A Cationic Fluorocarbon Surfactant DEFUMACl and Its Mixed Systems with Cationic Surfactants: ¹⁹F NMR and Surface Tension Study

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A cationic fluorocarbon surfactant system of diethanolheptadecafluoro-2-undecanolmethylammonium chloride (DEFUMACl) and both mixed systems of DEFUMACl/cationic dodecyltrimethylammonium chloride (DTACl) and DEFUMACl/cationic Gemini copolymer was investigated by ¹⁹F NMR spectroscopy and surface tension measurements. The critical micelle concentration (cmc) of DEFUMACl by ¹⁹F NMR is about 3.40 mmol/L, which is completely consistent with that obtained by the surface tension method. The studies of salt and temperature on the cmc values of DEFUMACl suggest that both salt addition and temperature increase decrease the cmc values of DEFUMACl. ¹⁹F NMR measurements provide much richer information on both mixed systems. For the DEFUMACl−DTACl system, two break points were observed with increased total surfactant concentration. The first break point means the DEFUMACl and DTACl mixed micelles and the second one implies the individual DEFUMACl micelles. Results of ¹⁹F NMR and surface tension measurements for DEFUMACl/cationic Gemini copolymer mixtures show three peculiar break points, corresponding to the critical association concentration (cac) of DEFUMACl, the concentration where cationic Gemini copolymer molecules become saturated by DEFUMACl micelles, and the concentration where DEFUMACl micelles and cationic Gemini copolymer coexist. These peculiar points in the cationic−fluorocarbon and cationic−copolymer systems were first reported by ¹⁹F NMR and surface tension measurements. These results should broaden the useful information for a better understanding of the mechanism of interaction and the behavior of surfactant−polymer mixtures.

Introduction

Fluorinated surfactants containing a fluoromethylene chain have a number of special properties such as chemical and biological inertness, thermal stability, and oleophobicity that offer some advantages over their hydrocarbon counterparts.[1] Their outstanding chemical and thermal stability allows applications under the extreme conditions that would be too severe for hydrocarbon amphiphiles. Due to the larger volume and higher electronegativity of fluorine than those of hydrogen, the introduction of fluorine atoms into the hydrophobic chains of a surfactant greatly increases its amphiphilic character, resulting in the enhanced surface activity and lower critical micelle concentration (cmc). Abundant applications of fluorinated surfactants have been developed in different fields. Fluorosurfactants were recently used in nonaqueous media of fluorocarbon solvents[1] and supercritical carbon dioxide.[2] They are used in blood substitute formulations,[3] oxygen and drug delivery systems,[4] and adhesive formulations and as antifogging and antistatic agents, cleaners, cosmetics, emulsions, fire-fighting foams, herbicide formulations, and so forth.[5]

One often constructs hydrocarbon/fluorocarbon surfactant mixed systems for obtaining some desired performances, for studying phase behavior and self-assembled structures including in aqueous or nonaqueous solution. Mainly anionic or nonionic

fluorocarbon surfactants have been investigated[6−10] and there have been few studies on cationic fluorinated surfactants,[11−13] especially cationic/cationic fluorocarbon- hydrocarbon surfactant mixed systems.[14]

It is well-established that the experimental techniques such as surface tension measurements, conductivity, and fluorescence measurements are available for the study of fluorinated surfactants and their mixed systems with hydrocarbon surfactants,[9,10] polymers,[11,12] proteins,[6,13] and so forth. Self-assembled structures of fluorinated surfactants at a molecular level can also be well-obtained by NMR measurements.[9,10,15,16] This powerful tool takes advantage of the separate observation of the two nuclei present at the same time in mixed solutions and, as a consequence, can provide useful information on the physical−chemical environment of each component. ¹⁹F NMR offers the advantage to independently observe the behavior of the fluorinated derivatives in the mixtures due to no overlapping of the ¹H signals of hydrocarbon components. Thus, ¹⁹F NMR measurements allow one to determine the concentration at which the fluorinated amphiphiles form micelles and give information on the composition of the hydrocarbon−fluorocarbon surfactant mixed micelles.[9,10]

In the present work, ¹⁹F NMR and surface tension measurements were used to study the properties and the aggregation behavior of a cationic fluorocarbon surfactant, DEFUMACl, and its mixtures with a cationic hydrocarbon surfactant (DTACl) and a cationic Gemini copolymer. The influence of salt and temperature on the cmc of DEFUMACl was investigated in

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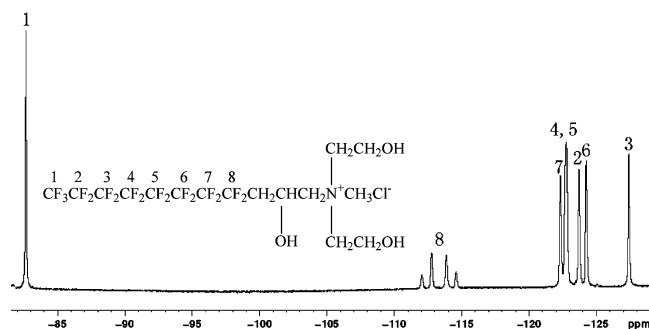† Shandong University.
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Figure 1. Chemical structure, ^{19}F NMR spectrum, and the assignment of the cationic fluorocarbon surfactant, DEFUMACl, $c_{DFUMACl} = 7.80$ mmol/L.
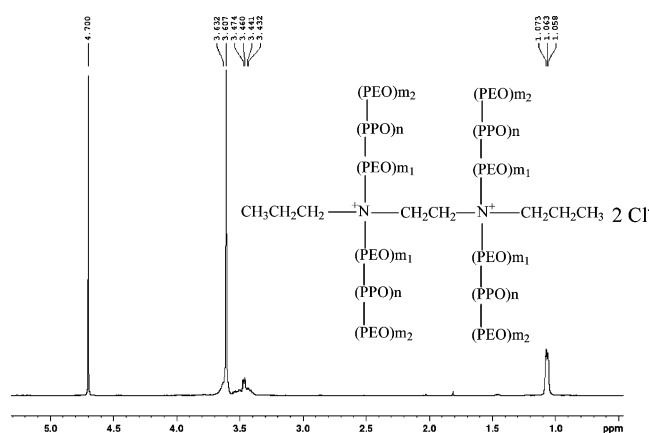

Figure 2. Chemical structure and ^1H NMR spectrum of the cationic Gemini copolymer, $c_{Gemi} = 1.0$ wt %.

detail. The interaction, the behavior, and the structural information on the mixed systems of DEFUMACl/DTACl and DEFUMACl/cationic Gemini copolymer were compared.

Experimental Section

Materials. Unless noted by exceptional circumstance, all reagents used in this study were analytical grade. Cationic fluorocarbon surfactant, DEFUMACl, was prepared by an anion-exchange method in methanol from the corresponding iodine salt supplied by Daikin Industries, Ltd. (Japan), which was kindly provided by Professor Dr. Heinz Hoffmann at Physikalische Chemie I, Bayreuth University, Germany. The crude product was recrystallized more than three times with an isopropanol/hexane mixed solvent. The complete chloride ion exchange and the composition were checked by elemental analysis. The ^{19}F NMR spectrum and the chemical structure of DEFUMACl are shown in Figure 1, including the assignments of each group. Cationic surfactant dodecyltrimethylammonium chloride (DTACl) was purchased from Sigma Chemical Co., U.S.A, and used without further purification. Cationic Gemini copolymer, as shown in Figure 2, including the ^1H NMR spectrum, was synthesized by our own Lab, MW $\approx$ 30000 g/mol.[17] Three-time drilled water was used to prepare all sample solutions.

Surface Tension Measurements. Surface tension was measured by a Processor Tensiometer K12 (Swiss). The surface tensions at various concentrations were measured after stirring and equilibration at a constant temperature of 25 ± 0.1 °C. The surface tension value reported at each concentration is the average value from three measurements, and the results are within $\pm$ 0.01 mN·m^{-1}.
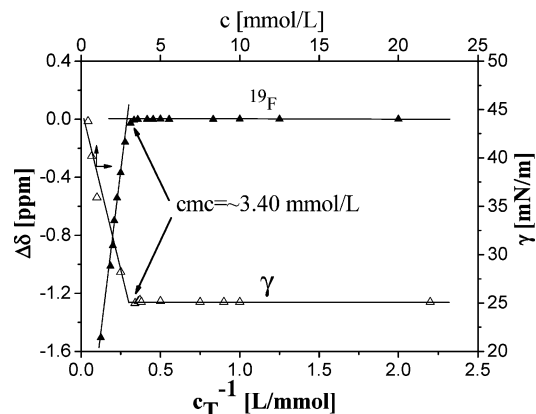

Figure 3. ^{19}F chemical shift ($\Delta\delta$, ppm) of the $-CF_3$ group of DEFUMACl in D_2O and surface tensions versus the reciprocal of the DEFUMACl concentration. $T = 25.0 \pm 0.1$ °C.

TABLE 1: Chemical Shifts, δ (ppm), of Fluorine Atoms Bound to the Different Carbons of DEFUMACl at Different DEFUMACl Concentrations, $T = 25.0 \pm 0.1$ °C

c (mM)	δ_{C1}	δ_{C2}	δ_{C3}	$\delta_{C4,5}$	δ_{C6}	δ_{C7}	δ_{C8}
0.5	−80.78	−122.69	−126.01	−121.87	−123.85	−121.56	−111.86
1.0	−80.78	−122.69	−126.01	−121.87	−123.85	−121.56	−111.88
2.2	−80.78	−122.69	−126.02	−121.87	−123.85	−121.58	−111.88
2.8	−80.78	−122.69	−126.02	−121.87	−123.85	−121.58	−111.88
3.0	−80.78	−122.67	−126.02	−121.88	−123.85	−121.59	−111.88
3.2	−80.80	−122.71	−126.04	−121.89	−123.86	−121.60	−111.88
3.6	−80.93	−122.80	−126.15	−121.97	−123.92	−121.67	−111.97
4.0	−81.15	−122.93	−126.33	−122.09	−123.99	−121.78	−112.12
4.4	−81.32	−123.02	−126.45	−122.17	−124.03	−121.83	−112.20
4.8	−81.48	−123.11	−126.56	−122.24	−124.08	−121.90	−112.27
5.0	−81.65	−123.17	−126.65	−122.29	−124.11	−121.96	−112.33
5.4	−81.79	−123.27	−126.78	−122.37	−124.17	−122.03	−112.42
8.0	−82.28	−123.52	−127.14	−122.60	−124.30	−122.21	−112.67

^{19}F NMR Measurements. All of the samples were dissolved in D_2O (Aldrich product, $\geq$ 99.9%). ^{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 1D spectra were reported in the range from +30 to −170 ppm (digitized points = 32K, 90° pulse = 7.4 ms, relaxation delay = 2 s).

The ^{19}F NMR chemical shifts are reported relative to external trifluorotoluene at −62.73 ppm. Each group of the DEFUMACl fluorocarbon chain for the ^{19}F NMR spectra was assigned as shown in Figure 1. All spectra reported in this work display solely the $-CF_3$ terminal regions of the ^{19}F NMR spectra. Unless the influence of the temperature on the micellization of DEFUMACl in solution was studied, all of the experiments were operated at 25.0 ± 0.1 °C.

Results and Discussion

1. DEFUMACl System. *cmc of DEFUMACl.* The physicochemical environment of a surfactant molecule surrounded by other surfactant molecules in self-assembled structures such as micelles is expected to be quite different from that existing as a free monomer surrounded by water molecules. In Figure 1, as a typical example, the spectrum of DEFUMACl at $T = 25.0 \pm 0.1$ °C is shown. A set of sharp resonance signals was observed in the ^{19}F NMR spectrum, indicating that the exchange of DEFUMACl molecules between different states is invariably fast on the NMR time scale, reflecting the time-averaged environment of the cationic fluorocarbon DEFUMACl. The shifts of the signals can be explained by the variation of the local dielectric constant experienced by each monomer,[18] which
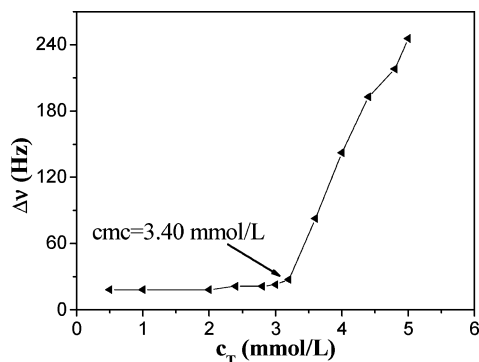
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Figure 4. Half-line width ($\Delta\nu$, Hz) of the ^{19}F resonance of the $-CF_3$ group as a function of the DEFUMACl concentration, $T = 25.0 \pm 0.1$ °C.
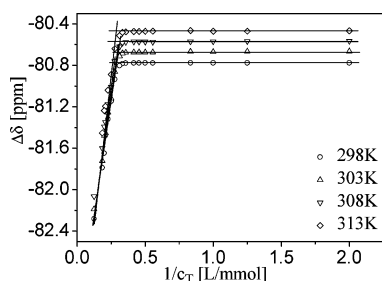

Figure 5. ^{19}F chemical shift ($\Delta\delta$) of the $-CF_3$ group of DEFUMACl versus the reciprocal of the DEFUMACl concentration in D_2O at different temperatures.
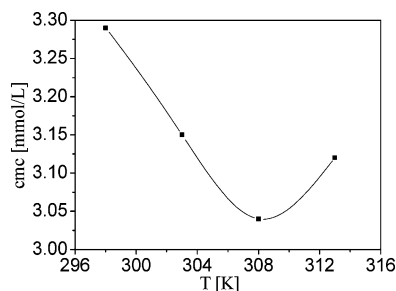

Figure 6. Temperature dependence on the cmc values of DEFUMACl.

could be used to determine the important parameters such as the cmc of the surfactants.[19] ^{19}F NMR chemical shifts are known to be sensitive to the surrounding environment and is an excellent means of studying fluorinated surfactants.[20−22] Basically, the physicochemical microenvironment of a surfactant molecule depends on its self-organization in aqueous solution. Depending on its concentration, the amphiphiles can exist as a single monomer and/or self-assembled structures such as micelles. Single monomers are in a hydrophilic environment, while surfactant hydrophobic tails are in a low-polarity environment within a micelle. Consequently, the fluorocarbon nuclei resonance shows an upfield shift upon micellization. The peak of the terminal $-CF_3$ group is the strongest, and its chemical shift is the most sensitive to the micellization. It must be underlined that the exchange rate of a surfactant between monomeric and micellar states is greater than the NMR relaxation rate.[9,23] Therefore, despite the coexistence of monomeric molecules and micelles, the observed chemical shift (δ_{obs}) is a weighted average value of the monomeric shift (δ_{mo}) and of the micelle shift (δ_{mic}). The variation of the chemical shifts of the $-CF_3$ group as a function of surfactant concentration can be conveniently expressed relative to the monomer shift δ_{mo} by using the difference $\Delta\delta$ between the observable chemical
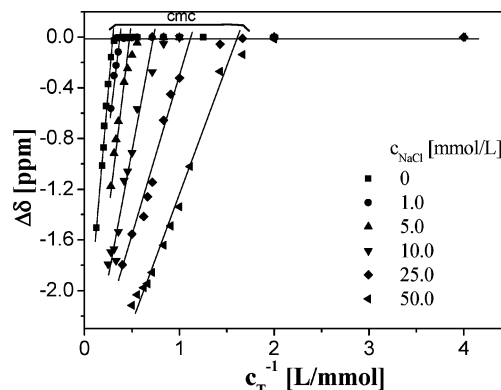

Figure 7. ^{19}F chemical shift ($\Delta\delta$) of the $-CF_3$ group of DEFUMACl versus the reciprocal of the DEFUMACl concentration in D_2O with different NaCl concentrations, $T = 25.0 \pm 0.1$ °C.
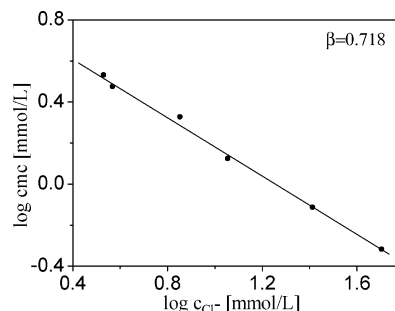

Figure 8. Logarithmic cmc of DEFUMACl versus the logarithmic concentration of the counterion ($c_{Cl^-} = cmc + c_{NaCl}$) at $T = 25.0 \pm 0.1$ °C.

shift at a given concentration and that measured at low concentration (below the cmc), that is, (eq 1)[9]

$$\Delta\delta = \delta_{obs} - \delta_{mo} \tag{1}$$

Micelle formation with a negative $\Delta\delta$ value indicates an upfield shift from the monomeric state.

For systems involving only one fluorinated surfactant, above the cmc, the chemical shift of the $-CF_3$ group of a fluorinated surfactant is given by eq 2, with the assumption that the monomer concentration is approximately equal to the cmc

$$\delta_{obs} = \frac{cmc}{c_T}(\delta_{mo} - \delta_{mic}) + \delta_{mic} \tag{2}$$

where cmc is the critical micelle concentration, c_T is the total surfactant concentration, that is, the sum of the amphiphile concentration both in the monomeric and the micellar states, and δ_{mo} and δ_{mic} are the chemical shifts of the $-CF_3$ in the monomeric and micellar states, respectively.

To determine the cmc from NMR data, $\Delta\delta$ is plotted versus the reciprocal concentration. According to eqs 1 and 2, a plot of $\Delta\delta$ versus c_T^{-1} is linear above the cmc, and δ_{obs} below the cmc corresponds to δ_{mo}. The break point gives the cmc.[20] The ^{19}F chemical shift ($\Delta\delta$) of DEFUMACl as a function of reciprocal concentration, at $T = 25.0 \pm 0.1$ °C, is shown in Figure 3. As expected, this curve shows the characteristic feature of a typical ionic fluorocarbon surfactant solution, that is, a constant value at low concentration where δ_{mo} is identified with δ_{obs}, followed by a drop in $\Delta\delta$ at higher concentration. The $\Delta\delta$ versus c_T^{-1} curve can be linearly fitted by two lines where the intersection point corresponds to the cmc, 3.40 mmol/L, which is completely consistent with the value determined
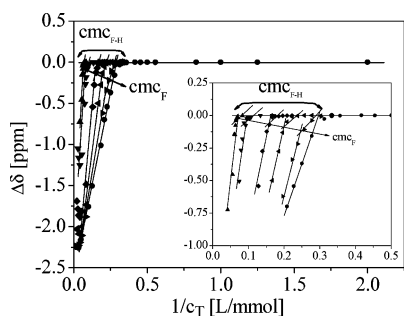
Figure 9. [19]F chemical shifts of the $-CF_3$ of DEFUMACl versus c_T^{-1} at different α_F's: 1.0 (●), 0.05 (▲), 0.1 (▼), 0.3 (◆), 0.5 (left arrow), and 0.7 (right arrow); $T = 25.0 \pm 0.1$ °C.
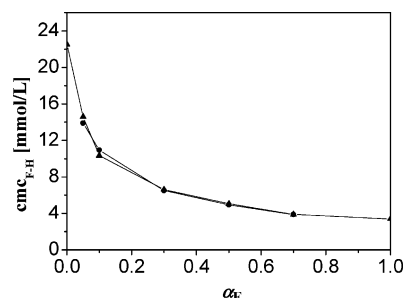

Figure 10. Experimental (▲) and calculated (●) cmc_{F-H} values of the DEFUMACl/DTACl mixed system at different α_F's.

by the surface tension method (the inset data in Figure 3), cmc = 3.38 mmol/L.

It has been hypothesized[6,24−26] that the surfactant molecules undergo a conformational variation in the micellization process. Such a conformational variation does occur in the DEFUMACl solution from free monomers to micelles, shown in Table 1. We observed constant values of the chemical shifts of all of the fluorine atoms bound to the different carbons in dilute solution (below the cmc); however, above the cmc, the chemical shifts of the total fluorine atoms move upfield at around 3.40 mmol/L, suggesting the cmc of DEFUMACl is around 3.40 mmol/L.

The DEFUMACl micellization process can be confirmed by the obvious broadening for F atoms linked to the different carbons of the DEFUMAC molecule, which provides useful information on the dynamics of the DEFUMACl system by analyzing the variation of the half-line width ($\Delta\nu$, Hz) for the ^{19}F resonance of the $-CF_3$. One can see from Figure 4 that $\Delta\nu$ increases above the cmc from 18 to 240 Hz. The observed broadening can be interpreted in terms of a fast exchange between two states of monomers and micelles of DEFUMACl molecules.

Influence of Temperature on the cmc of DEFUMACl. It is well-known that, for ionic surfactants, with the increase of temperature, the cmc value decreases slightly at first and then increases slowly at higher temperatures.[5,27] The influence of temperature on the chemical shifts ($\Delta\delta$, ppm) of the DEFUMACl aqueous solution is shown in Figure 5. The cmc values of DEFUMACl at different temperatures determined from the break points are shown in Figure 6. It can be seen that the cmc values of DEFUMACl have a minimum value at $T = \sim308$ K, and it is well-known that the cmc−temperature curve of other fluorocarbon surfactants has such a minimum point at ~308 K.[25]

Influence of Salt (NaCl) on the cmc of DEFUMACl. The addition of inorganic salt into the surfactant aqueous solution strongly decreases the cmc values of the ionic hydrocarbon

surfactant systems; however, there are few reports on the influence of inorganic salts on cationic fluorocarbon surfactants. The influence of added NaCl on the DEFUMACl solution was investigated by ^{19}F NMR. Results obtained for chemical shifts of the $-CF_3$ group versus the DEFUMACl concentration are shown in Figure 7. For different NaCl concentrations, one can see, with the increase of the DEFUMACl concentration, the chemical shift difference ($\Delta\delta$, ppm) has constant values below the cmc of DEFUMACl. Above the cmc, the difference of chemical shifts keeps decreasing with the increase of the sum of NaCl, and the cmc values can be determined from the intersections accordingly. The degree of counterion binding (β) at 25.0 ± 0.1 °C could be determined from the plots of the logarithmic concentration of the counterion ($c_{Cl^-} = cmc + c_{NaCl}$), that is, the so-called Corrin−Harkins plots.[28] As shown in Figure 8, we determined the $\beta = 0.718$.

2. DEFUMACl/DTACl Mixed System. The polarity of the fluorocarbon and hydrocarbon chains is completely different. Consequently, in mixtures made of fluorocarbon and hydrocarbon surfactants, if contacts occur between the two types of tails within mixed micelles, the chemical shift of the $-CF_3$ will be effected by the presence of the hydrocarbon tails. Thus, compared with the pure fluorocarbon surfactant micelles, the presence of the hydrocarbon moieties within the micelles induces an upfield shift of the signal.[9,29] Depending on the degree of compatibility or incompatibility between the surfactants, two cases must be distinguished, (i) the formation of a single type of completely miscible micelles or (ii) the formation of two types of partially demixed micelles. In a mixed system consisting of fluorocarbon and hydrocarbon surfactants, despite the incompatibility between CH and CF tails, co-micellization frequently induces either a negative or a positive deviation from the ideal case.[30,31]

The observed ^{19}F NMR chemical shift for a given α_F (the molar fraction of the fluorocarbon surfactant in a mixture) can be expressed as[9,10]

$$\delta_{obs} = \frac{c_{Fmo}}{c_T \alpha_F}(\delta_{mo} - \delta'_{mic}) + \delta'_{mic} \quad (3)$$

where the c_{Fmo} represents the concentration of the fluorinated surfactant in the monomer state and δ'_{mic} is the ^{19}F NMR chemical shift of the $-CF_3$ group in mixed micelles.

Regular solution theory (RST)[30a,32] for describing the behavior of liquid mixtures predicts that demixing will occur for $P_m > 2$, where P_m is an interaction parameter. The nature and the strength of the interaction between two surfactants can be determined by P_m. For a binary fluorocarbon−hydrocarbon surfactant mixed system, the P_m value can be calculated from the Rubingh's eq 4[33a] and eq 5[33]

$$\frac{X_F^{m2} \ln(\alpha_F cmc_{F-H}/X_F^m cmc_F)}{(1 - X_F^m)^2 \ln[(1 - \alpha_F)cmc_{F-H}/(1 - X_F^m)cmc_H]} = 1 \quad (4)$$

$$P_m = \frac{\ln(\alpha_F cmc_{F-H}^m/X_F^m cmc_F^m)}{(1 - X_F^m)^2} \quad (5)$$

where X_F^m is the mole fraction of the fluorocarbon surfactant in the mixed micelle. The cmc_F, cmc_H, and cmc_{F-H} are the critical micelle concentrations (cmc) for fluorocarbon and hydrocarbon surfactants and their mixture, respectively, at the mole fraction α_F of the fluorocarbon surfactant in solution. For the DEFUMACl/DTACl mixed system, positive P_m values, around (1.0
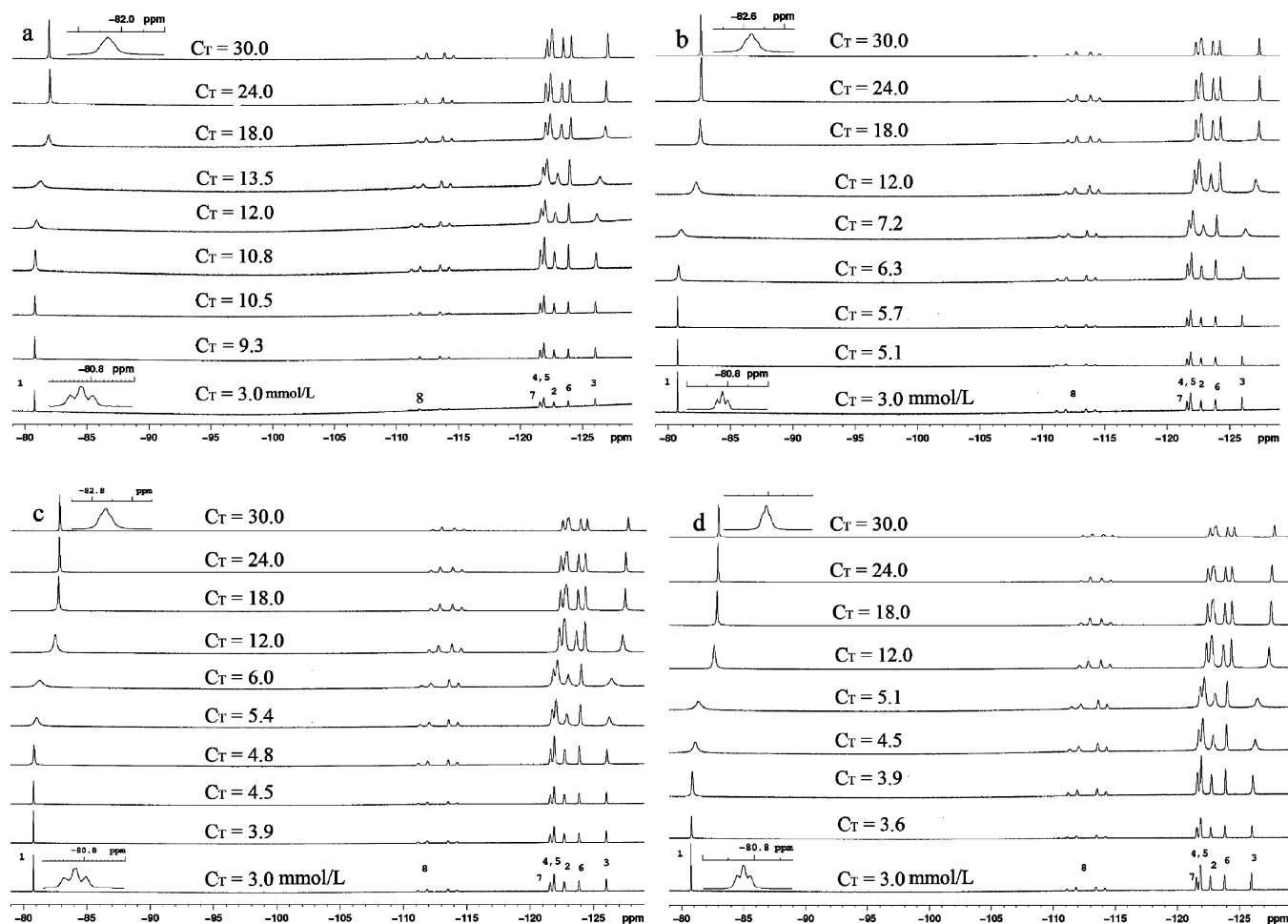
Figure 11. ^{19}F NMR spectra of DEFUMACl/DTACl mixtures at different mole fractions: $\alpha_F = 0.1$ (a), 0.3 (b), 0.5 (c), and 0.7 (d); $T = 25.0 \pm 0.1$ °C.

TABLE 2: The cmc$_{F-H}$ and X_F^m of the DEFUMACl/DTACl Mixed System at Different α_F's, $T = 25.0 \pm 0.1$ °C

α_F	cmc$_{F-H}$ [mmol/L]	cmc$_{F-H}$ [mmol/L]	X_F^m	
	(experimental data)	(calculated data)	(experimental)	(calculated)
0	22.5			
0.05	14.60	13.88	0.05	0.0493
0.1	10.31	10.93	0.34	0.361
0.3	6.62	6.49	0.624	0.617
0.5	5.05	4.94	0.71	0.708
0.7	3.89	4.03	0.784	0.802
1.0	3.40			

$\pm$ 0.1), were obtained from the application of eqs 4 and 5, implying the repulsive interaction but the possibility of formation of mixed micelles.

The chemical shift difference of $-$CF$_3$ ($\Delta\delta$, ppm) at different α_F's against the total concentration (c_T) are plotted in Figure 9, providing much richer information of the mixed system. Below the cmc, the chemical shift of $-$CF$_3$ is constant and coincident with that observed in the pure DEFUMACl system ($\alpha_F = 1.0$), indicating that hydrogenated and fluorinated monomers do not affect each other. At different ratios of DEFUMACl and DTACl, with increasing total concentration, one finds the DEFUMACl/DTACl mixed micelles at the first break point. Then, at the second break point, the individual DEFUMACl micelles are formed. The concentrations of DEFUMACl and DTACl at the mixed critical micelle concentration (cmc$_{F-H}$) are lower than their cmc values. At different α_F's, the cmc$_{F-H}$ values are

different, accordingly, and are tabulated in Table 2 together with the mixed micellar composition X_F^m calculated by applying these cmc$_{F-H}^m$ values to eq 4.

To identify the compatibility of the DEFUMACl/DTACl mixed system, the cmc values of the systems were calculated by employing the relation between the cmc$_{F-H}$ of the mixture and the cmc$_i$ of a single surfactant ($i = F$ and H) for ideal mixtures[34]

$$\frac{1}{\text{cmc}_{F-H}^{1+\beta_{F-H}}} = \frac{X_F}{\text{cmc}_F^{1+\beta_F}} + \frac{X_H}{\text{cmc}_H^{1+\beta_H}} \tag{6}$$

where cmc$_{F-H}$ represents the cmc of the mixed micelles, cmc$_F$ and cmc$_H$ are the cmc values of the fluorocarbon and hydrocarbon surfactants, respectively, β_{F-H} is the binding constant of the counterions of the mixed micelles, and β_F and β_H are binding constants of the counterions of single surfactant micelles, respectively. For the DEFUMACl/DTACl mixed system, $\beta_F = 0.72$, $\beta_H = 0.66$, and $\beta_{F-H} = 0.70$ were employed.[35] The calculated cmc$_{F-H}$ values of the DEFUMACl/DTACL mixtures at different α_F's are listed in Table 2 and plotted in Figure 10. One can clearly see that experimental cmc$_{F-H}$ values are in good agreement with the calculated ones at different α_F's, implying a good compatibility of the two surfactants for forming the mixed micelles at a range of surfactant concentrations. The mixed micellar composition, X_F^m, from experiment and theory tabulated in Table 2, could also imply the same good compatibility of the two surfactants for forming the mixed micelles.
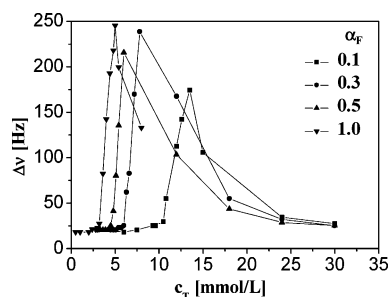
Figure 12. Half-line width ($\Delta\nu$, Hz) of the ^{19}F resonance of $-CF_3$ as a function of the total concentration of the DEFUMACl and DTACl mixtures.

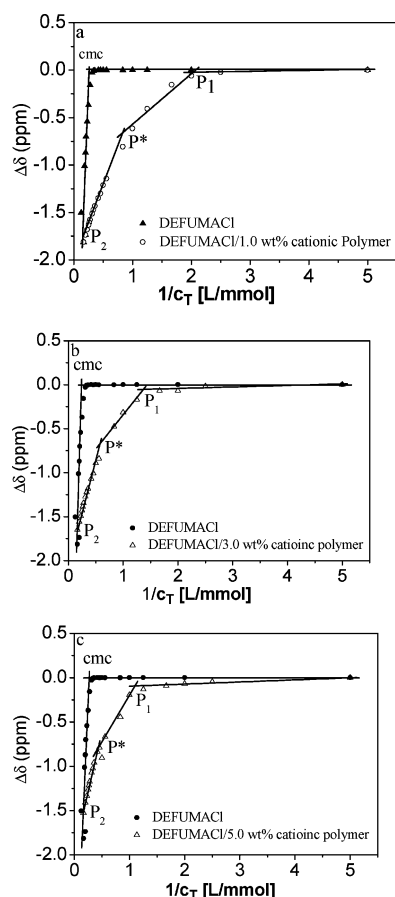**Figure 14.** Surface tension γ (mN·m^{-1}) versus surfactant concentrations: (a) SDS ($\triangle$) and SDS/1.0 wt % cationic Gemini copolymer ($\blacktriangle$); (b) DEFUMACl ($\triangle$) and DEFUMACl/ 1.0 wt % cationic Gemini copolymer ($\blacktriangle$); $T = 25.0 \pm 0.1$ °C.

aggregation. This regression of the ^{19}F NMR peaks to the DEFUMACl micelles at higher total DEFUMACl concentrations can be rationalized assuming that the carbons positioned at the 1, 2, and 3 of the fluorocarbon chain enter into a more hydrophobic environment, that is to say, the mixed micelles at lower total surfactant concentration separate into individual micelles of surfactants, that is, DEFUMACl micelles above a definite total surfactant concentration.

Combining Figures 9 and 11 and Table 2, one can see that the cmc values of DEFUMACl in the mixtures with different ratios of DEFUMACl and DTACl are much lower than the cmc of the pure DEFUMACl. It could be explained that at a higher concentration, DTACl's do not form micelles but exist as monomers which act like a salt to lower the cmc of DEFUMACl.

The behavior of the half-line width of the $-CF_3$ group of DEFUMACl in the DEFUMACl/DTACl mixed system, as shown in Figure 12, provides useful information on the understanding of DEFUMACl/DATCl mixed micelles and the individual DEFUMACl micelles. Comparing with Figure 2, one can observe that the values of the half-line width of the $-CF_3$ group of DEFUMACl in the DEFUMACl/DTACl mixed system at different α_F's increase above the cmc and thereafter decrease to a constant value. The constant values of the half-line width of the ^{19}F resonance of $-CF_3$ at $c_T \sim 24.0$ mmol/L clearly demonstrate the formation of individual DEFUMACl micelles, which also has been demonstrated from the ^{19}F NMR spectra in Figure 11.

3. DEFUMACl/Cationic Gemini Copolymer Mixed System. Gemini surfactants consisting of two or multiple conventional surfactant units linked at their polar head groups by a spacer are attracting a lot of attention because of the many unusual properties and applications.[36] Combining the triblock copolymer Pluronic (PEO)$_m$(PPO)$_n$(PEO)$_m$, which was investigated as a surfactant,[37] we named the compound having the chemical structure, as shown in Figure 2, to be cationic Gemini copolymer surfactant.[17] The interaction between DEFUMACl and the novel cationic Gemini copolymer was investigated by ^{19}F NMR spectroscopy and surface tension measurements. We selected three mixed systems with the fixed $c_{Gemi} = 1.0, 3.0,$ and 5.0 wt %. At these three concentrations, the cationic Gemini copolymer can form micelles on its own in the solution because the PPO group acts as the hydrophobic part, and the PEO group is the hydrophilic part.[17,37] ^{19}F chemical shifts ($\Delta\delta$, ppm) of $-CF_3$ in the three mixed systems as a function of DEFUMACl concentration are shown in Figure 13a, b, and c. Some peculiar DEFUMACl concentrations, assigned to be P_1, P^*, and P_2, could be obtained. The three break points indicate, respectively, the critical association concentration (cac) of DEFUMACl, the concentration where cationic Gemini copolymer molecules become saturated by DEFUMACl micelles, and the concentra-

Figure 13. ^{19}F chemical shifts versus the reciprocal of the DEFUMACl concentration at different c_{Gemi}'s: 1.0 (a), 3.0 (b), and 5.0 wt % (c); $T = 25.0 \pm 0.1$ °C.

The compatibility of the DEFUMACl/DTACl mixtures for forming mixed micelles was demonstrated by ^{19}F NMR spectra. From the corresponding ^{19}F NMR spectra at different α_F's, as shown in Figure 11, one can see that the ^{19}F chemical shifts move upfield pronouncedly, and the signals of the fluorine atoms at the 1, 2, and 3 positions of the DEFUMACl molecule broaden strongly at a range of total surfactant concentrations. These observations clearly imply that the $-CF_3$ group of the DEFUMACl molecule is strongly in contact with the hydrocarbon chains, that is, the interaction occurs among DEFUMACl and DTACl molecules, demonstrating the formation of mixed micelles. However, when c_T is above a definite total surfactant concentration, the broadened ^{19}F NMR peaks turn to be sharper that the original ones as obtained in a pure DEFUMACl micelle solution (Figure 1), reflecting that the fluorine atoms at the 1, 2, and 3 positions of the DEFUMACl molecules experience a much greater change of the environment upon the procedure of
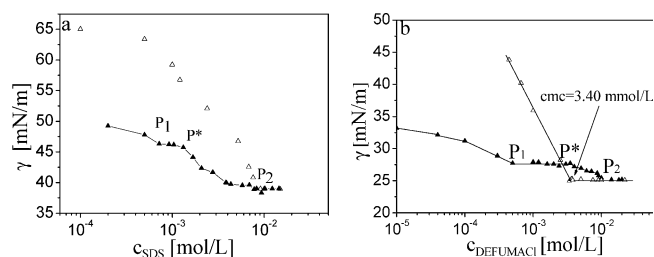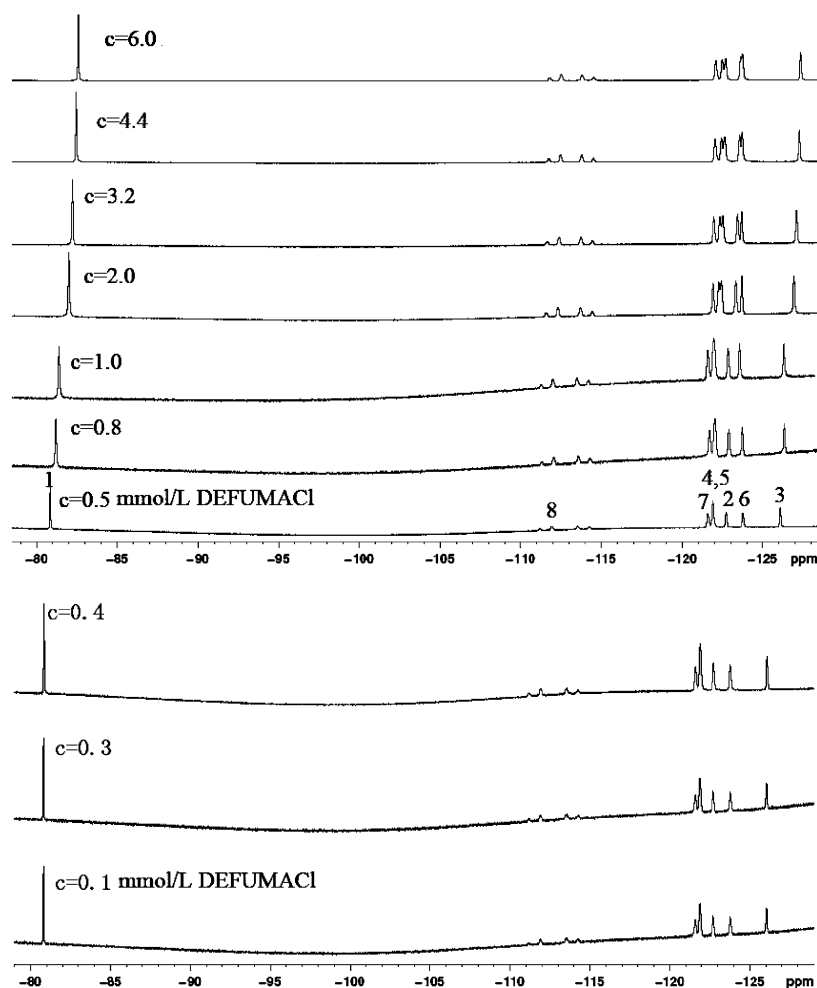
Figure 15. ^{19}F NMR spectra of DEFUMACl for the mixtures of the varied DEFUMACl concentrations at $c_{Gemi} = 1.0$ wt %, $T = 25.0 \pm 0.1$ °C.

tion where DEFUMACl micelles and micelles of cationic Gemini copolymers coexist. A similar significant change determined by surface tension measurements for hydrocarbon surfactant−polymer systems has been revealed previously.[36] At a very low concentration of DEFUMACl, the chemical shifts of the −CF$_3$ of DEFUMACl remain constant with the increase of the DEFUMACl concentration, indicating that the DEFU-MACl's are in their molecular states below the P_1 point. After the P_1 point, the resonance curves of the three systems deviate greatly from the pure DEFUMACl, implying a strong interaction and the strongly synergistic effect between DEFUMACl and the copolymer, that is, the air/water interface becomes saturated with DEFUMACl−cationic Gemini copolymer mixtures. At P^*, cationic Gemini copolymers become saturated with DEFUMACl molecules to form mixed aggregates.[36] With an increasing DEFUMACl concentration, at P_2, the chemical shifts of the −CF$_3$ of DEFUMACl in mixed systems are practically coincident with those of pure DEFUMACl in water. One can hypothesize that the surface monolayer is entirely held by only DEFUMACl molecules at P_2. Thereafter, further addition of DEFUMACl only causes an increase of the number of DEFU-MACl micelles.

Surface tension measurements, as shown in Figure 14 for both systems of an anionic surfactant (sodium dodecyl sulfate, SDS)/cationic Gemini copolymer and DEFUMACl/cationic Gemini copolymer, have been carried out. From Figure 14, one can clearly see that the three peculiar break points, P_1, P^*, and P_2 were observed in both systems, corresponding to the transition points observed in Figure 13. The behavior of hydrocarbon

surfactants and ionic or nonionic polymers have been widely observed.[38,39] These peculiar break points observed by ^{19}F NMR and surface tension measurements are being reported for the first time, to our knowledge, for the cationic fluorinated surfactants/cationic Gemini copolymers.

^{19}F NMR spectra of DEFUMACl/Gemini copolymer mixtures at $c_{Gemi} = 1.0$ wt % but at different DEFUMACl concentrations are shown in Figure 15. An interesting phenomenon can be observed. When the DEFUMACl concentration is below 0.40 mmol/L (this concentration is below P_1 for the DEFUMACl/1.0 wt % cationic Gemini copolymer mixture), the resonance signals of the fluorine atoms linked to all carbons are sharp, and the signals of the 2, 6 positions remain apart. At a DEFUMACl concentration above 0.5 mM, the signal peaks of the ^{19}F NMR spectra start to broaden slightly (from 18 to 36 Hz). The signal peaks of the fluorine atoms at the 2, 6 positions get closer and, at a higher concentration, overlap each other, while the signal at the 4, 5 position splits from one signal into two, implying that DEFUMACl and Gemini copolymers can form mixed aggregates and that fluorine atoms at the above positions experience a quite different microenvironment. Fluorine atoms at the 4, 5 positions turn from the same chemical microenvironment to a different one upon micellization, while the 2, 6 positions undergo a similar procedure too.

Finishing the analysis of the ^{19}F NMR spectra, we would like to determine the characteristic time of exchange τ, which could be determined by using 1D polarization transfer or 2D exchange spectroscopy.[40] NMR line-shaped analysis of the broadened signals gives the lifetime of monomeric and ag-

gregated species at various concentrations and the characteristic time of exchanging τ.[40] An estimate can be very simply obtained from line-shaped analysis of a sample at a concentration $c_{DEFUMACl} = 2 \times cmc = 6.8$ mmol/L. At this concentration, the lifetimes of the monomeric and aggregated species are both equal to τ, whose value is then given as[40]

$$1/\tau = \pi\Delta\Delta\nu \tag{7}$$

where $\Delta\Delta\nu$ is the line width difference between the monomer signal at 6.8 mmol/L (broadened by exchange) and below the cmc (no exchange). For the DEFUMACl/1.0 wt % cationic Gemini copolymer mixed system, $\tau = 0.02$ s was calculated, which is slower than that of most single-chain surfactants whose characteristic time of exchange are generally on the order of 1 ns to 1 ms.[40] The possible explanation lies in the existence of the Gemini copolymer surfactant and an unusual type of aggregate formed, which need to be studied further.

Conclusion

DEFUMACl, DEFUMACl/DTACl, and DEFUMACl/cationic Gemini copolymer mixtures can form individual surfactant micelles and the mixed micelles. Both salt addition and temperature increase decrease the cmc of the DEFUMACl aqueous solution. Specific behavior of the DEFUMACl/cationic Gemini copolymer mixtures appears, demonstrated by ^{19}F chemical shifts and surface tension measurements. The detailed investigations on the present cationic−fluorocarbon surfactant and the cationic−cationic surfactant mixtures should be helpful for an understanding of the peculiar behavior of cationic−cationic surfactant systems and the special evaluation for constructing mixed micelles of cationic−fluorocarbon and cationic−hydrocarbon amphiphilic mixtures.

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