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Adsorption Behavior of Fluorocarbon Surfactants on Polytetrafluoroethylene Surface

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Abstract: By using the sessile drop method, the wetting properties of nonionic fluorocarbon surfactants (FNS-1 and FNS-2) and anionic fluorocarbon surfactant (FAS) solutions on the surface of polytetrafluoroethylene (PTFE) were investigated. Meanwhile, the effects of surfactant concentration on the contact angle, adhesion tension, PTFE–liquid interfacial tension, and work of adhesion of the fluorocarbon surfactant with different structures were detected. The results demonstrate that the adsorption amount of the three fluorocarbon surfactants at the air–liquid interface is 1.5~2 times higher than their adsorption amount at the PTFE–solution interface. Before critical micelle concentration (CMC), the fluorocarbon surfactant molecules rely on their hydrophobic groups to adsorb on the PTFE surface. The smallest molecular size of FNS-2 results in the largest adsorption amount, while electrostatic repulsion and large steric hindrance result in the smallest adsorption amount for FAS. Above CMC, the fluorocarbon surfactants form semi-micelles to adsorb on the PTFE surface. The hydrophilic modification ability of the three fluorocarbon surfactants for the PTFE surface is stronger than that of reported surfactants, and the contact angle can be reduced to about 20° at high concentrations. The order of the hydrophilic modification ability is FNS-2 > FNS-1 > FAS. Hydrophilic EO groups can effectively enhance the hydrophilicity of FNS-1 and FNS-2. Due to the hydrophobic -CH_3 group and the smaller adsorption amount, FNS-1 possesses a weaker hydrophilic modification ability than FNS-2. Investigating the adsorption behavior of fluorocarbon surfactants on the PTFE surface can help us to better utilize fluorocarbon surfactants. This could have broad implications for colloid and interface science.

Keywords: fluorocarbon surfactant; wettability; contact angle; polytetrafluoroethylene; adsorption mechanism

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1. Introduction

The wettability of solid surfaces involves multiple areas in industrial production and daily life, such as daily necessities, medical devices, coatings, paints, and nanomaterials. Surfactants can adsorb on the surface of solid materials, thus changing the solid surface's wettability [1–3]. By investigating the wettability of solid surfaces, the surface chemistry, physical properties, hygroscopicity, and other characteristics of solid materials can be explored [4].

Polytetrafluoroethylene (PTFE) is a solid surface with low surface energy. In addition, PTFE exhibits high hydrophobicity, strong non-stickiness, good corrosion resistance, and heat resistance abilities. Accordingly, these unique surface properties enable PTFE to play a vital role in non-adhesive coatings and anti-stick materials. Since water and many solvents have difficulty wetting the surface of PTFE, it is of great significance to investigate the wetting properties of PTFE surfaces by surfactants. Zhou et al. [5] determined the contact angles of zwitterionic surfactants (betaines $C_{16}PB$, $C_{16}GPB$, $C_{16}(EO)_3PB$, $C_{16}G(EO)_3PB$) on the PTFE surface, and it was found that the branched structure and polyoxyethylene (EO) units can significantly increase the adhesion tension of these zwitterionic surfactants. Wang et al. [6] found that cationic surfactant dodecyltrimethylammonium bromide ($C_{12}TAB$) and anionic surfactant sodium dodecyl sulfate (SDS) exhibited a synergistic effect in wetting the PTFE surface. Since the SDS-$C_{12}TAB$ mixture was compactly arranged at the PTFE–water interface, the hydrophilic modification of the PTFE surface was significantly improved. Du et al. [7] investigated the effect of the polyoxypropene (PO) chain's length on the wettability and adsorption properties of extended anionic surfactants on the PTFE surface. It was found that the extended surfactants relied on hydrophobic groups to adsorb on the PTFE surface and formed a compacted interfacial film. Zhi et al. [8] explored the adsorption behaviors of different didecyl quaternary ammonium salts on the PTFE surface by using the sessile drop method, and it was found that the contact angle of didecyl quaternary ammonium salts initially decreased, and then increased with increasing size of the counterions.

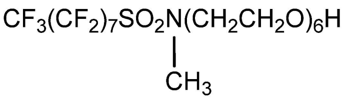
As a type of surfactant whose hydrophobic tails are totally replaced with fluorine atoms or partially fluorinated, fluorocarbon surfactants are widely applied in coatings, foaming, and lubricants. Fluorocarbon surfactants exhibit strong wettability, low surface tension, excellent stability, and both hydrophobic and oleophobic characteristics [9]. So far, the wettability of a variety of fluorocarbon surfactants with different structures on PTFE surfaces has been investigated. Szymczyk et al. calculated the Lifshitz–van der Waals components and the parameters of electron-acceptor and electron-donor of PTFE surfaces when fluorocarbon surfactants Zonyl FSN-100 (FSN100) and Zonyl FSO-100 (FSO100) were adsorbed on the PTFE surface [10]. Subsequently, they compared the differences in adsorption parameters between fluorocarbon surfactants (FSN100, FSO100) and traditional hydrocarbon surfactants on the PTFE surface [11,12]. Shen et al. [13] synthesized perfluoropolyether amide propyl betaine (PFPE-B) with higher surface activity than hydrocarbon surfactants, and PFPE-B exhibited effective spreading on the PTFE surface after CMC. The nonionic hydro-fluorocarbon hybrid surfactants ($C_9F_{19}CONH(CH_2)_3N(C_mH_{2m+1})_2$) prepared by Peng et al. could reduce the contact angle from 107.7° to 3.6° on the PTFE surface [14]. Chen et al. [15] noted that Gemini nonionic fluorocarbon surfactants (MN-2C_9F_{19}, EN-2C_9F_{19}) were able to wet the PTFE surface completely at low concentrations. Peng et al. [16] reported that the mixture of SDS and the amine-oxidized nonionic fluorocarbon surfactant also can wet PTFE surfaces completely. Zhou et al. reported that the tri-block nonionic short-chain fluorocarbon surfactant ($F_9EG_{13}F_9$) has synergistic effects with sodium dodecylbenzene sulfonate (SDBS) and SDS, and their mixtures could, respectively, reduce the contact angles to 70.2° [17] and 58.7° [18] on the PTFE surface. However, most of the research only focuses on the contact angle of fluorocarbon surfactants on PTFE surfaces, and the adsorption mechanism of fluorocarbon surfactants at the PTFE–liquid interface is ignored.

To figure out the effect of molecular structure on the adsorption behavior of fluorocarbon surfactants on the PTFE surface, three fluorocarbon surfactants (FNS-1, FNS-2, and FAS) with different branch degrees were chosen in this work. Among them, FNS-1 and FNS-2 are nonionic surfactants, while FAS is an anionic surfactant. Therefore, the differences in the electrical properties can also be examined for their effects on the adsorption behavior of the fluorocarbon surfactants on the PTFE surface. The differences in the adhesion tension, PTFE–liquid interfacial tension, and the work of adhesion of the three fluorocarbon surfactants were also examined. Investigating the effects of structural differences on wettability can help us to better utilize fluorocarbon surfactants to regulate the properties of PTFE surfaces. This is of great significance for the application of fluorocarbon surfactants in non-adhesive coatings and anti-adhesive materials. Specifically, understanding the effect of structural differences on adsorption behavior can help optimize the formulation of fluorocarbon surfactants, thereby improving the adsorption performance of fluorocarbon surfactants on the PMMA surface. This is critical for improving surface wettability, water resistance, and corrosion resistance. Since fluorocarbon surfactants play a key role in coatings and lubricants, this can also help us design coatings and lubricants with better lubricity, wear resistance, and corrosion resistance. Fluorocarbon surfactants have strong chemical stability, so they are difficult to degrade. Fluorocarbon surfactants may enter water bodies after use, affecting water quality and accumulating in organisms. Therefore, fluorocarbon surfactants may be transmitted through the food chain, which has a detrimental impact on human health and ecosystems. Therefore, the study of the influence of molecular structure on the adsorption behavior of fluorocarbon surfactants on the PMMA surface can help us to design more environmentally friendly products and promote the development of environmentally friendly fluorocarbon surfactants.

2. Materials and Methods

2.1. Materials

The two nonionic fluorocarbon surfactants (N-(methyl) perfluorooctane sulfonamide polyoxyethylene ether FNS-1 and perfluorohexane ethyl polyoxyethylene ether FNS-2) and anionic fluorocarbon surfactant (sodium perfluorononyloxy benzene sulfonate FAS) were all obtained from Shanghai Futian Chemical Technology Co. Ltd. (Shanghai, China), with active substance content higher than 95%. Figure 1 depicts the molecular structures of FNS-1, FNS-2, and FAS molecules. It must be pointed out that the number of oxyethylene groups in FNS-1 and FNS-2 is a distribution with a mixture of homologs and is just a nominal value. The critical micelle concentration (CMC), surface tension at CMC (γ_{CMC}), saturated adsorption amount (Γ_{max}), and saturated adsorption area (A_{min}) of the three fluorocarbon surfactants are shown in Table 1 [19]. Additionally, all the fluorocarbon surfactants were dissolved in double-distilled water (resistivity > 18.2 MΩ.cm) with the addition of 1% NaCl to simulate the application environment.

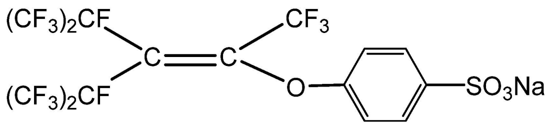


$$\underset{\displaystyle CH_3}{CF_3(CF_2)_7SO_2N(CH_2CH_2O)_6H}$$

FNS-1

$CF_3(CF_2)_6CH_2O(CH_2CH_2O)_5H$

FNS-2



FAS

Figure 1. Structures and abbreviations of the three fluorocarbon surfactants.

Table 1. The CMC, γ_{CMC}, Γ_{max}, and A_{min} of three fluorocarbon surfactants.

Surfactants	**CMC ($mol\cdot L^{-1}$)**	**γ_{CMC} ($mN\cdot m^{-1}$)**	**$10^{10}\Gamma_{max}$ ($mol\cdot cm^{-2}$)**	**A_{min} (nm^2)**
FNS-1	2.86×10^{-5}	20.7	2.48	0.67
FNS-2	5.56×10^{-5}	22.4	3.39	0.49
FAS	5.43×10^{-5}	20.9	2.64	0.63

2.2. Contact Angle Measurements

Before the contact angle measurements, the PTFE plate was first washed with a small amount of detergent and then rinsed with a large amount of water. Next, the washed PTFE plate was soaked in the HCl solution (1:1). Subsequently, the PTFE plate was rinsed with distilled water. Finally, the above PTFE plate was ultrasonicated in ultrapure water for 20 min and dried.

The contact angles of fluorocarbon surfactant solutions on the PTFE surface were determined by the sessile drop method using a LAUDA Scientific GmbH machine (SurfaceMeter machine, Würzburg, Germany) [19]. First, a droplet of fluorocarbon surfactant solution (2.0 μL) was used to make contact with the PTFE plate. Meanwhile, the shape of the droplet was photographed and processed by the software. Thus, the contact angles of the fluorocarbon surfactant solutions were obtained. Each contact angle measurement was conducted at least 5 times at 25.0 °C, and the measurement error of the contact angles was <3.0°.

3. Results

3.1. Contact Angles

Figure 2 shows the contact angles of fluorocarbon surfactant solutions on the PTFE surface. With the increase of the concentration, the contact angles of the three fluorocarbon surfactants change little in a wide concentration range (1×10^{-8}~1×10^{-5} mol/L), and their contact angles remain approximately 120°. However, the contact angles decrease dramatically when approaching the CMC value. This indicates that the three fluorocarbon surfactant molecules continue to adsorb on the PTFE surface after CMC. Szymczyk et al. [20,21] noticed that the contact angles of some fluorocarbon surfactants on the PTFE surface also decreased sharply near the CMC value, which is in agreement with the result of the three fluorocarbon surfactants in this work. However, this phenomenon is quite different from conventional surfactants. For conventional surfactants, their contact angles on PTFE surfaces generally decrease to plateau values near CMC.

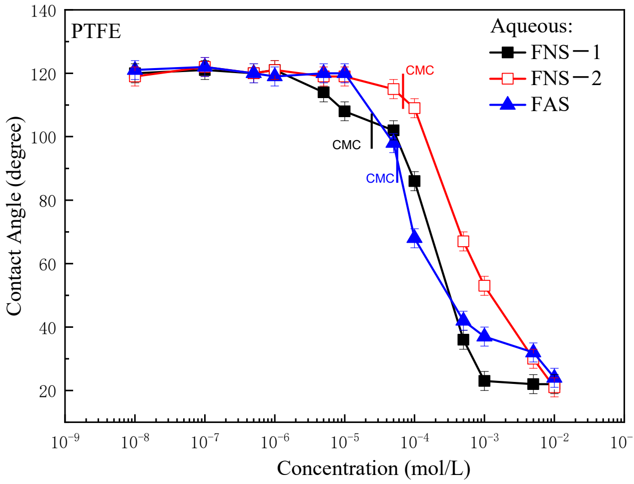


Figure 2. Contact angles of fluorocarbon surfactant solutions on the PTFE surface.

It is visible that the contact angles of the three fluorocarbon surfactants on the PTFE surface exhibit a similar trend. Notably, the contact angle of FNS-1 starts to decrease at a lower concentration than that of FNS-2. The contact angle of FNS-1 is obviously lower than that of FNS-2 at the same concentration. What is more, the decrease in contact angles for FAS is faster than FNS-2, but slower than FNS-1. It is worth noting that the contact angles of the three fluorocarbon surfactants are able to reduce to about 20° at high concentrations. According to the previous reports, traditional anionic surfactants (SDS and SDDS) and cationic surfactants (C_{12}TAB) can merely decrease the contact angles to approximately 80° on the PTFE surface [6,22]. Cationic surfactants (C_{16}GPC and $C_{16}G(EO)_3PC$) can reduce the contact angle to 55° [23]. Zwitterionic surfactants ($C_{16}G(EO)_3PB$ and C_{16}GPB) can also reduce the contact angle to about 55° [5]. Additionally, the extended anionic surfactants (L-$C_{12}PO_4S$ and L-$C_{12}PO_{11}S$) can decrease the contact angle to about 65° on the PTFE surface [7]. Even the fluorocarbon surfactants reported in the literature (FSN100 and FSO100) can only reduce the contact angle to 68° and 48° on the PTFE surface [20]. As shown in Table 2, the contact angles of reported surfactants in the literature are all higher than 48° on the PTFE surface. As the three fluorocarbon surfactants can reduce the contact angles to about 20° in Figure 2, the hydrophilic modification ability of the three fluorocarbon surfactants on the PTFE surface in this work is significantly better than the reported surfactants in the literature.

Table 2. The contact angles of three fluorocarbon surfactants and other reported surfactants on the PTFE surface.

Fluorocarbon Surfactants	Contact Angles	Other Surfactants	Contact Angles
FNS-1	20°	SDDS [6]	80°
FNS-2	20°	SDS [22]	80°
FAS	20°	C_{12}TAB [22]	80°
FSN100 [20]	68°	C_{16}GPC [23]	55°
FSO100 [20]	48°	$C_{16}G(EO)_3$PC [23]	55°
-	-	$C_{16}G(EO)_3$PB [5]	55°
-	-	C_{16}GPB [5]	55°
-	-	L-C_{12}PO4S [7]	65°
-	-	L-$C_{12}PO_{11}$S [7]	65°

3.2. Adhesion Tension

As known, the difference between the solid–air interfacial free energy (γ_{SV}) and the solid–liquid interfacial free energy (γ_{SL}) is the adhesion tension. Based on Young's equation, the air–liquid interfacial free energy (γ_{LV}) can be calculated by Equation (1).

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta \tag{1}$$

The value of the adhesion tension is $\gamma_{LV}\cos\theta$. In addition, according to the Gibbs equation and Young's equation, the relationship between the solid–air interfacial adsorption amount (Γ_{SV}), the solid–liquid interfacial adsorption amount (Γ_{SL}), and the air–liquid interfacial adsorption amount (Γ_{LV}) is shown in Equation (2).

$$\frac{d(\gamma_{LV}\cos\theta)}{d\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}} \tag{2}$$

Because the solid–air interfacial adsorption amount of the surfactants (Γ_{SV}) is zero, the absolute value of slope of the $\gamma_{LV}\cos\theta$-γ_{LV} curve in Figure 3 is exactly the value of Γ_{SL}/Γ_{LV}.

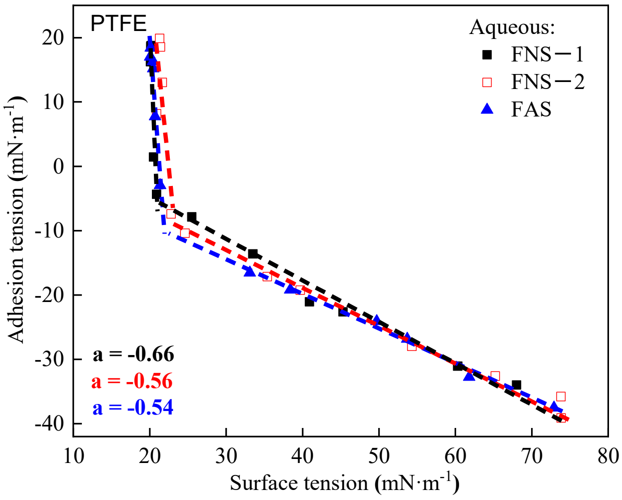


Figure 3. The adhesion tension of three fluorocarbon surfactants varies with surface tension on the PTFE surface.

As shown in Figure 3, the adhesion tension of the three fluorocarbon surfactants on the PTFE surface decreases as the surface tension increases. Meanwhile, the adhesion tension curve can be divided into two stages. Obviously, the adhesion tension decreases sharply at first and then decreases slowly. Szymczyk et al. [20,21] found that the adhesion tension of the conventional hydrocarbon surfactants (TX100, TX165, TX114, and CTAB) decreased linearly with the increase of surface tension. On the contrary, the adhesion tension of fluorocarbon surfactants (FSN100, FSO100), or even their mixtures with conventional surfactants on the PTFE surface, decreased sharply at first and then decreased slowly with the increase of surface tension. This trend, reported by Szymczyk et al., is consistent with the result in Figure 3.

Since PTFE is a nonpolar surface with low surface energy, the γ_{SV} value of PTFE is relatively low. Pure water with high polarity or the fluorocarbon surfactant solution with a low concentration has a significant difference with PTFE, resulting in a high γ_{SL} value. As a result, the value of adhesion tension is negative at low concentrations. When the concentration of fluorocarbon surfactants increases, the fluorocarbon surfactant molecules adsorb on the PTFE surface through hydrophobic interactions. Once the fluorocarbon surfactants adsorb on the PTFE surface by hydrophobic interactions, the hydrophilic groups of the fluorocarbon surfactants will point toward the aqueous phase. This causes the polarity of the PTFE surface to increase, and therefore the solid–liquid interfacial free energy (γ_{SL}) decreases. Thus, the adhesion tension increases as the surface tension decreases in Figure 3. In other words, the adhesion tension increases when the concentration of the fluorocarbon surfactant solution increases. Moreover, there is a linear relationship between the surface tension and adhesion tension. When the concentration of the three fluorocarbon surfactants exceeds the CMC value, the surface tension remains constant. Owing to the further adsorption of fluorocarbon surfactants on the PTFE surface, the adhesion tension rises significantly. In this stage, the adhesion tension of the three fluorocarbon surfactants shows a vertical upward trend.

The theoretical values of the saturated adsorption area (Amin, theo) of the three fluorocarbon surfactants before CMC can be calculated by the slope of the adhesion tension curve ($\Gamma_{\mathrm{SL}}/\Gamma_{\mathrm{LV}}$) in Table 3. The Amin, theo values of FNS-1, FNS-2, and FAS surfactants are 1.01 nm^2, 0.88 nm^2, and 1.17 nm^2, respectively. Based on the surface tension–adhesion tension curves of the three fluorocarbon surfactants, the slopes of FNS-1, FNS-2, and FAS solutions before CMC are, respectively, −0.66, −0.56, and −0.54. This suggests that the adsorption amount of the three fluorocarbon surfactants at the air–liquid interface is 1.5~2 times higher than that at the PTFE–solution interface. Szymczyk et al. [21] noticed that the adsorption amount of fluorocarbon surfactants (FSN100, FSO100) at the PTFE–solution interface was also less than their adsorption amount at the air–liquid interface, which is quite different from the adsorption behavior of other conventional hydrocarbon surfactants on the PTFE surface.

Table 3. The $\Gamma_{\mathrm{SL}}/\Gamma_{\mathrm{LV}}$ value of three fluorocarbon surfactants and other reported surfactants before CMC.

Special Surfactants	$\Gamma_{\mathrm{SL}}/\Gamma_{\mathrm{LV}}$	Conventional Surfactants	$\Gamma_{\mathrm{SL}}/\Gamma_{\mathrm{LV}}$
FNS-1	−0.66	TX-100 [20]	−1
FNS-2	−0.56	TX-114 [20]	−1
FAS	−0.54	SDS [22]	−1
$C_{16}(EO)_3PC$ [23]	−0.41	CTAB [24]	−1
$C_{16}G(EO)_3PB$ [5]	−0.62	CPyB [24]	−1
L-$C_{12}PO_4S$ [7]	−0.45	C_{12}(EDMAB) [25]	−1
$C_{16}GPC$ [26]	−0.47	BDDAB [25]	−1
Gemini C3 [27]	−0.29	DDAB [28]	−0.74
BSB [19]	−0.39	AOT [28]	−0.74
18S [29]	−0.36		

To facilitate the comparison, the slopes (Γ_{SL}/Γ_{LV}) of the adhesion tension curves of other reported surfactants and the three fluorocarbon surfactants in this work at the PTFE surface are summarized in Table 3. For the conventional anionic, cationic, and nonionic surfactants with linear structures, such as SDS, CTAB, and TX-100, their slopes are all -1. This indicates that the adsorption amount of these conventional surfactants on the PTFE surface is the same as their adsorption amount at the air–liquid interface. In contrast, the slopes of the three fluorocarbon surfactants in this work are all higher than -1, which is completely different from conventional surfactants. It was reported that the ΓSL/ΓLV of surfactants with special structures would be higher than -1 when the surfactants adsorbed on the PTFE surface, such as anionic extended surfactant L-C12PO4S, double carbon chain anionic surfactant AOT, branched-chain cationic surfactant C16GPC, dimethylphenyl substituted sulfobetaine BSB, linear sulfobetaine 18S, and cationic Gemini surfactant C3. These special surfactants possess branched alkyl chains, double alkyl chains, or multifunctional groups, which creates a large steric hindrance and leads the surfactant molecules to be more likely to adsorb on the air–liquid interface [7]. In this work, the FNS-1 molecule has multifunctional groups such as the EO group, -SO_2-, amino group, and the branched structure. The FNS-2 molecule has multiple EO groups. Additionally, the FAS molecule has large branched chains and the -SO^{3-} group. Therefore, it is reasonable that the three fluorocarbon surfactants in this work have slopes higher than -1.

3.3. PTFE–Solution Interfacial Tension

Figure 4 shows the effect of the concentration for the three fluorocarbon surfactants on the PTFE–solution interfacial tension. The PTFE–solution interfacial tension of the three fluorocarbon surfactants decreases with the increase of the concentration, and the PTFE–solution interfacial tension curves can be divided into three stages. When the concentration of the fluorocarbon surfactants is low (Stage I), the interfacial tension decreases slowly as the concentration increases. This phenomenon can be attributed to the fluorocarbon surfactants that adsorb on the PTFE surface by hydrophobic interactions. In this stage, the hydrophilic head of fluorocarbon surfactants directs toward the aqueous phase, resulting in an increase in the hydrophilicity of the PTFE surface and a decrease in the solid–liquid interfacial tension. When approaching the CMC value (Stage II), the interfacial tension decreases sharply as the concentration increases. In this stage, the fluorocarbon surfactant molecules continue to adsorb at the PTFE–solution interface, and the PTFE–solution interfacial tension continues to decrease. It is noteworthy that the slopes of the interfacial tension curves in the two stages are quite different. The slope of the second stage is significantly smaller than that of the first stage, demonstrating that the adsorption of fluorocarbon surfactants on the PTFE surface is significantly enhanced in the second stage. This trend is similar to the interfacial tension of extended anionic surfactants reported by Du et al. [7] When the concentration is high (Stage III), the adsorption of fluorocarbon surfactant molecules on the PTFE surface reaches saturation and the interfacial tension reaches the plateau value. Szymczyk et al. [30] found that the variation of the interfacial tension for fluorocarbon surfactants (FSN100 and FSO100) at the PTFE–solution interface can also be divided into two stages. However, the interfacial tension of FSN100 and FSO100 decreased sharply at first and then decreased slowly with the increase of the concentration, which is slightly different from this work. In contrast, the interfacial tension curves of conventional surfactants such as TX-100 and TX-165 have no turning point [30], which implies that there is no special adsorption behavior for these conventional surfactants on the PTFE surface.

The saturated adsorption amounts (Γ_{below}, Γ_{above}) and adsorption areas (A_{below}, $_{Aabove}$) of fluorocarbon surfactants at the PTFE–solution interface before and after the CMC value are calculated and listed in Table 4. It can be seen that the saturated adsorption area before CMC (A_{below}) calculated by Gibbs equations in Table 4 (0.99 nm^2, 0.86 nm^2, and 1.14 nm^2, respectively) is consistent with the theoretical saturated adsorption area ($A_{min,theo}$) obtained from the slope of adhesion tension in Table 3 (1.01 nm^2, 0.88 nm^2, and 1.17 nm^2, respectively). This demonstrates that the experimental results are reliable. As shown in Table 4, FNS-2 possesses the highest adsorption amount (1.93×10^{-10} mol·cm^{-2}) and the smallest adsorption area (0.86 nm^2) before CMC. This is due to the smallest molecular size of the FNS-2 molecule among the three fluorocarbon surfactants. However, large branched chains and electrostatic repulsion result in the smallest adsorption amount (1.46×10^{-10} mol·cm^{-2}) and the largest adsorption area (1.14 nm^2) of the anionic FAS molecules. When the concentration of the three fluorocarbon surfactants exceeds the CMC value, the adsorption amount increases nearly two times and the adsorption area decreases obviously. According to the literature, there are two adsorption behaviors for the surfactants at the PTFE–solution interface: (1) surfactant molecules rely on hydrophobic tails to adsorb on the PTFE surface; (2) surfactant molecules form aggregates to adsorb on the PTFE surface [7]. Therefore, it is inferred that the three fluorocarbon surfactants may form semi-micelles at the PTFE–solution interface after CMC. As a result, the adsorption amount of the fluorocarbon surfactants after CMC is nearly two times higher than their adsorption amount before CMC.

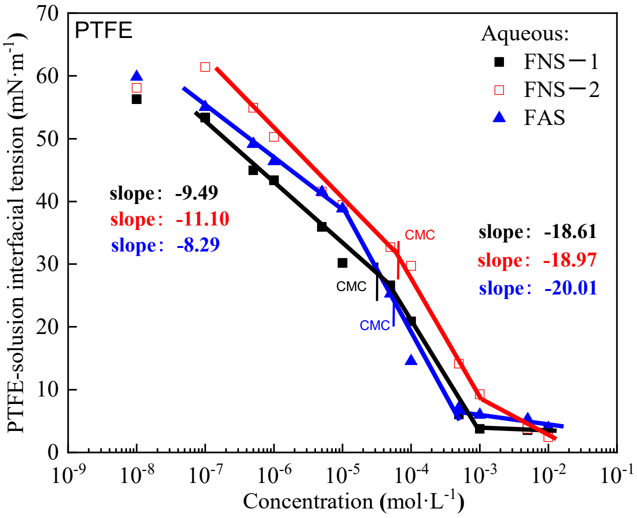


Figure 4. Effect of concentration for fluorocarbon surfactants on PTFE–solution interfacial tension.

Table 4. Adsorption parameters of fluorocarbon surfactants on PTFE surface.

Abrr.	$10^{10}\Gamma_{below}$ (mol·cm^{-2})	A_{below} (nm^2)	$10^{10}\Gamma_{above}$ (mol·cm^{-2})	A_{above} (nm^2)
FNS-1	1.68	0.99	3.26	0.51
FNS-2	1.93	0.86	3.32	0.50
FAS	1.46	1.14	3.53	0.47

The minimum interfacial tension reflects the hydrophilic modification ability of fluorocarbon surfactants on the PTFE surface. In Figure 4, the minimum interfacial tension values of FNS-1, FNS-2, and FAS are 3.6 mN/m, 2.4 mN/m, and 3.9 mN/m, respectively. Noticeably, the three fluorocarbon surfactants have a strong hydrophilic modification ability on the PTFE surface. What is more, the order of the hydrophilic modification ability for the three fluorocarbon surfactants is FNS-2 > FNS-1 > FAS. On the one hand, the -CH_3 group affects the hydrophilic modification ability of the FNS-1 molecule. On the other hand, the adsorption amount of FNS-2 after CMC is higher than that of FNS-1, and more hydrophilic groups of FNS-2 molecules stretch toward the aqueous phase. Consequently, the hydrophilic modification ability of FNS-2 is stronger than that of FNS-1. In addition, the hydrophilic modification ability of nonionic fluorocarbon surfactants (FNS-1 and FNS-2) is stronger than that of the anionic fluorocarbon surfactant (FAS). Although there is little difference in the adsorption amount of the three fluorocarbon surfactants, FNS-1 and FNS-2 have more hydrophilic EO groups to effectively enhance their hydrophilicity.

The minimum interfacial tension values of three fluorocarbon surfactants and other reported surfactants on the PTFE surface are summarized in Table 5. By comparison, the hydrophilic modification ability of the three fluorocarbon surfactants in this work is significantly stronger than that of other published surfactants with special structures. When the EO group exists in the surfactant molecule, the hydrogen bond formed by EO groups can promote the formation of aggregates on the PTFE surface. The EO group can also effectively improve the hydrophilic modification ability of surfactants on the PTFE surface. Therefore, the minimum interfacial tension of extended betaine $C_{16}(EO)_3PB$ can also be reduced to 4.5 mN/m.

Table 5. The minimum interfacial tension of three fluorocarbon surfactants and other reported surfactants on the PTFE surface.

Surfactants	The Minimum Interfacial Tension (mN/m)
FNS-1	3.6
FNS-2	2.4
FAS	3.9
C16(EO)3PB [5]	4.5
C16G(EO)3PB [5]	9.5
C16PB [5]	19.5
L-C12PO4S [7]	8.6
L-C12PO11S [7]	9.6
C16GPB [26]	7
C16GPC [26]	7
BCB [19]	23
BSB [19]	32

3.4. Work of Adhesion

The work of separating the surfactant solution from the solid surface is known as the work of adhesion, and the work of adhesion (W_A) can be computed by Equation (3). Based on Young's equation, the sum of surface tension and adhesion tension is the work of adhesion; accordingly, Equation (4) can also calculate the work of adhesion.

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{3}$$

$$W_A = \gamma_{LV}(\cos\theta + 1) \tag{4}$$

Figure 5 shows the effect of concentration on work of adhesion for fluorocarbon surfactants on the PTFE surface. At low concentrations, the adsorption of fluorocarbon surfactants at the air–liquid and PTFE–liquid interfaces increases with increasing concentration. In consequence, both the surface tension and the interfacial tension decrease. Since the decrease in surface tension is larger than the decrease in interfacial tension, the work of adhesion of the three fluorocarbon surfactants begins to decrease. When the concentration exceeds the CMC value, the adsorption of the three fluorocarbon surfactants on the air–liquid interface is saturated and the surface tension changes little. However, the fluorocarbon surfactants will continue to adsorb at the PTFE–solution interface through hydrophobic interaction. Consequently, the interfacial tension decreases, which results in the increase of the work of adhesion. Once the adsorption of fluorocarbon surfactants on the PTFE–solution interface reaches saturation, the work of adhesion of fluorocarbon surfactants reaches a plateau value. This trend is consistent with the effect of concentration on work of adhesion for fluorocarbon surfactants (FSN100 and FSO100) at the PTFE–solution interface obtained by Szymczyk et al. [20].

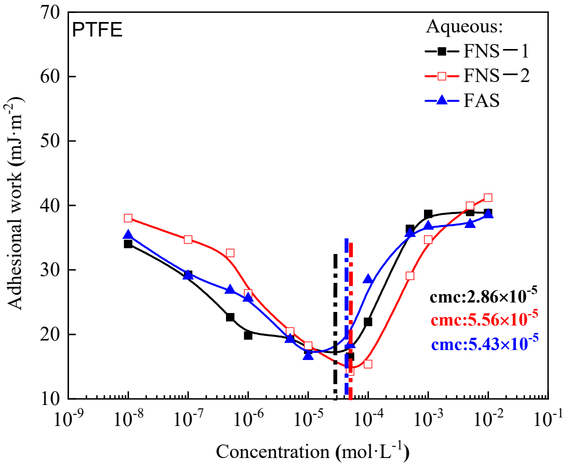


Figure 5. Effect of concentration on work of adhesion for fluorocarbon surfactants on the PTFE surface.

3.5. Adsorption Mechanism

The concentration dependence of adsorption parameters for the three fluorocarbon surfactants on the PTFE surface is depicted in Figure 6. It is visible that the adsorption processes of the three fluorocarbon surfactants on the PTFE surface are similar and all can be divided into four stages. Taking the FNS-1 molecule as an example, its adsorption behavior is as follows:

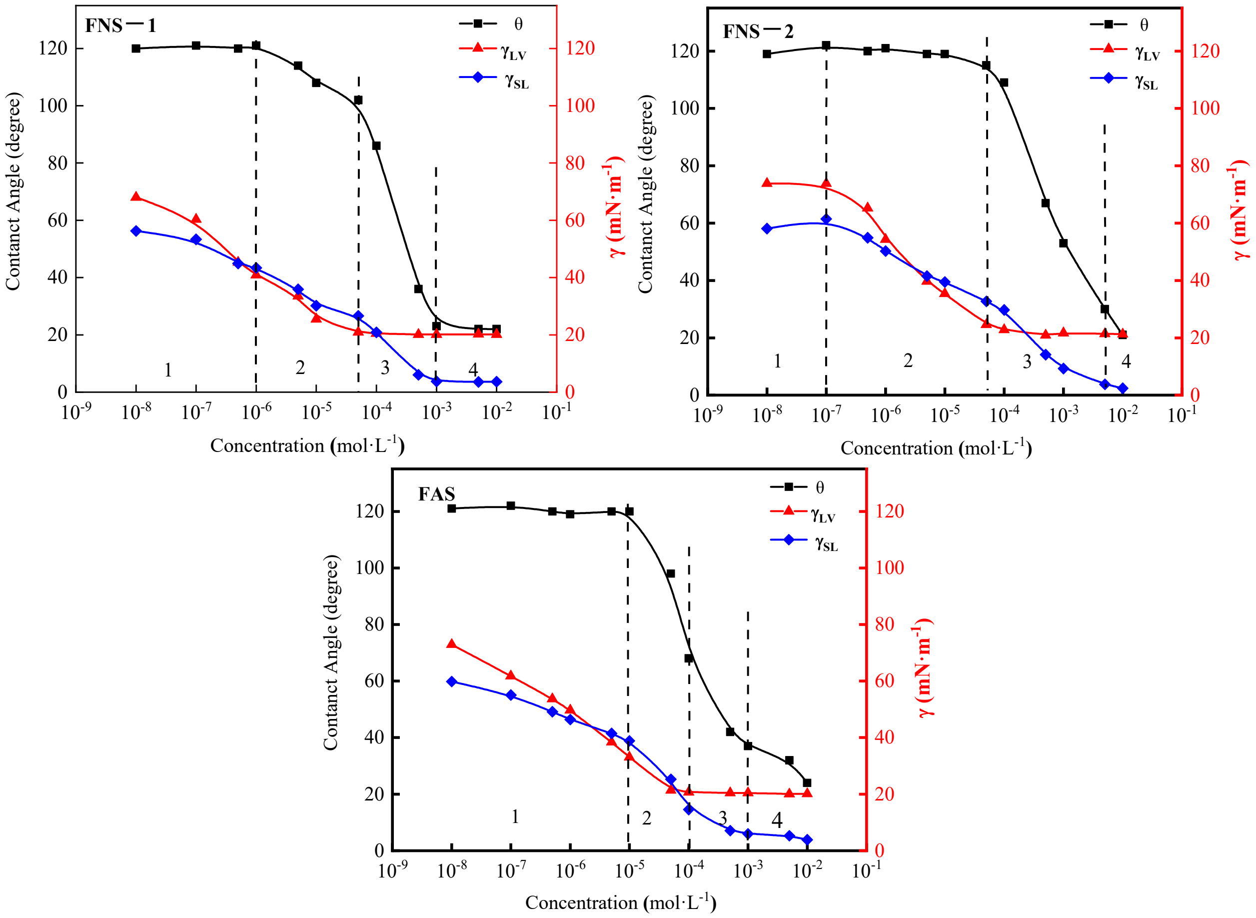


Figure 6. Concentration dependence of adsorption parameters for the three fluorocarbon surfactants on the PTFE surface.

(1) In the first stage (1×10^{-8}~1×10^{-6} mol/L), the adsorption of FNS-1 at the air–liquid and PTFE–liquid interfaces increases with the increase of the concentration. Thus, both the surface tension and PTFE–liquid interfacial tension of FNS-1 decrease in the first stage. The decrease of surface tension is beneficial for the increase of contact angle, while the decrease of PTFE–liquid interfacial tension is conducive to the decrease of contact angle. Since the effects of surface tension and interfacial tension on the contact angle cancel each other out, the contact angle is almost constant. In the first stage, the fluorocarbon surfactants rely on their hydrophobic groups to adsorb at the PTFE–liquid interface, and their hydrophilic groups point to the solution. Consequently, the PTFE surface is modified to be hydrophilic.

(2) In the second stage (1×10^{-6}~5×10^{-5} mol/L), the FNS-1 molecules continue to adsorb at the air–liquid and PTFE–liquid interfaces. The surface tension and interfacial tension of FNS-1 continue to decrease until reaching the CMC value (2.86×10^{-5} mol/L). However, the decrease of PTFE–liquid interfacial tension plays the dominant role, and the contact angle decreases with increasing concentration.

(3) In the third stage (5×10^{-5}~1×10^{-3} mol/L), the concentration of the FNS-1 solution exceeds its CMC value (2.86×10^{-5} mol/L). The adsorption of FNS-1 molecules at the air–liquid interface tends to be saturated, and the surface tension approaches the plateau value. However, the contact angle decreases significantly due to the obvious decrease in interfacial tension. At this stage, the adsorption behavior of fluorocarbon surfactants changes dramatically. FNS-1 molecules tend to form aggregates on the PTFE surface by hydrogen bonding of EO groups, resulting in a significant increase in the adsorption amount of fluorocarbon surfactants.

(4) In the fourth stage (1×10^{-3}~1×10^{-2} mol/L), the adsorption of FNS-1 at the solid–liquid and air–liquid interfaces tends to be saturated. Accordingly, the contact angle is almost constant.

Figure 7 depicts the adsorption mechanism of the three fluorocarbon surfactants on the PTFE surface. At low concentrations, the fluorocarbon surfactant molecules rely on hydrophobic groups to adsorb at the PTFE–solution interface. FNS-2 possesses the highest adsorption amount due to its smallest molecular size. On account of the electrostatic repulsion and large steric hindrance of FAS, FAS has the smallest adsorption amount. At high concentrations above CMC, fluorocarbon surfactant molecules form aggregates on the PTFE surface, and the interfacial adsorption amount increases significantly. Owing to the hydrophilic EO groups of FNS-1 and FNS-2 molecules, the hydrophilic modification ability of FNS-1 and FNS-2 is stronger than that of FAS. Because of the smaller adsorption amount and the -CH_3 group of FNS-1, the hydrophilic modification ability of FNS-1 is weaker than that of FNS-2 at high concentrations.

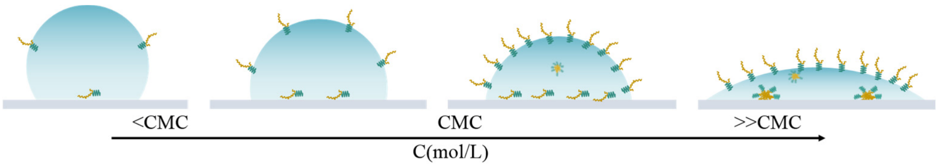


Figure 7. Representative adsorption mechanism of the fluorocarbon surfactants on the PTFE surface.

4. Conclusions

The adsorption behaviors of different fluorocarbon surfactants (FNS-1, FNS-2, and FAS) on the PTFE surface were investigated using the sessile drop method, and the following conclusions can be drawn:

(1) At low concentrations, the contact angles of the three fluorocarbon surfactants on the PTFE surface are approximately 120°. Above CMC, the three fluorocarbon surfactants continue to adsorb at the PTFE–solution interface by hydrophobic interactions and can reduce the contact angle to about 20°, indicating that the hydrophilic modification ability

of the fluorocarbon surfactants for the PTFE surface is significantly stronger than that of other reported surfactants.

(2) As the surface tension increases, the adhesion tension of the three fluorocarbon surfactants decreases sharply at first and then decreases slowly. The adsorption amount of the three fluorocarbon surfactants at the air–liquid interface is 1.5~2 times higher than that at the PTFE–solution interface.

(3) When the concentration increases, the interfacial tension of the PTFE–solution interface decreases slowly at first and then decreases sharply. At concentrations lower than CMC, FNS-2 has the highest adsorption amount due to its smallest molecular size, while FAS possesses the smallest adsorption amount due to its large steric hindrance and electrostatic repulsion. Above CMC, semi-micelles are formed at the PTFE–solution interface, and thus the adsorption amount of the fluorocarbon surfactants increases nearly two times.

(4) At high concentrations, the order of hydrophilic modification ability on the PTFE surface is FNS-2 > FNS-1 > FAS. The hydrophilicity of FNS-1 and FNS-2 is effectively enhanced by their hydrophilic EO groups. The hydrophobic -CH_3 group and lower adsorption amount endow FNS-1 with a weaker hydrophilic modification ability than FNS-2.

Investigating the effects of structural differences on wettability is beneficial for the regulation of fluorocarbon surfactants' properties on PTFE surfaces. In our future work, we will explore the stability of the adsorption layer over time and test the performance of these fluorocarbon surfactants on other low-energy surfaces.

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