohols as raw materials for the synthesis of surfactants with various hydrophilic and hydrophobic chain lengths by means of sequential substitution and ring-opening reactions. We then measured the static and dynamic surface tension of aqueous solutions of the surfactants and used the resulting data to develop structure–activity relationships.

2. MATERIALS AND METHODS

2.1. Chemicals and Instruments

mPEG-1000 (m = 22) were purchased from Innochem Co., Ltd. (Beijing, China); mPEG-500 (m = 11) was purchased from Macklin Co., Ltd. (Shanghai, China) and mPEG-200 (m = 4) and 2-methoxyethanol were purchased from 3A Co., Ltd. (Shanghai, China). 1H,1H-perfluoro-1-heptanol (n = 5) was purchased from J&K Co., Ltd. (Beijing, China); 1H,1H-perfluoro-1-hexanol (n = 4) and 1H,1H-perfluoro-1-

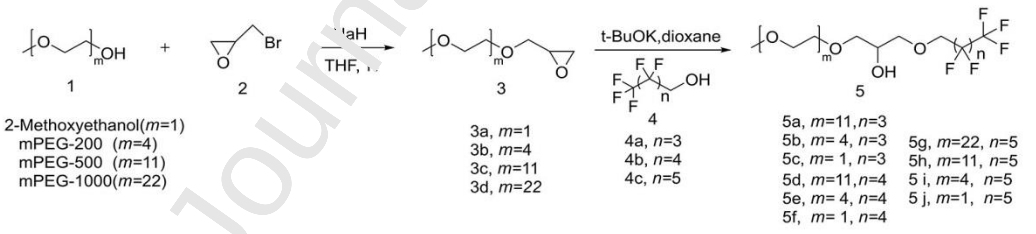
pentanol (n = 3) were purchased from 3A Co., Ltd. (Shanghai, China). All reagents were used as received. All the reactions were performed under Ar atmosphere. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Bruker AV 400 spectrometer. Surfactant molar masses and their distributions were determined by gel permeation chromatography (GPC) on a Waters 1525 instrument with THF as the mobile phase.

2.2. Surface Tension Measurements

Static surface tension values for aqueous solutions were measured by means of a platinum ring test at 25 ± 1 °C on an automatic processor tensiometer (JK99M). Reported values were averages of three measurements. Dynamic surface tension values were measured by means of the maximum bubble pressure method at 25 ± 1 °C on a Kruss BP100 tensiometer. Both instruments were calibrated with pure water prior to sample measurements.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Surfactants and Determination of Their Structures



Scheme 1. Synthesis of surfactants **5**

Nonionic fluorinated surfactants **5a**–**5j** were obtained by reactions of epibromohydrin **2** with mPEGs or 2-methoxyethanol **1** at room temperature and subsequent ring-opening reactions of the resulting mono-epoxide-functionalized mPEGs or 2-methoxyethanol **3** with perfluoroalkyl alcohols **4** (Scheme 1). Because the surfactant products have a hydroxyl group, they can also undergo ring-opening reactions with **3**. To minimize these side reactions, we screened various reaction temperatures and **3**:**4** feed ratios and monitored the results by means of GPC and ^{1}H NMR spectroscopy. In Table 1, the optimal conditions for the synthesis of each surfactant were listed. In the GPC spectra of **5g** (m = 22, n = 5, Figure 1) obtained under the optimized condition, the product peak appeared at retention times between 25 and 27.5 min, and there were no peaks with shorter retention times, which indicate that the side reactions were essentially prevented. The purities of surfactants **5a, 5d, 5h** were also determined by GPC spectra (see Figure S23).

entry	3	4	feed ratio (**3**:**4**)	temperature (°C)	surfactants (5)
1	**3a**	**4a**, **4b**, **4c**	1:3	80	**5c**, **5f**, **5j**
2	**3b**	**4a**, **4b**, **4c**	1:3	50	**5b**, **5e**, **5i**
3	**3c**	**4a**, **4b**, **4c**	1:4	70	**5a, 5d**, **5h**
4	**3d**	**4c**	1:5	90	**5g**

[a] *t*-BuOK(1 equiv.) was used, the reaction time was 24 h.

Table 1. Ring opening conditions of intermediates **3**$^{\mathbf{a}}$

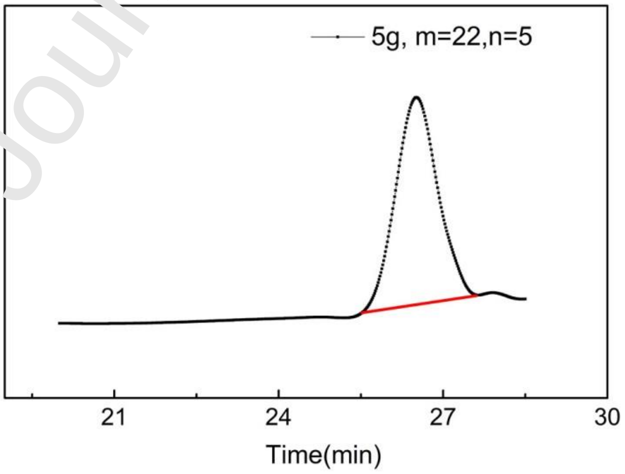


Figure 1. GPC spectra of **5g**

The structures of products with m = 4 or 1 could easily be determined by ^{1}H

NMR spectroscopy. For example, in the spectrum of **5b** (*m* = 4, *n* = 3; Figure 2), H3 appeared as a triplet at δ 4.20 with an integration value of 2, and the integration values for H1 and H2 were 2.96 and 0.90, respectively; these values are consistent with the expected H3/H1/H2 ratio (2:3:1). The purities of surfactants **5** were determined by ^{1}H NMR and ^{19}F NMR (see Figure S3 - S22).

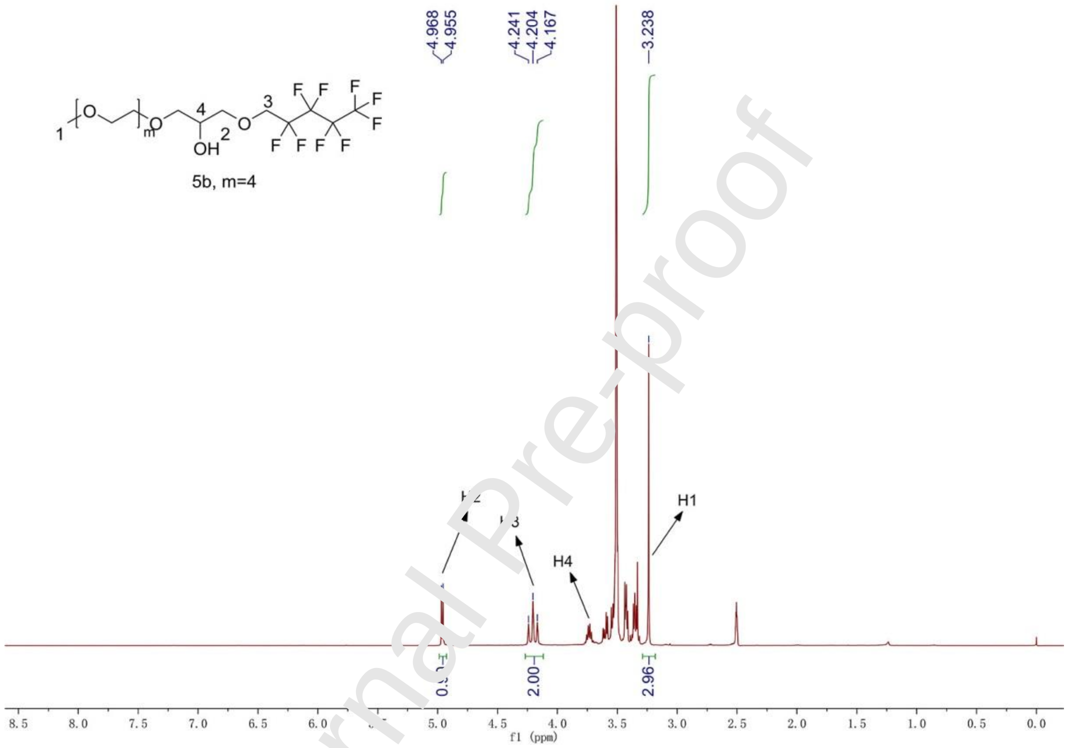


Figure 2. ^{1}HNMR spectrum of **5b**

3.2. Static Surface Tension

For each surfactant **5**, we plotted surface tension (*γ*) versus the logarithm of surfactant concentration (*C*, millimolar) to determine the CMC and the lowest surface tension ($\gamma_{\min}$); representative plots are shown in Figure 3. In addition, we calculated maximum surface excess concentrations ($\Gamma_{\max}$) and minimum areas per surfactant molecule ($A_{\min}$) by using the Gibbs adsorption isotherm equations [30, 31]. The formulas for calculating these quantities are as follows:

$$\Gamma_{\max} = \frac{-1}{2.303\, n\, R\, T}\left(\frac{\partial \gamma}{\partial \lg C}\right) \qquad (1)$$

$$A_{\min} = \frac{10^{18}}{N_{\mathrm{A}}\, \Gamma_{\max}} \qquad (2)$$

Where γ is the surface tension of surfactant solution, C is the bulk concentration of surfactant, n is a constant (for nonionic surfactants, $n = 1$), R is the gas constant (8.314 J/(mol• K)), T is absolute temperature (K), and N_A is the Avogadro constant (6.022×10^{23} mol^{-1}). The value of $\partial\gamma/\partial \lg C$ is determined from the slope of the linear fitting of the surface tension and lg C curve before CMC. The values determined from the plots and equations are shown in Table 2.

surfactant	n	m	CMC[b] (mmol/L)	$\gamma_{\min}$[c] (mN/m)	$\Gamma_{\max}$[d] (mol/m^2)	$A_{\min}$[e] (nm^2)
5a	3	11	4.46	23.05	4.94×10^{-3}	3.36×10^{-4}
5b	3	4	4.27	18.41	6.07×10^{-3}	2.74×10^{-4}
5c	3	1	—	34.89[a]	—	—
5d	4	11	1.21	22.62	5.47×10^{-3}	3.04×10^{-4}
5e	4	4	0.95	18.10	6.18×10^{-3}	2.69×10^{-4}
5f	4	1	—	24.42[a]	—	—
5g	5	22	0.77	34.51	3.36×10^{-3}	4.90×10^{-4}
5h	5	11	0.35	23.21	5.99×10^{-3}	2.77×10^{-4}
5i	5	4	0.20	17.89	6.28×10^{-3}	2.65×10^{-4}
5j	5	1	—	18.26[a]	—	—

[a]The γ of the surfactant at 0.5 mmol/L. [b]The critical micelle concentration. [c]The lowest surface tension measured. [d]The maximum excess surface concentration. [e]The minimal area per surfactant molecule.

Table 2. $\gamma_{\min}$, CMCs, $\Gamma_{\max,}$ and $A_{\min}$ of surfactants **5**

The data provided in Figure 3 show that for a given concentration, surface tension decreased with decreasing mPEG molecular weight. In table 2, $\gamma_{\min}$ also decreased as mPEG molecular was decreasing. For example, when *n* was 5, decreasing *m* from 22 to 4 decreased $\gamma_{\min}$ from 34.51 (**5g**) to 17.89 (**5i**) mN/m, respectively. The reason for this trend may have been that changing the size of the hydrophilic group changed the adsorption density of the surfactant; that is, decreasing the size of the mPEG chain may have increased the ability of the surfactant molecules to replace water molecules at the water–air interface, resulting in tighter gathering of the surfactant molecules at the interface [27].

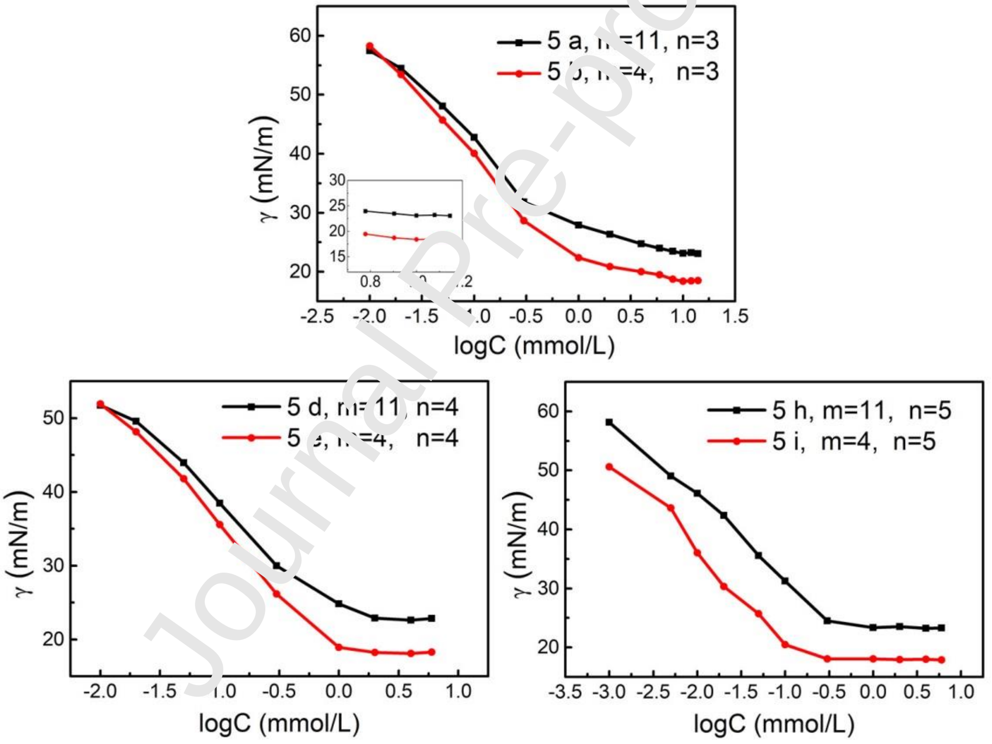


Figure 3. Surface tension as a function of logC for aqueous solutions of **5a**, **5b**, **5d**, **5e**, **5h** and **5i**

Plots of surface tension versus surfactant concentration for surfactants with a given mPEG molecular weight and different numbers of fluorocarbon atoms are compared in Figure 4. These plots show that for a given concentration, surface tension decreased with increasing number of fluorocarbon atoms. As shown in Table 2, γ_{min} also decreased as the number of fluorocarbon atoms was increased. For example, for surfactants with $m = 4$, increasing n from 3 to 5 decreased γ_{min} from 18.41 (**5b**) to 17.89 (**5i**) mN/m, respectively.

Further analysis of the data in Figure 4 and Table 2 shows that surfactants with $m = 11$ or 4 exhibited the same trend, the γ_{min} values for **5a**, **5d**, **5h** ($n = 3$–5) were all approximately 23 mN/m and all the surfactants with $m = 4$ (**5b**, **5e**, **5i**, $n = 3$–5) had similar γ_{min} values of approximately 18 mN /m. These results indicate that mPEG molecular weight was the main determinant of γ_{min}, a result that differs from that for previously reportedly surfactants prepared by reactions of fluorinated mercaptan and polyethylene glycol [28], probably because when there are fewer fluorocarbon atoms, the hydrophobicity is much lower than when there are eight. It was worth noting that for $m = 1$ (**5c**, **5f**, **5j**), when the concentration was higher than 0.5 mmol/L, the sample would not dissolve completely, but the surface tension would still decrease slowly. The surface tension was not balanced before 0.5 mmol/L; therefore, we could not calculate the CMC and γ_{min} values.

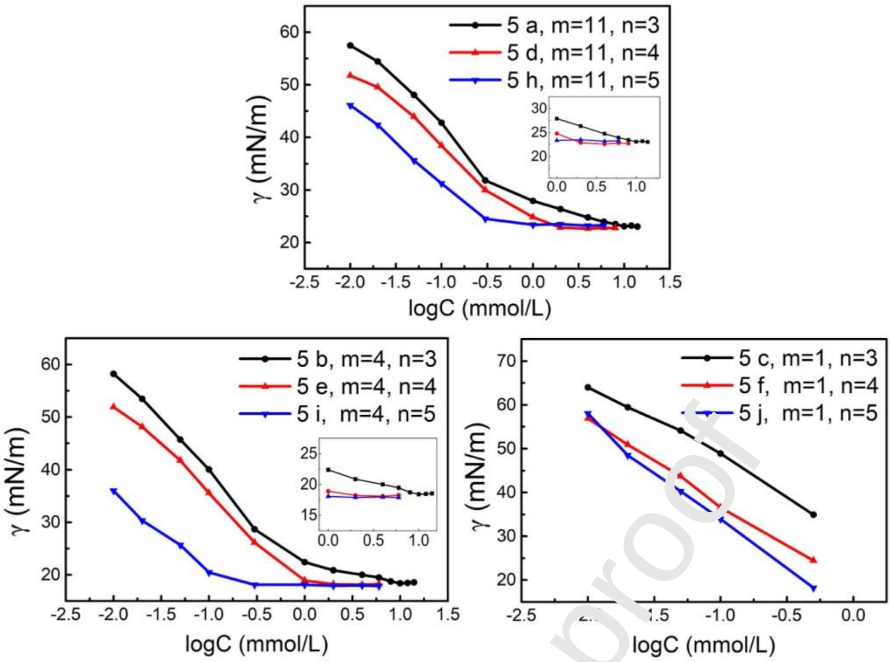


Figure 4. Surface tension against logC for aqueous solutions of **5a**, **5b**, **5c**, **5d**, **5e**, **5f**, **5h**, **5i** and **5j**

The value of γ_{min} can be an indication of a surfactant's effectiveness at reducing surface tension. From Table 2, when *n* was 3, 4, or 5 and *m* was 4, γ_{min} dropped below 20 mN/m. Surfactant **5i** had the greatest effect on surface tension, reducing γ_{min} to as low as 17.89 mN/m.

As shown in Table 2, CMC decreased with increasing fluorocarbon chain length but increased with increasing mPEG molecular weight. For example, the CMCs of **5b**, **5e** and **5i** (*m* = 4) were 4.27, 0.95, and 0.20 mmol/L, respectively; and the CMCs of **5g**, **5h**, and **5i** (*n* = 5) were 0.77, 0.35, and 0.20 mmol/L, respectively. These results can be explained by the fact that an increase in the length of the hydrophilic chain enhanced the solubility of the surfactant and therefore hindered micelle formation; shorter mPEG chains seem to favor micelle formation [28]. In addition, increasing the fluorocarbon chain length increased the steric bulk of the surfactant, which led to an increase in the aggregation number and favored micelle formation [32]. Further analysis of the data in Table 2 indicates that for a given fluorocarbon chain length (**5a**, **5b** (*n* = 3); **5d**, **5e** (*n* = 4); and **5g**, **5h**, **5i** (*n* = 5)), there was little variation in CMC. For example, the CMCs of **5a** and **5b** were 4.46 and 4.27 mmol/L. However, for a given mPEG molecular weight, CMC varied considerably; for example, the CMCs of **5a**, **5d**, and **5h** (*m* = 11) were 4.46, 1.21, and 0.35 mmol/L, respectively. These results suggest that the number of fluorocarbon atoms was the main determinant of CMC.

For surfactants with a given fluorocarbon chain length, the saturated adsorption capacity ($\Gamma_{\max}$) decreased with increasing mPEG molecular weight (Table 2). For surfactants with a given mPEG molecular weight, $\Gamma_{\max}$ increased as the number of fluorocarbon atoms increased. Accordingly, $A_{\min}$ decreased with decreasing mPEG molecular weight and increasing number of fluorocarbon atoms. This result can be explained by noting that increasing the size of the mPEG increases the head group size and thus lowers surfactant adsorption and that increasing the fluorocarbon chain length results in closer packing of the surfactant molecules [32–34].

In short, the structures of both the hydrophobic and the hydrophilic portions of the surfactants markedly affected their adsorption at the air–water interface. The molecular weight of mPEG was the main determinant of $\gamma_{\min}$, and the number of fluorocarbon atoms was the main determinant of CMC.

3.3. Dynamic Surface Tension

For the three surfactants with the same hydrophobic chain (*n* = 5, **5i**, **5h** and **5g**) and the three surfactants with the same hydrophilic chain (*m* = 4, **5b**, **5e**, **5i**), the temporal dependences of surface tension at concentrations of 0.1, 0.5, 1, and 2 times the CMC are plotted in Figures 5 and 6, respectively. The plots indicate that as the surfactant concentration increased, both the rate and the magnitude of the reduction in dynamic surface tension increased.

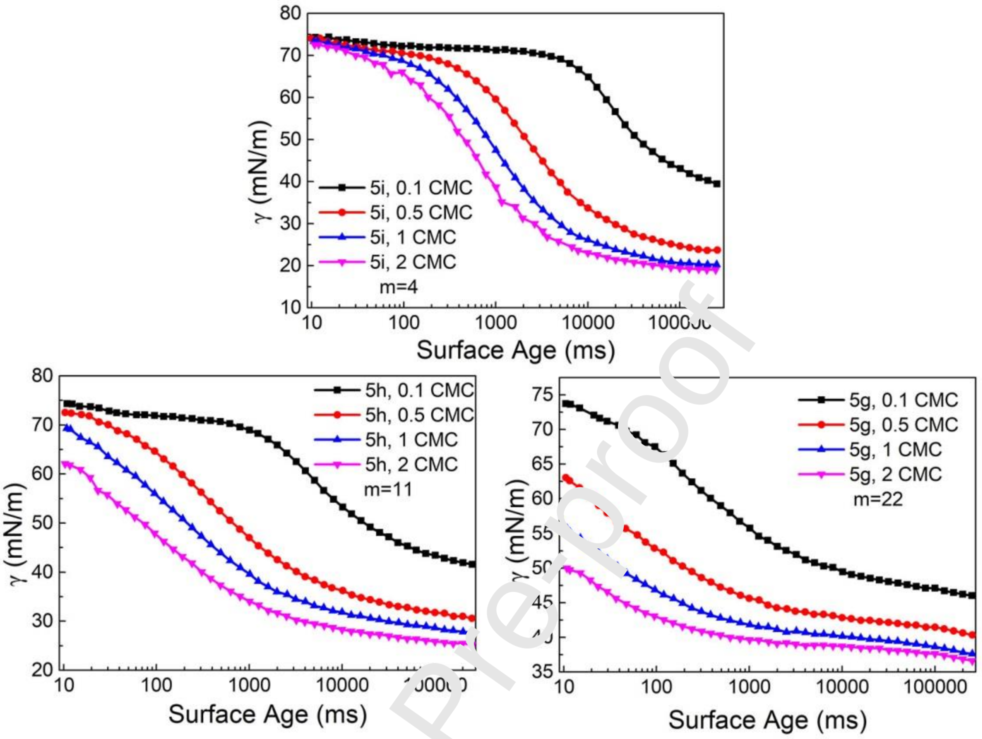


Figure 5. Dynamic surface tension data for **5i**, **5h** and **5g** at various concentrations

As shown in Figure 5, the trends for surfactants **5h** and **5g**, which have relatively large hydrophilic groups (*m* = 11 and 22, respectively), were similar to each other. The initial surface tension decreased with increasing concentration; for example, at 10 ms, the surface tension of an aqueous solution of **5g** at a concentration of 2 times the CMC was 50 mN/m, versus 73 mN/m at 0.1 times the CMC. However, when the hydrophilic group was small (*m* = 4 for **5i**), regardless of the concentration, the surface tension dropped more slowly. For example, the surface tension of an aqueous solution of **5i** with 2 times the CMC was 65 mN/m at 100 ms.

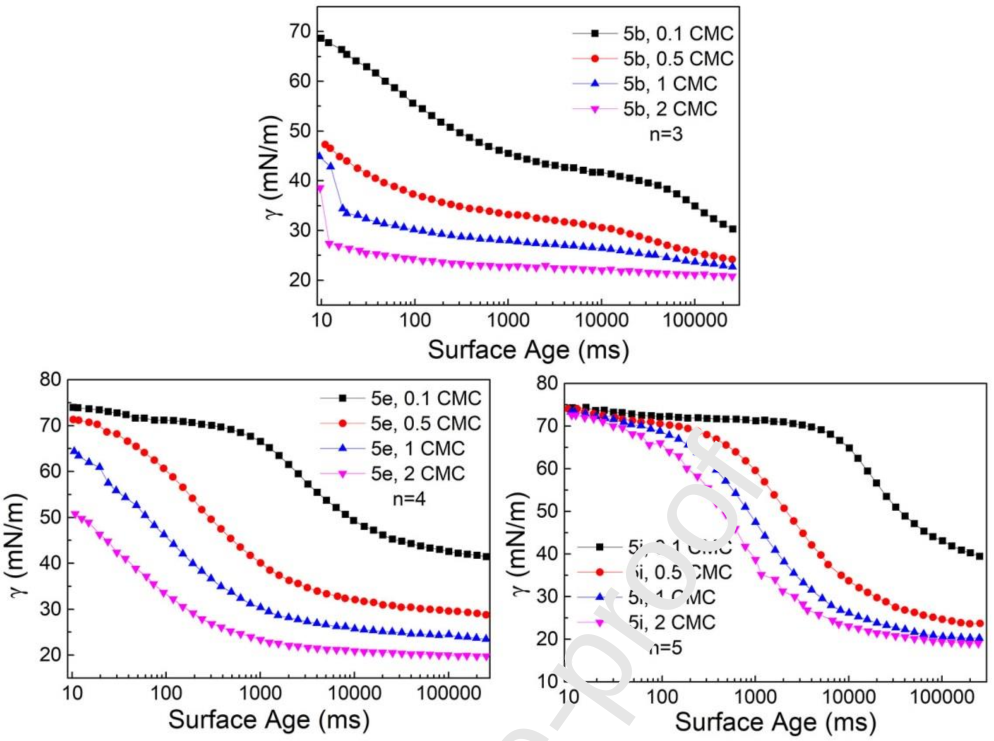


Figure 6. Dynamic surface tension data for **5b**, **5e** and **5i** at various concentrations

As shown in Figure 6, when the number of fluorocarbon atoms was small (n = 3 for **5b**), surface tension dropped quickly to below the solvent surface tension regardless of the concentration. For example, when the concentration of **5b** was 0.5 times the CMC, the surface tension dropped to about 50 mN/m at 10 ms. When the concentration of **5e** (n = 4) was 0.5 times the CMC, at 10 ms, the surface tension was close to that of water. For surfactants with n = 5, the surface tension dropped more slowly, regardless of the concentration. These results indicate that the structure of a surfactant strongly affected its diffusion rate; surfactants with large mPEGs and short fluorocarbon chains diffused faster at the air–water interface and were adsorbed more efficiently than surfactants with small mPEGs and long fluorocarbon chains. The effects of surfactant structure on diffusion in aqueous solution will be discussed later.

The curves in Figures 5 and 6 can be divided into four regions: the induction region, the rapid-fall region, the meso-equilibrium region, and the equilibrium region. The first three regions can be described by Eq. 3. Take the logarithm of both sides of Eq. 3 to get Eq. 4. Ploting log t with $\log[(\gamma_0-\gamma_t)/(\gamma_t-\gamma_m)]$, We can obtain n and t* values from slope and intercept, respectively[35].

$$\frac{\gamma_0-\gamma_t}{\gamma_t-\gamma_m}=(\frac{t}{t^*})^n \qquad (3)$$

$$\log[(\gamma_0-\gamma_t)/(\gamma_t-\gamma_m)]=n\log t-n\log t^* \qquad (4)$$

Where γ_0 is the surface tension of water; γ_t is the surface tension of the solution at time t; and γ_m is the surface tension at the meso-equilibrium. The values of parameters t^* and n can be used to understand the characteristics of the surfactant. These values can be obtained by fitting the surface tension value at different times. The t^* value depends on how fast the surfactant diffuses from the bulk solution to the subsurface, a lower t^* value indicates a smaller diffusion barrier and faster diffusion of the surfactant. The n value reflects the difference between the energies of surfactant adsorption and desorption. The larger the n value, the higher the potential barrier of surfactant adsorption and the slower the molecular diffusion [32].

As can be seen from the data in Table 3, for solutions of surfactants **5i**, **5h**, and **5g** (n = 5), whose surface tension values reached equilibrium in 200,000 ms, t^* decreased as the molecular weight of mPEG increased, regardless of concentration. This result shows that the larger the hydrophilic group, the faster the surfactant diffused at the air–water interface and the more efficiently it was adsorbed. The reason for this phenomenon may be that increasing the size of the hydrophilic group increased the solubility of the surfactant in the aqueous solution, which in turn accelerated diffusion of the surfactant molecules from the bulk phase to the air–water interface [36].

surfactant (n = 5)	Conc (time of CMC)	n	t^* (ms)	γ_m (mN/m)
5i, m = 4	0.1CMC	1.69	17246	43.06
	0.5CMC	1.23	1980	28.77
	1CMC	1.15	1068	22.24
	2CMC	1.04	647	19.96
5h, m = 11	0.1CMC	1.25	6194	43.44
	0.5CMC	0.79	636	31.64
	1CMC	0.71	237	28.64
	2CMC	0.65	84	26.36
5g, m = 22	0.1CMC	0.84	601	47.07
	0.5CMC	0.57	43	41.46
	1CMC	0.55	10	39.41
	2CMC	0.47	3	37.65

Table 3. Dynamic surface tension parameters for aqueous solutions of **5i**, **5h**, and **5g** at various concentrations

surfactant (m = 4)	Conc (time of CMC)	n	t^* (ms)	γ_m (mN/m)
5b, n = 3	0.1CMC	0.70	151	37.36
	0.5CMC	0.47	3.75	30.32
	1CMC	0.30	0.11	24.99
	2CMC	0.41	0.06	21.88
5e, n = 4	0.1CMC	1.17	3225	42.98
	0.5CMC	0.94	294	30.39
	1CMC	0.76	81	24.49
	2CMC	0.70	21	20.19
5i, n = 5	0.1CMC	1.69	17246	43.06
	0.5CMC	1.23	1980	28.77
	1CMC	1.15	1068	22.24
	2CMC	1.04	647	19.96

Table 4. Dynamic surface tension parameters for aqueous solutions of **5b**, **5e** and **5i** at various concentrations

For surfactants **5b**, **5e**, and **5i** (*m* = 4), whose surface tension values reached equilibrium in 200,000 ms, *t** increased with increasing fluorocarbon chain length at all concentrations (Table 4), which shows that the surfactant with a short fluorocarbon chain diffused faster at the air–water interface and was adsorbed more efficiently than the surfactant with long fluorocarbon chains. The reason for this may be that the long-chain surfactant molecules are larger, which would hinder their diffusion from the bulk solution to the subsurface, making it difficult for them to be adsorbed from the solution to the air–water interface [37, 38].

3.4. Diffusivity Coefficients

The surfactant adsorption process includes two sequential steps: the surfactant molecules diffuse from the bulk aqueous phase to the subsurface and then they adsorb from the subsurface to the air–water interface [39]. The modified Ward–Tordai equation can be used to describe diffusion-controlled adsorption on a fresh surface. For the nonionic surfactants, corresponding simplified Eqs. (5) was obtained at the initial stage of the adsorption [40–42].

$$\gamma(t)_{t\to 0} = \gamma_0 - 2RTC_0\sqrt{\frac{Dt}{\pi}} \qquad (5)$$

where γ_0 is the surface tension of pure water; Γ_{eq} is the surface excess concentration, which can be obtained from the equilibrium surface tension measurements; C_0 is surfactant concentration; and *D* is the diffusion coefficient.

We evaluated the temporal dependence of surface tension for solutions of **5i**, **5h**, and **5g**, which have the same hydrophobic chain, at a concentration of 0.2 mmol/L and for solutions of **5b**, **5e**, and **5i**, which have the same hydrophilic chain, at a concentration of 0.6 mmol/L (Figure 7). These concentrations were chosen to ensure that the initial surface tension value of the surfactant solution was >65 mN/m and that the adsorption layer was a dilute solution; if these conditions are not met, the formula (5) is no longer applicable [37]. In addition, the concentration must be high enough to minimize lateral diffusion of the surfactant from the thick surface to the thin surface of a generated air bubble, known as the Gibbs–Marangoni effect [43], causing the dominance of the vertical surfactant diffusion from the bulk liquid to the new surface of a generated air bubble.

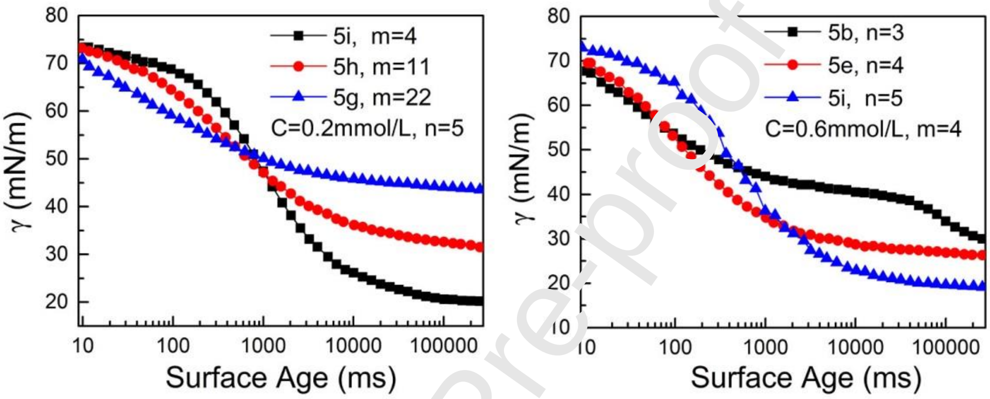


Figure 7. Dynamic surface tension data for **5i**, **5h**, **5g** at 0.2 mmol/L and **5b**, **5e**, **5i** at 0.6 mmol/L

According to Eq. (5), $\gamma(t)(t \rightarrow 0)$ of the solution is linearly related to $t^{1/2}$, therefore the D values can be determined from the slopes of the plots in Figure 8 and the values are listed in Table 5. During the initial stage of adsorption, D increased with increasing mPEG molecular weight and decreased as fluorocarbon chain length increased. These results indicate that increasing the size of the hydrophilic group increased surfactant solubility, enhanced surfactant mobility in the aqueous solution, and thus resulted in an increase in the diffusion rate. In contrast, increasing the hydrophobic chain length increased the size of a surfactant molecule and decreased its solubility, which reduced the its mobility in the aqueous solution, which in turn resulted in a decrease in the diffusion rate [32]; these results are the same as those obtained by comparing the *t** values.

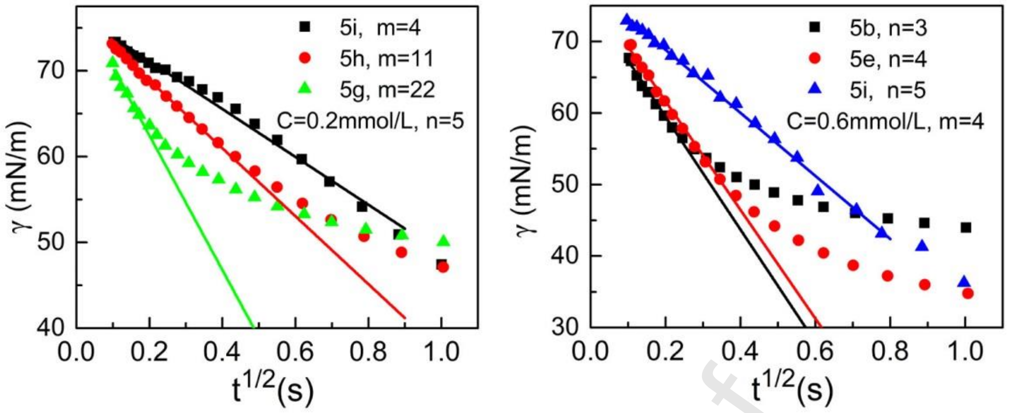


Figure 8. The linear behavior of γ(t)–t $^{1/2}$ determined by the short time of **5i**, **5h**, **5g** and **5b**, **5e**, **5i**

	surfactant	D (m^2/s)
Same hydrophobic chain (n = 5) C = 0.2 mmol/L	**5i**, m = 4	2.49×10^{-9}
	5h, m = 11	5.01×10^{-9}
	5g, m = 22	1.97×10^{-8}
Same hydrophilic chain (m = 4) C = 0.6 mmol/L	**5b**, n = 3	2.20×10^{-9}
	5e, n = 4	2.05×10^{-9}
	5i, n = 5	6.91×10^{-10}

Table 5. Diffusion coefficients of **5i**, **5h**, **5g** and **5b**, **5e**, **5i**

4. CONCLUSION

Ten nonionic surfactants with short fluorocarbon chains (≤6) and various mPEG molecular weights or 2-methoxyethanol were synthesized and characterized by ^{1}H NMR, ^{19}F NMR, and GPC. Detailed analysis of structure–activity relationships were conducted, which can provide a theoretical basis for designing nonionic fluorinated surfactants with practical applications. Measurement of the static and dynamic surface tension of the surfactants revealed that for a given number of fluorocarbon atoms, decreasing the mPEG molecular weight decreased the surface tension, CMC, and diffusion rate. In contrast, for a given mPEG molecular weight, increasing the number of fluorocarbon atoms decreased the surface tension, CMC, and diffusion rate. The molecular weight of mPEG was the main determinant of γ_{min}, and the number of fluorocarbon atoms was the main determinant of CMC. Surfactant **5i** reduced the surface tension the most, reducing γ_{min} to 17.89 mN/m. On the basis of the results of this structure–activity relationship study, we are exploring applications of the surfactants for pesticides.

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Notes

The authors declare no competing financial interest.

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Supplementary Material

Supporting Information of general synthesis procedure and characterization for **3a**–**3d** and **5a**–**5j**.

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Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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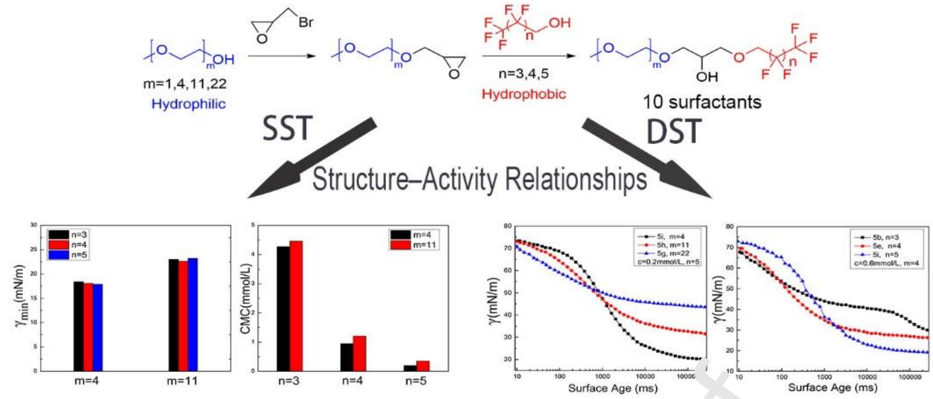
GRAPHICAL ABSTRACT



Highlights

1. Ten new nonionic fluorinated surfactants were designed and synthesized.

2. The synthesized surfactants exhibited a novel structure-activity relationship.

3. Methoxypolyethylene glycol molecular weight determines minimum surface tension.

4. The number of fluorocarbon atoms determines critical micelle concentration.