# Influence of Counterions on Micellization of Tetramethylammonium Perfluorononanoic Carboxylate in 1-Butyl-3-methylimidazolium Ionic Liquid

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Ⓢ *Supporting Information*

ABSTRACT: The influence of counterions on micellization of perfluorononanoic carboxylate ammonium salts in water and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]-BF_4) solutions was investigated by surface tension and ^{19}F NMR measurements and freeze-fracture transmission electron microscopy (FF-TEM) observations. Changes in the counterions of the fluorocarbon surfactants have different effects on the two solvents. With the increase of counterion volume, the critical micelle concentration (cmc) value of relevant fluorinated surfactant decreases in aqueous solutions. This is because the counterions with larger size, such as $^+N(CH_3)_4$, can be little hydrated, which can screen the electrostatic repulsion of the headgroups of the fluorocarbon surfactant and thus facilitate micelle formation. However, the fluorocarbon surfactants can dissolve and form micelles in [bmim]BF_4 only when they provide with largest counterion such as $^+N(CH_3)_4$. This is because the counterion, $^+N(CH_3)_4$, disperses the charge of the cations, which could weaken the electrostatic interaction between the ion pair of the surfactant, leading to a higher degree of counterion binding. The thermodynamic parameters estimated from the temperature dependence of the cmc values tell us that the micelle formation for tetramethylammonium perfluorononanoic carboxylate ($C_8F_{17}COON(CH_3)_4$, PFNT) in ionic liquids (ILs) is an entropy-driven process at low temperature but an enthalpy-driven process at high temperature. The driving force of the micellization for fluorocarbon surfactants in [bmim]BF_4 is the solvophobic effect, due to the hydrophobic and oleophobic properties of fluorocarbon chains.
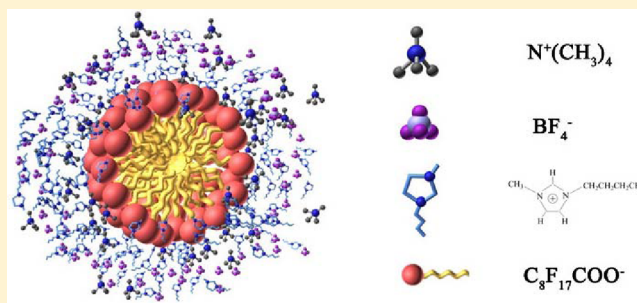
INTRODUCTION

Ionic liquids (ILs), as a class of environmentally friendly solvents, are stable over a large range of temperatures and have negligible vapor pressures.[1] Owing to their ability to undergo multiple solvation interactions with many molecules, ILs have been widely used in organic synthesis,[2] chemical separation,[3] nanomaterial preparation,[4−6] and polymer gel electrolytes[7] as complex solvents. The amphiphilic surfactant can self-assemble in ILs to form different aggregates such as micelles,[8] vesicles,[9] or liquid crystals.[10,11] Indeed, special attention to surfactant organization in ILs could open new research directions toward micellar catalysis into IL media, solvation enhancement for apolar entities, and lyotropic properties experimentally as well as theoretically during the past decades.[12] Up to now, various kinds of microemulsions containing IL have been prepared, including IL-in-oil and oil-in-IL microemulsions, IL-in-water and water-in-IL microemulsions, and IL-in-IL microemulsion.[13−16] Recently, the creation of microemulsions with IL as the continuous phase and CO_2 as the dispersed phase has been reported first.[17] The novel microemulsion including surfactant N-ethyl perfluorooctylsulfonamide and IL 1,1,3,3-tetramethylguanidinium acetate has many advantages such as the tunable size of dispersed CO_2 droplet and designable

features of ILs, which may be used in material synthesis, chemical reactions, and extraction.

Up to now, most of surfactant micelles investigated in ILs are formed by nonionic surfactants; for example, the aggregation behavior of a series of pure alkyl poly(ethylene glycol) ethers in 1-butyl-3-methyl-imidazolium (bmim) ILs with various counterions was studied by Patrascu et al.[18] The alterations/modifications by addition of a popular "hydrophobic" IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), in the properties of dilute aqueous micellar solutions of a nonionic surfactant, Triton X-100, were reported by Behera et al.[19] They also observed that several typical nonionic surfactants, Brij-35, Brij-700, Tween-20, and Triton X-100, could aggregate into micelles in a low-viscosity room-temperature IL 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([emim]Tf_2N).[8] However, no aggregation was observed for the cationic surfactant cetyltrimethylammonium bromide, and the anionic surfactant sodium dodecyl sulfate (SDS) does not appear to solubilize within emimTf_2N at ambient conditions. The micelle formation

of several traditional surfactants in two ILs, 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and [bmim]PF$_6$, was investigated by Armstrong et al. by using surface tension measurements and inverse gas chromatography.[20] Zheng's group has intensively investigated the thermodynamics of surfactant aggregation in ILs, including two aggregates for Tween 20 and aggregation behavior of a cationic fluorinated surfactant in different ILs.[21−24] Recently, Sarkar's group has intensively investigated the properties and applications of micelle systems in ionic liquids,[25−28] such as photophysical properties,[29] tunable drug delivery,[30] and synthesis of inorganic nanoparticle materials.[31]

In fact, the mechanism of surfactant aggregation in ILs has not been clear, and it would be of interest and importance from both practical and academic points of view to investigate more efficient ionic surfactants in ILs. However, most of ionic surfactants, especially anionic surfactants, are very difficult to dissolve in ILs. As is widely known, fluorocarbon amphiphiles are more surface active and more hydrophobic than their hydrogenated counterparts, due to their larger cross section and rigid fluorocarbon chains.[32,33] Reports on micellization of fluorinated surfactants in ILs are rare,[22,23] because of their insolubility in ILs. Unexpectedly, we discovered that the change of counterions can make the anionic fluorinated surfactants dissolve in ILs and self-assemble into aggregation. This is because the voluminous counterions, such as $^+N(CH_3)_4$, can weaken the electrostatic interaction between the ion pair of the surfactant. In the present paper, we describe the micellization of an anionic fluorocarbon surfactant, tetramethylammonium perfluorononanoic carboxylate ($C_8F_{17}COON(CH_3)_4$, PFNT), in IL 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]-BF$_4$). Surface tension was measured to investigate the surface properties of the fluorocarbon surfactant water and in IL. Freeze-fracture transmission electron microscopy (FF-TEM) indicated the micelle formation of PFNT in [bmim]BF$_4$. ^{19}F NMR chemical shifts revealed that the premicellar aggregates transform into micelles. On the basis of the additional parameters, such as the maximum surface excess concentration, Γ_{max}, and the minimum molecular sectional area, A_{min}, one can observe that the counterions ($^+N(CH_3)_4$) play an important role in the micelle formation of the fluorocarbon surfactant in ILs. The thermodynamic parameters estimated from the temperature dependence of the critical micelle concentration (cmc) values tell us that the micelle formation for PFNT in ILs is an entropy-driven process at low temperature but an enthalpy-driven process at high temperature.

EXPERIMENTAL SECTION

Chemicals and Materials. The IL, [bmim]BF$_4$, used here was purchased from the Center for Green Chemistry and Catalysis (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, >99%). Tetramethylammonium perfluorononanoic carboxylate ($C_8F_{17}COON(CH_3)_4$, PFNT), methylammonium perfluorononanoic carboxylate ($C_8F_{17}COONH_3CH_3$, PFNM), and dimethylammonium perfluorononanoic carboxylate ($C_8F_{17}COONH_2(CH_3)_2$, PFND) were gifts from Hoechst Aktiengesellschaft Werk, Gendorf (Frankfurt-am-Main, Germany). Ultrapure water, with a resistivity of 18.25 MΩ cm, was obtained using a UPH-IV Ultrapure water purifier (Chengdu Ultrapure Technology Co. Ltd., China).

In order to get an idea of the purity of the IL ([bmim]BF$_4$), ^{1}H NMR spectra and IR spectra of the IL were performed, and

the results are appended as Supporting Information (Figures S1 and S2). Both of the two data indicate that the pure [bmim]BF$_4$ solution does not contain impurity. Karl Fischer titration was performed to determine the amount of water in IL ([bmim]-BF$_4$), which is about 0.23%.

Methods and Characterization. Surface tension measurements were conducted on a Krüss K100 (Germany) surface tensiometer using the plate method. Temperature was controlled using a Haake K10 (Germany) superconstant temperature trough. All the surface tension data was repeated at least twice until the values were reproducible.

To characterize the micellar structure of PFNT in [bmim]-BF$_4$ samples, FF-TEM was carried out. A small amount of clear solution to be characterized was placed on a 0.1 mm thick copper disk covered with a second copper disk. The copper sandwich with the sample was immersed rapidly into the liquid ethane cooled by liquid nitrogen. They were transferred into liquid nitrogen after several seconds. The samples, after being transferred into the chamber of the freeze-etching apparatus (Balzers BAF-400D), were fractured at a temperature and pressure of −150 °C and 10^{-7} Pa. After being etched for 1 min, Pt−C was sprayed onto the fracture face at 45°, and then C was sprayed at 90°. The replicas were examined on a JEOL 100CX-II TEM operating at an accelerating voltage of 100 kV.

^{19}F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer equipped with pulse field gradient module (Z axis) using a 5 mm BBO probe operating at 376.72 MHz. The ^{19}F spectra are reported in the range from +30 to −170 ppm (digitized points = 32 K, 90° pulse = 7.4 ms, relaxation delay = 2 s). ^{19}F NMR measurements were performed at 25.0 ± 0.5 °C.

RESULTS AND DISCUSSION

Surface Tension Measurements. Surface tension measurements were performed to detect the surface absorption and micellization of the fluorocarbon surfactants in water and [bmim]BF$_4$. Figure 1 presents the surface tension versus
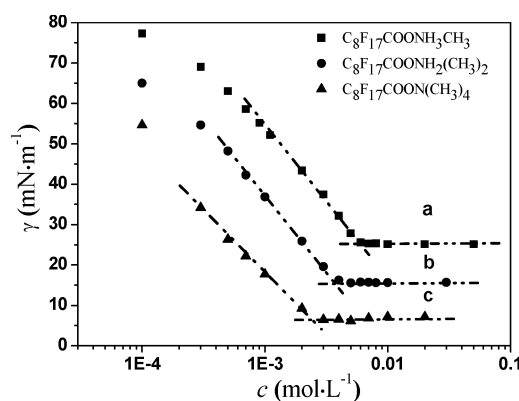
Figure 1. Surface tension vs concentration plots obtained for PFNM (a), PFND (b), and PFNT (c) in water at 25.0 ± 0.1 °C. Surface tension curves of PFNM (a) and PFNT (c) are drawn by shifting the surface tension values appropriately.
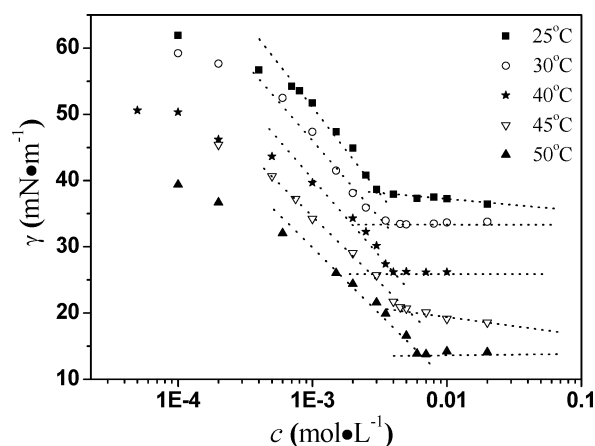
concentration plot obtained for the solutions of PFNT, PFND, and PFNM in water at 25.0 ± 0.1 °C, where the surface tension curves obtained for PFNT (Figure 1c) and PFNM (Figure 1a) are drawn by shifting the scale on the vertical axis appropriately in order to avoid the overlapping of data points. The surface tension decreases initially with increasing concentration of surfactants, suggesting that the surfactant molecules are

Table 1. Surface Properties and Micellization Parameters of PFNM, PFND, and PFNT in Aqueous Solutions at 25.0 ± 0.1 °C

surfactants	cmc (mmol·L^{-1})	γ_{cmc} (mN·m^{-1})	Γ_{max} (μmol·m^{-2})	pC$_{20}$	Π_{cmc} (mN·m^{-1})	A_{min} (Å^2)
C$_8$F$_{17}$COONH$_3$CH$_3$	6.00	15.3	3.409	3.29	57.3	48.7
C$_8$F$_{17}$COONH$_2$(CH$_3$)$_2$	3.73	15.6	3.324	3.45	57.0	50.0
C$_8$F$_{17}$COON(CH$_3$)$_4$	2.39	19.6	2.651	3.66	53.0	62.6

adsorbed at the air/solution interface. Then a plateau appears in the ($\gamma - c$) plot, indicating that the micelles have been formed, and the cmc is determined from the break point of the plot. The surface absorption and micellization parameters of the three surfactants are listed in Table 1. Changes in the counterions of the fluorocarbon surfactants have an effect on their surface activities. With the increasing of molecular bulk of the counterions, the cmc's of PFNM, PFND, and PFNT decrease successively, whereas the values of γ_{cmc} rise gradually. This is probably because the counterions with larger size, such as ($^+$N(CH$_3$)$_4$) can be little hydrated, which can screen the electrostatic repulsion of the headgroups of the fluorocarbon surfactant and thus facilitate micelle formation.[34,35] However, the large counterions may also adsorb at the air/solution interface and thus reduce the values of γ_{cmc}. At the same time, the A_{min} value for PFNT is rather higher than that of the other two surfactants, which means the fluorocarbon chains arrange rather loose at the air/solution interface. This is because the four methyls of counterion ($^+$N(CH$_3$)$_4$) disperse the charge of the cations, which could weaken the electrostatic interaction between the ion pair of the surfactant, leading to a higher degree of counterion binding.

The counterions of the fluorocarbon surfactants affect the micelle formation in [bmim]BF$_4$ solution, as the fluorocarbon surfactant with the largest counterions (PFNT) can form micelle in [bmim]BF$_4$ solution, but this is not the case for PFNM and PFND. The surface tension obtained for the solutions of PFNT in [bmim]BF$_4$ as a function of the concentration at different temperatures, where the surface tension curves obtained for temperatures different from 45 °C are drawn by shifting the scale on the vertical axis appropriately in order to avoid the overlapping of data points, are shown in Figure 2. At each temperature, the surface tension decreases initially with increasing concentration of surfactants, suggesting
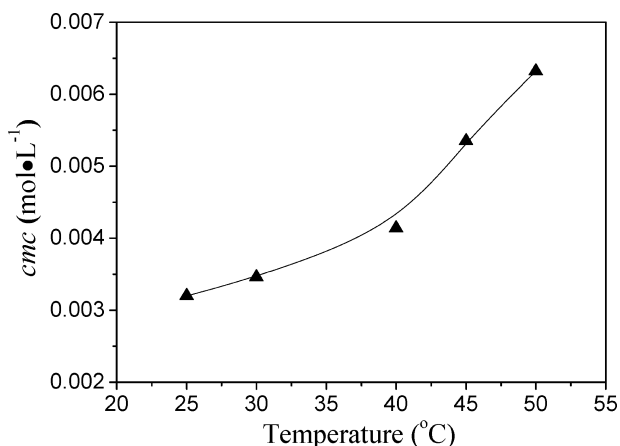
that the fluorocarbon surfactant molecules are adsorbed at the air/solution interface. The initial decrease of the surface tension with the addition of PFNT is followed by an abrupt change in the slope of the surface tension versus concentration curve. Similar to that observed for aqueous solutions of micelle-forming surfactants, then a plateau appears in the ($\gamma - c$) plot, indicating that the micelles have been formed in [bmim]BF$_4$ solution, and the cmc is determined from the break point of the plot. The values of cmc were determined from the intersection of two straight lines drawn in the low- and high concentration regions in the surface tension curves ($\gamma - \log c$ curves), and the surface absorption and micellization parameters of PFNT in [bmim]BF$_4$ solution at different temperatures are listed in Table 2. Compared to aqueous solution, IL species are known to be a rather poor solvent for micelle formation by surfactants, not only for hydrocarbon surfactants[18−20] but also for fluorocarbon ones[22,23] studied to date. The adsorption efficiency, pC$_{20}$, can be used to measure the adsorption efficiency of surfactant molecules at the air/IL solution interface, whereas the surface pressure at the cmc, Π_{cmc}, can be a measure of effectiveness of the surfactant in lowering the surface tension of the solvent. The values of the two parameters at various temperatures in [bmim]BF$_4$ solution are also shown in Table 2. The pC$_{20}$ for PFNT in [bmim]BF$_4$ is in the range of 2.58−2.78, and the Π_{cmc} value is range from 24.3 to 28.5 mN·m^{-1}, which are similar to the data for SDS, C$_{16}$E$_8$, and another cationic fluorinated surfactant from previously published reports.[18,20,23] This means that the temperature has little influence in the adsorption of the fluorocarbon surfactants at the air/IL solution interface.

The values of cmc are plotted as a function of temperature for PFNT in [bmim]BF$_4$, as shown in Figure 3. One can observe that the cmc value increases with temperature showing a concave curve. The cmc values of both hydrocarbon and fluorocarbon ionic surfactants in aqueous solutions have been as a function of temperature by many researchers.[36−38] The cmc value decreases slightly at first and then increases slowly at higher temperatures for ionic surfactants. This trend is similar to the temperature dependence obtained for the cmc of PFNT in [bmim]BF$_4$. It is of interest to compare the present results with those obtained for studied fluorocarbon surfactants in aqueous solution and in [bmim]BF$_4$ solution. It is well-known that the influence of temperature to the micelle formation of ionic surfactants in aqueous solutions is dependent on the combination of hydration interaction with headgroups and hydrophobic interaction with tail chains. However, we believe that the solvophobic interaction between the fluorocarbon tails of the surfactant molecules in [bmim]BF$_4$ is dominant in the micelle formation affected by increasing of temperature. This is because the increase of temperature has little influence on the electrostatic interaction between cationic and ionic pairs in IL solutions.

Thermodynamic Analysis on the Micelle Formation of PFNT in [bmim]BF$_4$. As is well-established in the thermodynamics of micelle formation, the standard Gibbs free energy of aggregate formation for an ionic surfactant is given as follows:[36]

Figure 2. Surface tension vs concentration plots obtained for PFNT in [bmim]BF$_4$ solutions at various temperatures. Surface tension curves at every temperature are drawn by shifting the surface tension values appropriately but not at 45.0 ± 0.1 °C. Temperatures are indicated in the figure.

Table 2. Surface Properties and Micellization Parameters of PFNT in [bmim]BF$_4$ Solutions at Various Temperatures

T (K)	cmc (mmol·L^{-1})	γ_{cmc} (mN·m^{-1})	Γ_{max} (μmol·m^{-2})	pC$_{20}$	Π_{cmc} (mN·m^{-1})	A_{min} (Å^2)
298	3.20	21.7	2.309	2.64	24.3	71.9
303	3.46	19.2	1.934	2.78	26.4	85.9
313	4.14	19.1	2.375	2.60	26.2	69.92
318	5.35	16.3	1.463	2.58	28.5	113.5
323	6.32	16.2	1.636	2.59	28.3	101.5

Figure 3. Temperature dependence on the cmc values of PFNT in [bmim]BF$_4$.

$$\Delta G_m^0 = (1 + \beta)RT \ln X_{cmc} \tag{1}$$

where X_{cmc} is expressed in mole fraction units, and it can be calculated from cmc. Herein, we consider that the fluorocarbon surfactant molecules are completely ionized in [bmim]BF$_4$ solution, due to the weak electrostatic interaction between cationic and ionic pairs, so the degree of counterion binding (β) can also be curtly considered as 1. Once ΔG_m^0 as a function of temperature is known, the standard enthalpy of micelle formation (ΔH_m^0) can be derived by applying the Gibbs–Helmholtz equation:

$$\left[\frac{\partial(\Delta G_m^0/T)}{\partial(1/T)} \right] = \Delta H_m^0 \tag{2}$$

Then the standard entropy of micelle formation (ΔS_m^0) is obtained through the following relation:

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \tag{3}$$

The thermodynamic parameters for PFNT in [bmim]BF$_4$ were thus obtained and are listed in Table 3.

It can be seen in Table 3 that the temperature dependence of ΔG_m^0 is rather weak. The plots of ΔH_m^0 and $-T\Delta S_m^0$ as a

Table 3. Critical Micelle Concentration (cmc) and Thermodynamic Parameters of Micelle Formation for PFNT in [bmim]BF$_4$ Solutions at Various Temperatures

T (K)	cmc (mmol·L^{-1})	ΔG_m^0 (kJ·mol^{-1})	ΔH_m^0 (kJ·mol^{-1})	$-T\Delta S_m^0$ (kJ·mol^{-1})	ΔS_m^0 (J·Kmol^{-1})
298	3.20	−36.88	−6.304	−30.576	102.6
303	3.46	−37.11	−22.19	−14.92	49.24
313	4.14	−36.80	−52.43	15.63	−50.75
318	5.35	−36.10	−66.83	30.73	−96.64
323	6.32	−35.76	−80.80	45.04	−139.4

function of temperature for PFNT in [bmim]BF$_4$ are shown in Figure 4. In the range of temperatures investigated, the value of
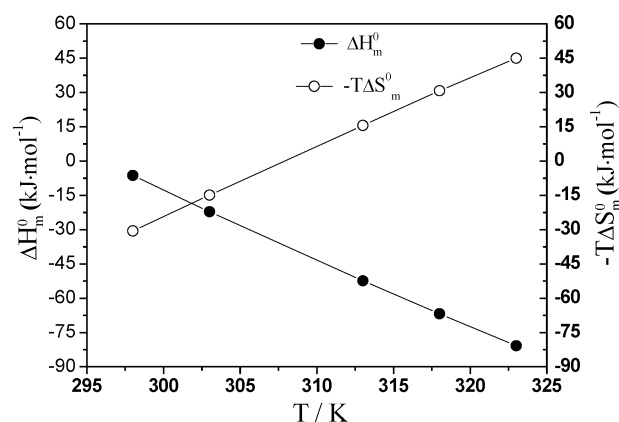
Figure 4. Thermodynamic parameters of micelle formation as a function of temperature for PFNT in [bmim]BF$_4$ solution. Solid and hollow circles correspond to ΔH_m^0 and $-T\Delta S_m^0$, respectively.

ΔH_m^0 decreases with temperature, whereas the $-T\Delta S_m^0$ increases. As far as we know, the micelle formation for ionic surfactant in aqueous solution is an entropy-driven process at room temperature. However, one can observe from Figure 4 that the micelle formation for PFNT in ILs is an entropy-driven process at low temperature but an enthalpy-driven process at high temperature. We believe that the behavior of thermodynamic parameters associated with temperature with temperature rise is caused by solvophobic interaction between the solvophobic tails in the surfactant molecules. The electrostatic interaction between cationic and ionic pairs in IL solutions is slightly affected by the temperature rise.

^{19}F NMR Results. The NMR chemical shift is a parameter that in part depends on the intermolecular surrounding of the nucleus in question. Consequently, the fluorocarbon nuclei resonance shows an upfield shift upon micellization in aqueous solutions. The peak of the terminal −CF$_3$ group is the strongest, and its chemical shift is the most sensitive to the micellization. Herein, the ^{19}F NMR spectroscopy was also used to the monitor the micellization of PFNT in [bmim]BF$_4$ solution. In the case for the fluorocarbon surfactant in IL solutions, the observed ^{19}F NMR chemical shift for the terminal −CF$_3$ group of the fluorocarbon surfactant can be expressed as[38−40]

$$\delta_{obs} = \frac{c_{Fmo}}{c_T}(\delta_{mo} - \delta'_{mic}) + \delta'_{mic} \tag{4}$$

where c_{Fmo} represents the concentration of the fluorocarbon surfactant in the monomer state, c_T is the total concentration of the surfactants, and δ_{mo} and δ_{mic} are the ^{19}F NMR chemical shift of the −CF$_3$ group in monomeric and micellar states, respectively.
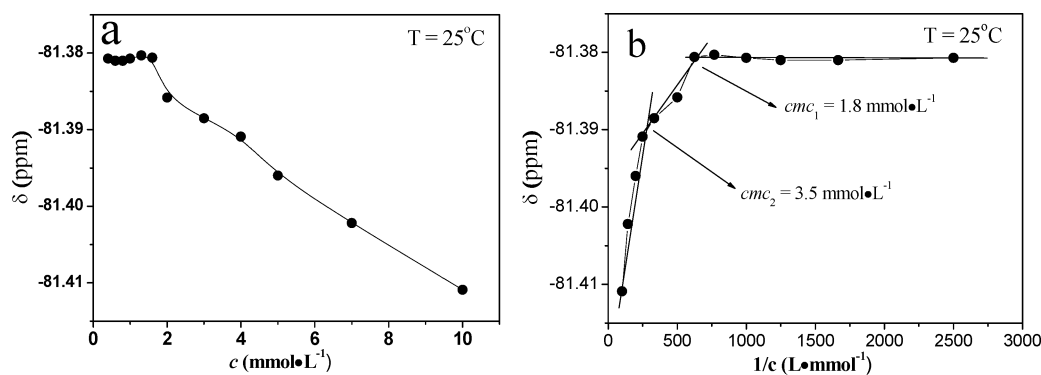
Figure 5. (a) Plot of the ^{19}F NMR chemical shift for the terminal CF_3 in the fluorocarbon chain of PFNT as a function of the surfactant concentration in [bmim]BF_4 solutions. (b) Plot of δ_{obs} against $1/c$. Temperature is 25.0 ± 0.5 °C.

The plot of chemical shift, δ, for terminal CF_3 fluorine as a function of PFNT concentration is shown in Figure 5a. It can be seen that δ remains constant up to about 1.5 mmol·L^{-1} and then decreases monotonously with the increase of PFNT concentration. The constant δ is invariable in the low-concentration region due to the free monomeric state of the surfactant molecules. However, when the concentration of PFNT is increased, molecular aggregates of PFNT molecules are formed, and the fluorocarbon chains contact each other in the aggregates. Then, the environment of the solution becomes less polar, due to the enhanced electron density around the fluorine nuclei, and the fluorocarbon nuclei resonance shows an upfield shift in IL solution, similar to the micelle formation for ionic fluorocarbon surfactant in aqueous solution. Unexpectedly, the constant δ starts to decrease at a concentration lower than the cmc, suggesting premicelle formation occurs below the cmc.[23] Figure 5b shows the plot of δ_{obs} against $1/c$ for the data presented in Figure 5a. The plots of δ_{obs} against $1/c$ can be linearly fit by three straight lines. The two break points provide concentrations corresponding to C_{pre} (premicelle formation concentration) and cmc, respectively. The values estimated from this plot are $C_{pre} = 1.8$ mmol·L^{-1} and cmc = 3.5 mmol·L^{-1}. The cmc value is almost consistent with that from surface tension measurements.

FF-TEM Observations. In the next experiment, we determined the microstructures of micelles formed by PFNT in [bmim]BF_4 solutions by FF-TEM measurements. The FF-TEM micrograph in Figure 6 clearly shows the spherical micelles of PFNT in [bmim]BF_4 solution. One can observe the
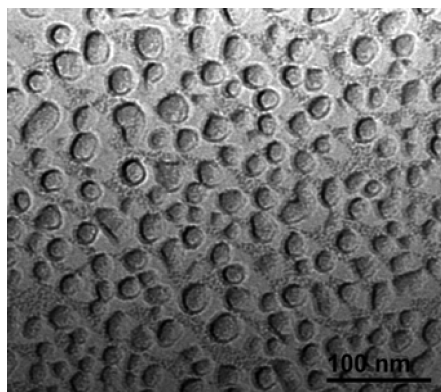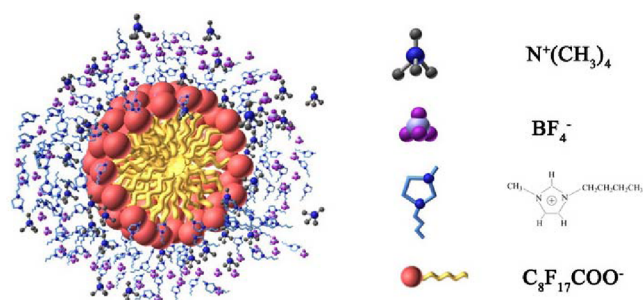
micelles formed in [bmim]BF_4 solution above the cmc in the surface tension versus concentration curve are small ranging from 10 to 20 nm. The diameter of the micelles formed by PFNT in [bmim]BF_4 solution is larger than that of fluorocarbon surfactant formed in aqueous solution[37] but smaller than that of cationic fluorocarbon surfactant formed in ILs.[22,23]

Proposed Mechanism of Micelle Formation of PFNT in [bmim]BF_4 Solution. Until now, the mechanism of micelle formation of fluorocarbon surfactants in ILs is disputable. Li et al. reported that a cationic fluorocarbon surfactant can form two different kinds of micelles in hydrophilic [bmim]BF_4 and hydrophobic [bmim]PF_6.[22] They claimed the driving force of the micellization for fluorocarbon surfactants in hydrophilic [bmim]BF_4 is the solvophobic effect (hydrophobic interaction), and the micelles formed in [bmim]BF_4 are regarded as traditional "micelles". However, the aggregates formed in hydrophobic [bmim]PF_6 are considered as nanodroplets composed of fluorocarbon surfactant molecules segregated from the IL solution, due to the weak solvophobic effect between fluorocarbon surfactant and [bmim]$PF6$. In addition, through the ion pair formation between the surfactant cation and the IL anion, the cationic fluorinated surfactant can form unusual micelles in an inconvenient solvent, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim]Tf_2N).[23] Actually, the speculated mechanism of these systems needs more experimental or theoretical evidence.

In the present work, because the voluminous counterions, such as $^+N(CH_3)_4$, which can weaken the electrostatic interaction between the ion pair of the surfactant in ILs, the fluorocarbon surfactant molecules can dissolve and completely ionize in [bmim]BF_4 solution. It is well-known that fluorocarbon chains are both hydrophobic and oleophobic, so we believe the solvophobic effect between fluorocarbon surfactants and normal ILs is dominant in the micelle formation. According to experimental data and the above analysis, a proposed mechanism of self-assembly of fluorocarbon surfactant into micelles is shown in Figure 7. As shown in the model, the fluorocarbon chains self-assemble to the solvophobic core first. Then, two cations, including $^+N(CH_3)_4$ and bmim$^+$, are fixed in the surface of the fluorocarbon core through the electrostatic interaction. Beyond the fixed counterion layer, the other three ions form the diffusing layer. So, the key of the micelle formation for fluorocarbon surfactants in ILs is weakening the electrostatic interaction between the ion pair of the surfactant, and increasing the volume of their counterions is an efficient way.

Figure 6. FF-TEM image obtained for PFNT in [bmim]BF_4 solutions. The surfactant concentration is 20 mmol·L^{-1}.

Figure 7. Schematic view of the self-assembly of PFNT into micelles in [bmim]BF$_4$ solution. The molecular models of correlative ions are indicated in the figure.

N$^+$(CH$_3$)$_4$

BF$_4^-$

C$_8$F$_{17}$COO$^-$

CONCLUSIONS

In summary, we investigated the micellization of perfluorononanoic carboxylate ammonium salts with different counterions (PFNM, PFND, and PFNT) in water and [bmim]BF$_4$ solutions. Changes in the counterions of the fluorocarbon surfactants have an effect on their surface activities in aqueous solution. With the increase of counterion volume, the cmc value of the relevant fluorinated surfactant decreases. This is because the counterions with larger size, such as ($^+$N(CH$_3$)$_4$), can be little hydrated, which can screen the electrostatic repulsion of the headgroups of the fluorocarbon surfactant and thus facilitate micelle formation. However, the fluorocarbon surfactants can dissolve and form micelles in [bmim]BF$_4$ only when they provide with largest counterion (PFNT). This is because the four methyls of counterion ($^+$N(CH$_3$)$_4$) disperse the charge of the cations, which could weaken the electrostatic interaction between the ion pair of the surfactant, leading to a higher degree of counterion binding. So, we believe that the key of the micelle formation for fluorocarbon surfactants in ILs is weakening the electrostatic interaction between the ion pair of the surfactant, and increasing the volume of their counterions is an efficient way. The driving force of the micellization for fluorocarbon surfactants in [bmim]BF$_4$ is the solvophobic effect, due to the hydrophobic and oleophobic properties of fluorocarbon chains.

ASSOCIATED CONTENT

Ⓢ Supporting Information
^{1}H NMR spectra and FT-IR spectra of [bmim]BF$_4$. 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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REFERENCES

(1) Xin, B.; Hao, J. Chem. Soc. Rev. 2010, 39, 769−782.
(2) Mehnert, C. P.; Cook, R. A.; Dispenziere, N. C.; Afeworki, M. J. Am. Chem. Soc. 2002, 124, 12932−12933.
(3) Anderson, J. L.; Armstrong, D. W. Anal. Chem. 2005, 77, 6453−6462.
(4) Zhou, Y.; Antonietti, M. Adv. Mater. 2003, 15, 1452−1455.
(5) Wang, Y.; Yang, H. J. Am. Chem. Soc. 2005, 127, 5316−5317.
(6) Bühler, G.; Feldmann, C. Angew. Chem., Int. Ed. 2006, 45, 4864−4867.
(7) Susan, M. A. B. H.; Kaneko, T.; Noda, A.; Watanabe, M. J. Am. Chem. Soc. 2005, 127, 4976−4983.
(8) Fletcher, K. A.; Pandey, S. Langmuir 2003, 20, 33−36.
(9) Hao, J.; Song, A.; Wang, J.; Chen, X.; Zhuang, W.; Shi, F.; Zhou, F.; Liu, W. Chem.—Eur. J. 2005, 11, 3936−3940.
(10) Araos, M. U.; Warr, G. G. J. Phys. Chem. B 2005, 109, 14275−14277.
(11) Wang, L.; Chen, X.; Chai, Y.; Hao, J.; Sui, Z.; Zhuang, W.; Sun, Z. Chem. Commun. 2004, 2840−2841.
(12) Hao, J.; Zemb, T. Curr. Opin. Colloid Interface Sci. 2007, 12, 129−137.
(13) Eastoe, J.; Gold, S.; Rogers, S. E.; Paul, A.; Welton, T.; Heenan, R. K.; Grillo, I. J. Am. Chem. Soc. 2005, 127, 7302−7303.
(14) Pramanik, R.; Sarkar, S.; Ghatak, C.; Rao, V. G.; Setua, P.; Sarkar, N. J. Phys. Chem. B 2010, 114, 7579−7586.
(15) Wu, H.; Wang, H.; Xue, L.; Li, X. J. Colloid Interface Sci. 2010, 353, 476−481.
(16) Cheng, S.; Zhang, J.; Zhang, Z.; Han, B. Chem. Commun. 2007, 2497−2499.
(17) Zhang, J.; Han, B.; Li, J.; Zhao, Y.; Yang, G. Angew. Chem., Int. Ed. 2011, 50, 9911−9915.
(18) Patrascu, C.; Gauffre, F.; Nallet, F.; Bordes, R.; Oberdisse, J.; de Lauth-Viguerie, N.; Mingotaud, C. ChemPhysChem 2006, 7, 99−101.
(19) Behera, K.; Dahiya, P.; Pandey, S. J. Colloid Interface Sci. 2007, 307, 235−245.
(20) Anderson, J. L.; Pino, V.; Hagberg, E. C.; Sheares, V. V.; Armstrong, D. W. Chem. Commun. 2003, 2444−2445.
(21) Wu, J.; Li, N.; Zheng, L.; Li, X.; Gao, Y.; Inoue, T. Langmuir 2008, 24, 9314−9322.
(22) Li, N.; Zhang, S.; Zheng, L.; Wu, J.; Li, X.; Yu, L. J. Phys. Chem. B 2008, 112, 12453−12460.
(23) Li, N.; Zhang, S.; Zheng, L.; Inoue, T. Langmuir 2009, 25, 10473−10482.
(24) Li, N.; Zhang, S.; Zheng, L.; Dong, B.; Li, X.; Yu, L. Phys. Chem. Chem. Phys. 2008, 10, 4375−4377.
(25) Seth, D.; Sarkar, S.; Sarkar, N. Langmuir 2008, 24, 7085−7091.
(26) Pramanik, R.; Sarkar, S.; Ghatak, C.; Rao, V. G.; Mandal, S.; Sarkar, N. J. Phys. Chem. B 2011, 115, 6957−6963.
(27) Pramanik, R.; Ghatak, C.; Rao, V. G.; Sarkar, S.; Sarkar, N. J. Phys. Chem. B 2011, 115, 5971−5979.
(28) Pramanik, R.; Sarkar, S.; Ghatak, C.; Rao, V. G.; Sarkar, N. Chem. Phys. Lett. 2011, 512, 217−222.
(29) Ghatak, C.; Rao, V. G.; Pramanik, R.; Sarkar, S.; Sarkar, N. J. Phys. Chem. B 2011, 115, 6644−6652.
(30) Ghatak, C.; Rao, V. G.; Mandal, S.; Ghosh, S.; Sarkar, N. J. Phys. Chem. B 2012, 116, 3369−3379.
(31) Setua, P.; Pramanik, R.; Sarkar, S.; Ghatak, C.; Rao, V. G.; Sarkar, N.; Das, S. K. J. Mol. Liq. 2011, 162, 33−37.
(32) Fontell, K.; Lindman, B. J. Phys. Chem. 1983, 87, 3289−3297.
(33) Hoffmann, H.; Würtz, J. J. Mol. Liq. 1997, 72, 191−230.
(34) Kim, D. C. Biophys. Chem. 2006, 119, 271−281.
(35) Kim, D. C. Methods 2004, 34, 300−311.
(36) Shi, L.; Li, N.; Yan, H.; Gao, Y.; Zheng, L. Langmuir 2011, 27, 1618−1625.
(37) Li, X.; Dong, S.; Jia, X.; Song, A.; Hao, J. Chem.—Eur. J. 2007, 13, 9495−9502.
(38) Dong, S.; Li, X.; Xu, G.; Hoffmann, H. J. Phys. Chem. B 2007, 111, 5903−5910.
(39) Dong, S.; Xu, G.; Hoffmann, H. J. Phys. Chem. B 2008, 112, 9371−9378.

(40) Nordstierna, L.; Furó, I.; Stilbs, P. *J. Am. Chem. Soc.* **2006**, *128*, 6704−6712.