

Study of Micelle Formation by Fluorocarbon Surfactant *N*-(2-hydroxypropyl)perfluorooctane Amide in Aqueous Solution

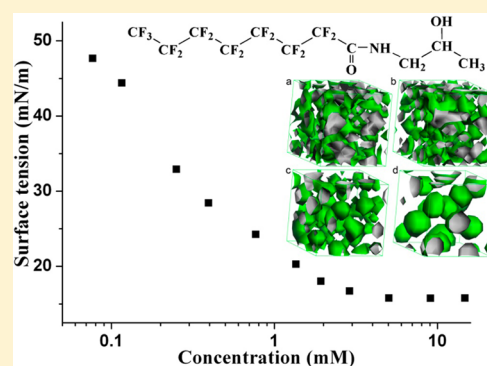
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ABSTRACT: Micelles formed by fluorocarbon surfactant *N*-(2-hydroxypropyl)perfluorooctane amide in aqueous solution were studied through surface tension, dynamic light scattering (DLS), isothermal titration calorimetry (ITC), and dissipative particle dynamic (DPD) simulations. Through surface tension measurements, the effectiveness of surface tension reduction, the maximum surface excess concentration, and the minimum area occupied per surfactant molecule at the air/water interface were investigated. The critical micelle concentration (cmc) at different temperatures and a series of thermodynamic parameters (ΔG_m^0 , ΔH_m^0 , ΔS_m^0 , ΔG_{ads}^0 , ΔH_m^A and ΔC_{pm}^0) of micellization were evaluated. The thermodynamic parameters showed that the micelle formation was entropy-driven. The micelle formation was also confirmed by ITC and DLS. In addition, the DPD simulations were conducted to simulate the whole process of micelle formation to make micelle formation better understood.



■ INTRODUCTION

Self-assembled aggregates have attracted a large amount of attention and shown application to drug delivery, cosmetics, the food industry, life science, and enhanced oil recovery.¹⁻⁵ The investigation of these self-assembled aggregates has been of fundamental interest over these past 20 or 30 years. In general, the most common self-assembled aggregates are micelles formed by various surfactants in aqueous solution. These surfactants are generally divided into four kinds: anionic,⁶ cationic,⁷ nonionic,⁸ and amphoteric,⁹ which are all thoroughly studied. In recent years, a new kind of surfactant has been synthesized and received much interest.¹⁰⁻²¹ The hydrophobic hydrocarbon tails of conventional surfactants are all or partly replaced by perfluorocarbon tails, which has superior surface activity and many interesting properties. This new kind of surfactant is traditionally called fluorocarbon surfactant.

In the molecular structure of fluorocarbon surfactants, appearance of fluorocarbon atoms supports a number of new properties, such as high thermal and chemical stability. Fluorocarbon surfactants are therefore designed and synthesized according to our needs with different molecular structures, including hydrophilic headgroups and fluorocarbon tails. Marchant and co-workers synthesized a series of fluorocarbon surfactant polymers with hydrophilic dextran oligosaccharides and hydrophobic perfluoroundecanoyl groups attached on a poly(vinylamine) backbone.¹⁰ They could tune the properties of fluorocarbon surfactant polymers through adjusting the ratio of hydrophilic dextran to hydrophobic

fluorocarbon branch. Lazzara and Piccionello synthesized a newly fluorinated surfactant 5-hydroxyamino-3-perfluoroheptyl-1,2,4-oxadiazin-6-one (PFHO) and studied its physicochemical behavior in aqueous solution.¹¹ The PFHO showed high thermal stability and enhanced self-assembling behavior. The Koper group designed and synthesized two novel homologous aromatic moiety bearing hybrid fluorocarbon surfactants.¹² Aggregation behaviors and thermodynamic properties were described, and the results showed super surface activity. Our group previously studied a cationic fluorinated surfactant FC-4 and the micelle formation in different ionic liquid solvents, such as 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄), hexafluorophosphate (bmimPF₆), and bis-(trifluoromethylsulfonyl)imide (bmimTf₂N).^{13,14} With the exception of these ionic fluorocarbon surfactants, nonionic fluorocarbon surfactants have also received much attention, due to their high stability to salinity. Fung and Mamrosh synthesized a new class of fluorinated nonionic surfactants (C_nF_{2n+1}C(O)NH(CH₂CH₂O)_mH; *n* = 3, 6–8; *m* = 2–4) and indicated a number of unusual micellar characteristics in aqueous solution.¹⁹ The Revey group synthesized a new series of nonionic fluorinated surfactants CF₃(CF₂)_{*m*}–C₂H₄–(SC₂H₄)–(OC₂H₄)_{*n*}OH and studied their surface activity in aqueous solution. The results indicate that the fluorocarbon

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chains are very densely packed at the air/water interface, and the presence of one inserted SC_2H_4 group in the hydrophilic chain cancels out the effect of two oxyethylene groups.²⁰ Eastoe group synthesized the fluorinated nonionic surfactants $\text{X}-(\text{CF}_2)_m-\text{CH}_2-\text{O}-(\text{C}_2\text{H}_4\text{O})_3-\text{CH}_3$, with X either H or F, and m either 4 or 6. The results clearly show the relationship between structure and activity, and effect of CF_3 - or $\text{H}-\text{CF}_2$ -terminal groups on the properties.²¹

In this work, we designed and synthesized a nonionic fluorocarbon surfactant *N*-(2-hydroxypropyl)perfluorooctane amide (PPFOA). The surface activity, adsorption, and thermodynamic parameters of micellization are investigated in detail. In addition, the dissipative particle dynamic (DPD) simulation is also conducted to study micelle formation. Through this work, we expect to gain more understanding of the phase behaviors of fluorocarbon surfactants.

EXPERIMENTAL SECTION

Chemicals. The nonionic fluorocarbon surfactant PPFOA was synthesized according to the reference reported;¹⁵ under protection of nitrogen atmosphere, 15.50 g perfluorocaprylic acid, 3.60 g methanol, and 0.0955 g acetic acid were added into a three-mouth flask. The temperature was heated to 40 °C and kept mixing for 2 h. Then, 4.50 g 1-amino-2-propanol and 0.1185 g sodium methoxide were added to the flask and temperature was kept at 80 °C. After mixing for 4 h, the reaction was finished. Then the flask was cooled, diluted with saturated saline solution, and extracted with ether. Then the ether extract was distilled, and the dark yellow products were obtained. The water used was deionized water.

Characterization. Surface Tension Measurement. Surface tension measurements were carried out on a Model JYW-200B surface tensiometer (Chengde Dahua Instrument Co. Ltd., accuracy ± 0.01 mN/m) using the ring method. Temperature was controlled by thermostat cell holder. The surface tension was determined with a single-measurement method and all measurements were repeated at least twice.

Dynamic Light Scattering (DLS). The DLS measurement was carried out to determine the hydrodynamic radius of micelles formed in aqueous solution using the Zetasizer Nano ZS (Malvern). The DLS measurement was conducted at 25.0 ± 0.1 °C. The scattering angle is 90° and the light of $\lambda = 632.8$ nm from a solid-state He–Ne laser (22 mW) was used as the incident beam. Each sample of 1.5 mL solution was transferred to a square cuvette and DLS data were presented as the mean of three times.

Isothermal Titration Microcalorimetry (ITC) Measurement. The ITC was employed on a nanowatt-scale isothermal titration microcalorimeter (Thermometric 2277 Thermal Activity Monitor, Thermometric, Sweden). The 1-mL sample cell of the calorimeter was initially loaded with water. The surfactant solution (the titrant with a concentration of five times the cmc) was injected into the stirred sample cell using a 500- μL Hamilton syringe controlled by a Thermometric 612 Lund Pump. The interval between adjacent injections was 50 min, which was sufficiently long for the signal to return to the baseline. The golden turbine stirrer in the ampule was at a constant speed of 50 rpm throughout the experiment. All experiments were performed at 25.0 °C and repeated twice to achieve the reproducibility within $\pm 2\%$.

RESULTS AND DISCUSSION

Surface Properties and Micellization. Surface tension measurement was carried out to investigate surface properties of PPFOA in aqueous solution. Figure 1 shows surface tensions

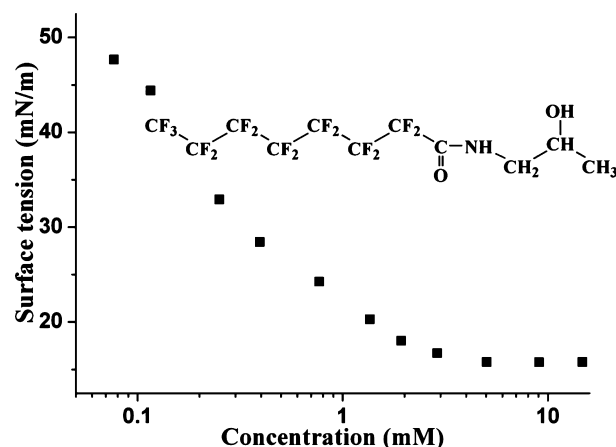


Figure 1. Surface tension isotherms at 25 °C as a function of PPFOA concentration (C) in aqueous solution. The inset image is the chemical formula of PPFOA.

of solutions versus concentrations at 25 °C. At the dilute solution, the surface tensions decrease sharply compared with the surface tension of pure water, indicating the adsorption of PPFOA molecules at the air/water interface. With the further increase of PPFOA concentrations, the surface tension gradually decreases. Until PPFOA concentration reaches a higher value, the surface tension no longer decreases and almost remains constant. This suggests the adsorption of PPFOA molecules at the air/water interface achieves saturation. The concentration of breakpoint in the surface tension curves is traditionally assigned to be the critical micellar concentration (cmc). With the further increase of PPFOA concentrations, the PPFOA molecules form the micelles in aqueous solution. From Figure 1, the cmc value of PPFOA in aqueous solution at 25 °C is about 3.09 mM, which is similar to the result obtained from ITC measurement (shown in the Supporting Information, SI). In general, the cmc values of surfactants are the sign of surface properties, which follows the principle: the smaller the cmc value, the better the surface activity. When comparing the cmc values with the typical conventional hydrocarbon nonionic surfactants with the same carbon atoms, including $\text{C}_8\text{H}_{17}\text{SOCH}_3$, $\text{C}_8\text{H}_{17}\text{O}(\text{C}_2\text{H}_4\text{O})\text{H}$, $\text{C}_8\text{H}_{17}\text{O}(\text{C}_2\text{H}_4\text{O})_2\text{H}$, and $\text{C}_8\text{H}_{17}\text{O}(\text{C}_2\text{H}_4\text{O})_3\text{H}$, their cmc values are 27, 4.57, 5.62, and 7.62 mM, respectively.²² Through this comparison, PPFOA has better surface activity than hydrocarbon surfactants. Compared with the other nonionic fluorocarbon surfactants with the same perfluorocarbon chain, such as $\text{C}_7\text{F}_{15}\text{COONa}$, $\text{C}_8\text{H}_{17}\text{SO}_3\text{NH}_3\text{C}_2\text{H}_4\text{OH}$,^{2,3} and $\text{C}_7\text{F}_{15}\text{C}(\text{O})\text{NH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$ ¹⁹ (their cmc values are 36, 4.6, and 0.069 mM, respectively), the surface activity of PPFOA is better than $\text{C}_7\text{F}_{15}\text{COONa}$, similar to $\text{C}_8\text{H}_{17}\text{SO}_3\text{NH}_3\text{C}_2\text{H}_4\text{OH}$, and worse than $\text{C}_7\text{F}_{15}\text{C}(\text{O})\text{NH}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$. This indicates the super surface activity of fluorocarbon surfactants.

For the fluorocarbon surfactants, the most attractive characteristic is their ability to decrease the surface tension. From Figure 1, the lowest surface tension can reach 15.78 mN/m due to the adsorption of PPFOA at the air/water interface.

Table 1. Surface Properties of PPFOA in Aqueous Solution at 25 °C

surfactants	cmc (mmol/L)	γ_{cmc} (mN/m)	Π_{cmc} (mN/m)	Γ_{max} ($\mu\text{mol}/\text{m}^2$)	A_{min} (\AA^2)	N
PPFOA	3.09	15.78	56.22	2.356	70.48	10

To show the surface activity, the effectiveness of surface tension reduction (Π_{cmc}) is proposed and determined as follows:

$$\Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (1)$$

where γ_0 is surface tension of water and γ_{cmc} is surface tension of solutions when the surfactant concentration is above cmc. For PPFOA molecules, the Π_{cmc} can be calculated according to the eq 1, and the value is about 56.22 mN/m. For conventional hydrocarbon surfactants, these three kinds of surfactants ($\text{C}_8\text{H}_{17}\text{N}(\text{CH}_3)_3 \cdot \text{C}_8\text{H}_{17}\text{SO}_4$, $\text{C}_{10}\text{H}_{21}\text{N}(\text{CH}_3)_3 \cdot \text{C}_{10}\text{H}_{21}\text{SO}_4$, and $\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_2\text{OH} \cdot \text{C}_{12}\text{H}_{25}\text{SO}_3$) have the prominent ability to decrease surface tension with Π_{cmc} values of 49, 50, and 48.5 mN/m.²² Through comparison, the PPFOA molecules have stronger ability to decrease surface tension. For the fluorocarbon surfactants ($\text{C}_7\text{H}_{15}\text{COONa}$, $\text{C}_7\text{H}_{15}\text{COOH}$, $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_4\text{COOH}$, and $\text{C}_7\text{F}_{15}\text{C}(\text{O})\text{NH}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$),²³ their lowest surface tensions of aqueous solutions are 24.2, 15.2, 15.5, and 17 mN/m, respectively. Through comparison, the ability to decrease surface tension of these three nonionic fluorocarbon surfactants is similar, and stronger than that of ionic fluorocarbon surfactants. In addition, to further indicate the surface activity of PPFOA in aqueous solution, the relative maximum reduction of surface tension ($\Pi_{\text{cmc}}/\gamma_0$) is introduced and regarded as a measure of surface activity of a surfactant in aqueous solution. In general, the larger the relative maximum reduction of surface tension, the better the surface activity of surfactant becomes. For PPFOA, the ($\Pi_{\text{cmc}}/\gamma_0$) value is about 0.78. For the cationic fluorosurfactant FC-4, its ($\Pi_{\text{cmc}}/\gamma_0$) value is about 0.74.²⁴ This also suggests superior surface activity of PPFOA.

As mentioned above, the decrease of surface tension in Figure 1 is ascribed to the adsorption of PPFOA at the air/water interface. So, the adsorption behavior is investigated. To indicate the adsorption behavior of PPFOA, two parameters are proposed, the maximum surface excess concentration Γ_{max} and the minimum area A_{min} occupied per surfactant molecule at the air/water interface. They can be calculated according to the following equations:²⁵

$$\Gamma_{\text{max}} = -\frac{1}{nRT} \left(\frac{d\gamma}{d \ln c} \right)_T \quad (2)$$

where n is the number of solute species whose concentration at the interface changes with the change of surfactant concentration c ; R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); T is the absolute temperature; γ represents the surface tension; and $d\gamma/d(\ln c)$ is the slope of surface tension γ vs $\ln c$ dependence when the concentration is near cmc. The value of n is taken as 1 for PPFOA in aqueous solution. Then A_{min} can be obtained from eq 3:

$$A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}} (\times 10^{23}) \quad (3)$$

where N_A is Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$). For the adsorption of PPFOA at the air/water interface at 25 °C, the values of Γ_{max} and A_{min} are $2.356 \mu\text{mol}/\text{m}^2$ and 70.48 \AA^2 , respectively, as listed in Table 1. For the other typical fluorocarbon surfactants, the A_{min} values of $\text{C}_7\text{F}_{15}\text{CH}_2\text{OP}(\text{O})-$

$[\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]_2$ and $[\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{NC}_5\text{H}_5]\text{Cl}$ are 59.9 and 54.2 \AA^2 . Through the comparison, PPFOA molecules have larger A_{min} , which relates to smaller Γ_{max} ,^{26–29} indicating that PPFOA molecules pack more sparsely at the air/water interface. Thus, the PPFOA molecules have a relatively lower packing density at the interface, which is due to the nature and structure of PPFOA molecules.

As is known to all, after the adsorption of PPFOA at the air/water interface reaches saturation, the micelles are formed by PPFOA molecules in aqueous solution. Then there is another question which appears: how many PPFOA molecules are necessary to form a micelle? To address this issue, the aggregation number (N) is usually employed. The values of N can be generally obtained through fluorescence quenching methods and ^1H NMR measurements.^{30,31} However, these methods are relatively complex and hard to calculate. In addition, the values of N can also be calculated according to the eq 4:¹²

$$N = \frac{4\pi L^2}{A_{\text{min}}} \quad (4)$$

where A_{min} is the minimum area occupied per surfactant molecule at the air/water interface obtained from eq 3; π is 3.14 and L is the hydrophobic length of surfactant. For PPFOA, the L is about 7.5 \AA according to the molecular structure simulation. This equation is based on a hypothesis: the formed micelles are spherical. As known to all, the morphologies of micelles include spherical, rodlike, wormlike, disclike, and cubic. When micelles begin to be formed at low concentrations, the micelles are generally regarded to be spherical. So the calculation of N is reliable. For PPFOA molecules, the value of N is about 10, which is slightly smaller than the fluorocarbon surfactants lithium perfluorooctylsulfonate with aggregation number of 36.^{27,31} This may be due to the steric hindrance effect induced by the PPFOA molecular structure.

To further investigate the micelles formed by PPFOA, DLS measurement was carried out. Figure 2 shows the DLS result of concentrated PPFOA solution, when the concentration is about 5 mM, a little larger than its cmc. The scattering peak is very sharp, indicating the micelles formation and the uniform size of micelles. The average hydrodynamic radius is about 3.77 nm

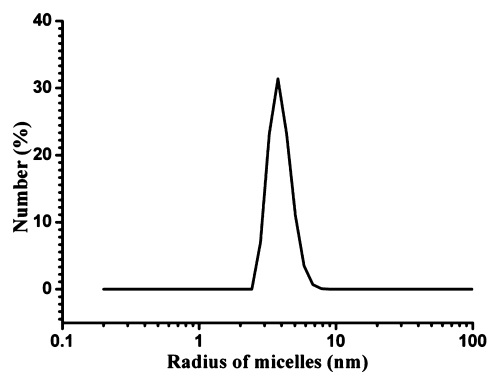


Figure 2. Radius and size distribution of PPFOA micelles in aqueous solution at 25 °C at PPFOA concentration of 5 mM.

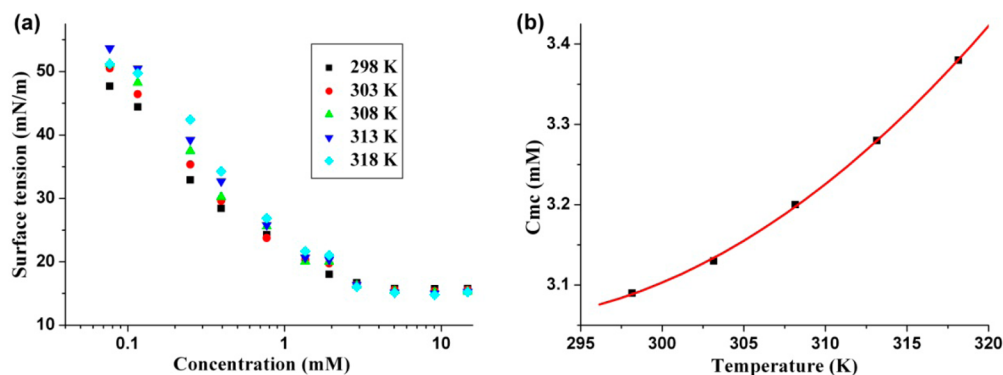


Figure 3. (a) Surface tensions versus the PPFOA concentration and (b) cmc values of PPFOA micelles at different temperatures.

Table 2. Thermodynamic Parameters of PPFOA Micelles Formed in Aqueous Solution at Different Temperatures

surfactants	<i>T</i> (K)	cmc (mM)	ΔG_m^0 (kJ/mol)	ΔH_m^0 (kJ/mol)	$-T\Delta S_m^0$ (kJ/mol)	ΔS_m^0 (J/molK)
PPFOA	298	3.09	−24.28	−1.658	−22.63	75.89
	303	3.13	−24.66	−2.656	−22.00	72.58
	308	3.20	−25.01	−3.621	−21.39	69.41
	313	3.28	−25.35	−4.555	−20.80	66.41
	318	3.38	−25.68	−5.460	−20.22	63.54

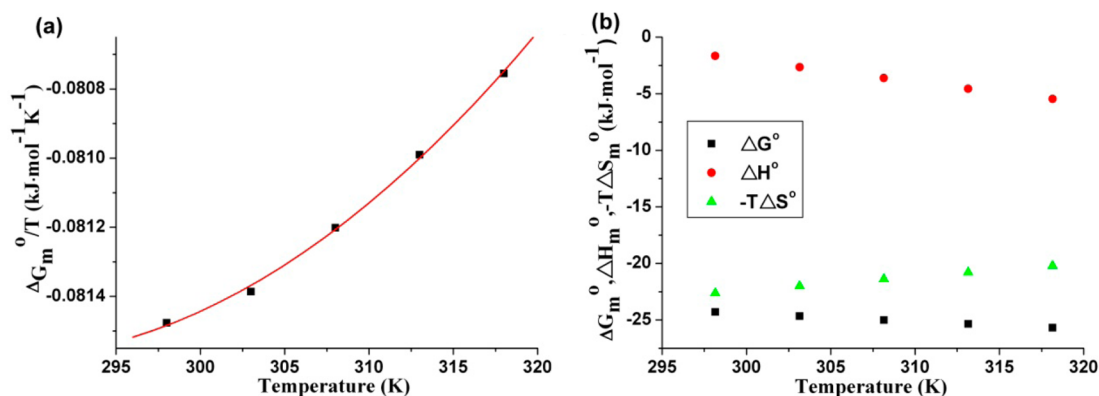


Figure 4. (a) The plots of $\Delta G_m^0/T$ and (b) thermodynamic parameters (ΔG_m^0 , ΔH_m^0 , and ΔS_m^0) in the micelles formation process at different temperatures.

with the polydispersity of 0.925, which is comparable to the size of conventional micelles (1–10 nm).²²

Thermodynamic Analysis on the Micelle Formation of PPFOA in Aqueous Solution. In general, temperature has a significant effect on the self-assembly behaviors of surfactant in aqueous solution. Figure 3a shows surface tensions versus PPFOA concentrations at different temperatures. From Figure 3a, these five curves show a similar tendency, and the final surface tensions γ_{cmc} are more or less the same. The cmc values at different temperatures can be easily obtained and listed in Table 2. Figure 3b shows the temperature dependence of cmc values. It is clear that the cmc values increase with temperature, and the plots fit a second-order polynomial, which agrees well with the other surfactants in aqueous solution.^{8,32,33}

For the thermodynamic parameters of micelles formed by PPFOA in water, the standard Gibbs free energy of micelle formation (ΔG_m^0) can be calculated according to the pseudophase model of micellization from the equation below:^{22,34}

$$\Delta G_m^0 = RT \ln X_{cmc} \quad (5)$$

where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T is absolute temperature; X_{cmc} is the cmc in molar fraction and can be transformed from cmc. Through eq 5, the values of ΔG_m^0 at different temperatures can be obtained and listed in Table 2. It is observed that the values of ΔG_m^0 are more negative with the increase of temperature, suggesting that the formation of micelles becomes more spontaneous. In addition, on the basis of the ΔG_m^0 , the standard Gibbs free energy of adsorption (ΔG_{ads}^0) can also be calculated using eq 6.¹² For PPFOA molecules, the value of ΔG_{ads}^0 at 25 °C is about −48.13 kJ/mol, which is similar to the fluorocarbon surfactants reported with the ΔG_{ads}^0 values of −35.8 and −41.8 kJ/mol.¹²

$$\Delta G_{ads}^0 = \Delta G_m^0 - \pi_{cmc} A_{min} \quad (6)$$

The standard enthalpy of micelle formation (ΔH_m^0) can also be determined according to the following Gibbs–Helmholtz equation:

$$\Delta H_m^0 = \left[\frac{\partial(\Delta G_m^0/T)}{\partial(1/T)} \right] \quad (7)$$

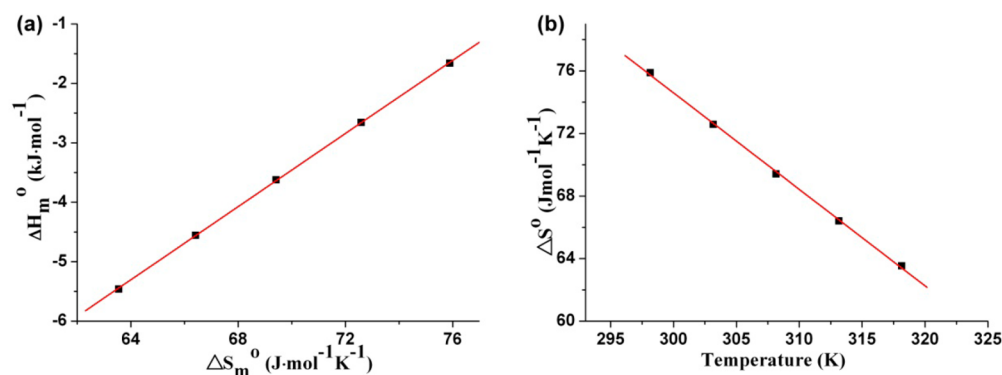


Figure 5. (a) The enthalpy–entropy compensation and (b) ΔS_m^0 versus temperature for PPFOA in aqueous solution.

From the eq 7, the values of $(\Delta G_m^0/T)$ are plotted as a function of $(1/T)$, and the curve is shown in Figure 4a. The curve fits a second-order polynomial. The values of ΔH_m^0 at different temperatures are determined from slopes of tangential lines and listed in Table 2.

Based on the calculation of ΔG_m^0 and ΔH_m^0 , the standard entropy of micelle formation (ΔS_m^0) can be obtained by applying the eq 8 and listed in Table 2.

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0)/T \quad (8)$$

Figure 4b describes the plots of thermodynamic parameters (ΔG_m^0 , ΔH_m^0 , and $-T\Delta S_m^0$) versus temperature (T). The ΔH_m^0 and $(-T\Delta S_m^0)$ means the contributions of enthalpy change and enthalpy change to the standard Gibbs free energy of micelle formation, respectively. From the plots in the temperature range from 25 to 45 °C, with the increase of temperature, the change of the Gibbs free energy is very slight, while the enthalpy change decreases and the entropy change increases remarkably. Comparing their contributions to ΔG_m^0 , the entropy change always plays a major role in the determination of ΔG_m^0 . Thus, the micelle formation of PPFOA in aqueous solution is largely entropy-driven, which is similar to the other kinds of surfactants in aqueous solution.²²

For the enthalpy change and entropy change in aqueous solution, some linear relationship exists and it is usually called the entropy–enthalpy compensation.^{35,36} This compels us to investigate the relationship between enthalpy and entropy change for micelle formation of PPFOA in water. The entropy–enthalpy compensation generally includes two parts: the desolvation part due to the dehydration of hydrophobic fluorocarbon chain and the chemical part due to the aggregation of surfactant tails to form micelles. Figure 5a shows the dependence of enthalpy change (ΔH_m^0) to entropy (ΔS_m^0). From this figure, the plots of ΔH_m^0 vs ΔS_m^0 show a good linear relationship. The entropy–enthalpy compensation can be described as the following form:

$$\Delta H_m^0 = \Delta H_m^A + T_c \Delta S_m^0 \quad (9)$$

where T_c is the compensation temperature and a measure of desolvation part; ΔH_m^A is the enthalpy belonging to the chemical part. From the fitting straight line, for PPFOA micelles formation, the values of ΔH_m^A and T_c are -25.00 kJ/mol and 307.8 K, respectively. This compensation temperature is similar to the fluorocarbon surfactants reported before with ΔH_m^A and T_c values of -24.6 kJ/mol and 301.5 K.³⁷ The parameter ΔH_m^A is the enthalpy when ΔS_m^0 is equal to 0, indicating the stability of micelles. The greater the value of

ΔH_m^A , the less stable the formed micelles. Thus, compared with the fluorocarbon surfactants mentioned before, the PPFOA micelles are slightly more stable.

Another thermodynamic parameter of micelles, the heat capacity of micellization (ΔC_{pm}^0), was determined from the curve of micellization entropy as a function of temperature.³⁸ As shown in Figure 5b, the plots fit a good linear relationship. The value of ΔC_{pm}^0 is equal to the slope of fitting line and about -0.62 kJ·mol⁻¹·K⁻¹, which is a little smaller than the other fluorocarbon surfactants, such as sodium perfluoroalkyl carboxylates (C_nFONa , $n = 6, 9, 10$ with ΔC_{pm}^0 values in the range of -0.21 to -0.58 kJ·mol⁻¹·K⁻¹).³⁸ The negative value of ΔC_{pm}^0 suggests that the hydration shell is lost during the micellization process due to organized water molecules around the hydrophobic chain of surfactant. The more negative the ΔC_{pm}^0 value, the larger the hydrophobic surface being exposed to water upon demicellization becomes. Through the above comparison, the ΔC_{pm}^0 value of PPFOA is more negative,¹² indicating more hydrophobic chains are exposed to water molecules upon demicellization.

Dissipative Particle Dynamic (DPD) Simulations on the Micelle Formation of PPFOA in Aqueous Solution.

DPD simulations were performed on Material Studio software. Detailed information for this simulation method can be seen in previous literature.^{39,40} In the simulation, the PPFOA molecule is represented by a dimeric model shown in Figure 6, in which this amphiphilic molecule is divided into two parts, the hydrophilic part H and the hydrophobic part C, which are connected by a harmonic spring. The water molecule is represented by the monomer particle W. The interaction parameters a_{ij} between different particles are determined by

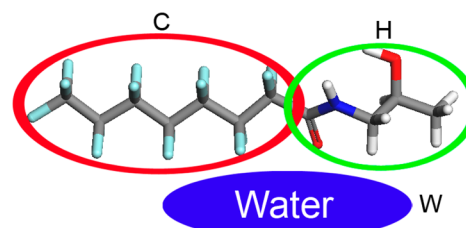


Figure 6. Schematic representation of the simulation model. The PPFOA molecule is divided into two DPD particles, fluorinated carbon chain (C) and headgroup (H), which are connected together by a harmonic spring. Water is represented by a single DPD particle W.

using the blends model. They were as follows: $a_{C-C} = a_{H-H} = a_{W-W} = 15$, $a_{C-H} = 80.5$, $a_{C-W} = 82.4$, and $a_{H-W} = 0$. The dynamics of 5000 DPD particles, starting from a random distribution, is simulated in a $10 \times 10 \times 10$ cubic box under periodical boundary conditions. The step size for the integration of the Newton equation is set to $\Delta t = 0.05$. The temperature is set to 298 K.

In order to get into the dynamic process for micelle formation, DPD simulations were performed on the system with 20% PPFOA content and the corresponding results were shown in Figure 7. At the very initial stage, the system is

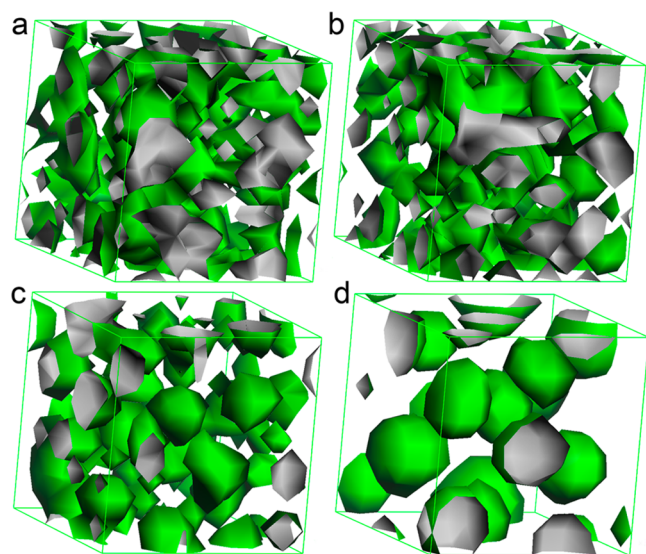


Figure 7. The simulated isodensity profiles for the micelles formed at room temperature at 20% PPFOA content at different time steps: (a) 3; (b) 10; (c) 100; and (d) 20 000. The size of the simulation box is $10 \times 10 \times 10$ in DPD units.

unstable, and the beads in the system display an unordered arrangement (Figure 7a,b), indicating no unordered structure was formed. With time evolution, premicelles with spherical structures were formed, but there still exists some unordered structure, as can be clearly seen in Figure 7c. Then, they transformed to more ordered spherical micelles with time steps increased to 20 000 (Figure 7d). Such an evolution process often happens in tens of μs and is very difficult to observe directly by experimental methods. The simulated results are therefore considered to be a great supplement for the experimental results and can provide more microphase separation information.

CONCLUSIONS

In summary, the micelles formed by a fluorocarbon surfactant PPFOA in aqueous solution were investigated in this work. A series of adsorption parameters at the air/water interface were calculated, which showed the superior surface activity of PPFOA. The DLS result confirmed the formation of PPFOA micelles and the radius was about 3.77 nm. The micelles formation is entropy-driven in the temperature region of 25 and 45 °C. The DPD simulation further simulated the formation process of PPFOA micelles in water. We expect that this work can deepen the basic understanding of fluorocarbon surfactants.

ASSOCIATED CONTENT

Supporting Information

The ITC results and discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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