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NMR Study of the Transformation of Perfluorinated Surfactant Solutions

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The formation of micelles and aggregates in D_2O solutions of the homologous series of surfactant cesium perfluoroalkanoates $C_nF_{2n+1}COO^-Cs^+$ (n = 5, 7, 9) and the other salts (Na^+, NH_4^+, and Rb^+) of perfluorooctanoic acids were studied at 30 and 50 °C by using some NMR techniques. The critical micelle concentrations (cmc) were determined by ^{19}F chemical shift measurements. The studies of Cs salts have shown that the effect of each CF_2 group on micelle formation is roughly equivalent to that of 1.5 CH_2 groups. Except for the $n = 5$ system at 50 °C, second breaks other than cmc at higher concentration were observed for α-CF_2 groups of all Cs salts, which suggest the transformation into a larger micelle, most likely ellipsoidal. In the case of ω-CF_3 groups these second breaks were not observed. Support for the ^{19}F results was furnished by ^{133}Cs chemical shift studies. The perfluorooctanoate surfactants with the Cs^+ as a counter ion showed the behavior that was different from the other salts of the same chain length. This could be explained in terms of electrostatic and hydrophobic interactions between the counter ions and the micelles. Additionally, the molecular motions in monomer and micellar states are discussed by means of the ^{19}F relaxation times of the fluorine nuclei in the micelles.

In general, perfluorinated surfactants exhibit a higher degree of hydrophobicity compared with hydrocarbon surfactants of the equal carbon chain length. Although various properties have been studied in the past, particular attention was focused on the nonideality of mixing with hydrocarbon surfactants,[1,2] on the lower critical micelle concentration (cmc) and their greater surface activity.[3—5] Recently, Boden and co-workers[6—10] have studied the phase behavior of binary fluorosurfactant/water (or D_2O) systems exhibiting mesophases at high surfactant concentration using microscopy, small-angle X-ray scattering (SAXS), and NMR, the surfactants being the cesium salts of the perfluoroalkanoic acids. Through these wide-ranging studies, the existence of what is now called a micellar nematic phase was established. On the other hand, it was found that changing the counter ion affected the phase behavior, as can be seen from the phase diagram for ammonium salts by Reizlein and Hoffmann.[11] Nevertheless, in regard to the properties of fluorocarbon surfactants in the isotropic micellar region near the isotropic/nematic phase transition, not much is known about micellar size and shape, compared with a large amount of information on the hydrocarbon surfactants. For some systems of the latter surfactants, the existence of rodlike micelles at higher concentration was inferred from the physical methods, e.g., light scattering,[12,13] proton NMR,[14] ultrasonic absorption,[15] and, most recently, small angle neutron scattering (SANS).[16,17]

Usually, ^{19}F NMR chemical shifts are very sensitive to the surrounding environment. In such cases, ^{19}F NMR is an excellent means for the study of fluorinated surfactants, determining the exact cmc values and structural properties of the aggregates.[18] In the present work, we have chosen a series of cesium salts of perfluoroalkanoic acid $C_nF_{2n+1}COO^-Cs^+$ (n = 5, 7, 9), which are typical perfluorinated surfactants. To explore the structural properties of the micelles in the isotropic micellar region above cmc, the major techniques used in this study were ^{19}F and ^{133}Cs NMR chemical shift measurements. ^{19}F spin-lattice relaxation times (T_1) were also measured to obtain some complementary information about the segmental motion of the fluorocarbon chain of the micellized surfactants. The results obtained for cesium salt of perfluorooctanoic acid were compared with those of its sodium, ammonium, and rubidium salts. Parallel to these works, we have undertaken a systematic examination of cmc values in a series of perfluorinated surfactants. Especially for cesium salts, the effect of chain length on the cmc values has been studied.

Experimental

Cesium perfluorohexanoate (CsPFH), cesium perfluorooctanoate (CsPFO), cesium perfluorodecanoate (CsPFD), and rubidium perfluorooctanoate (RbPFO) were prepared by neutralizing the corresponding perfluoroalkanoic acid with an appropriate base solution in acetone or ethanol. The salts obtained were purified by recrystallization twice from ethanol, and were then dried under vacuum. (Anal. Found: C, 15.7%. Calcd for CsPFH: C, 16.1%. Found: C, 18.24%. Calcd for CsPFD: C, 18.59%). Some of CsPFO was given as a gift by Prof. S. Harada.

Sodium perfluorooctanoate (SPFO, PCR inc.) was purified by recrystallization from water. Ammonium perfluorooctanoate (APFO, Fluka) was purified by recrystallization from carbon tetrachloride. Deuterium oxide was used as solvent. Most ^{19}F NMR chemical shift measurements were performed on a JEOL FX-90Q spectrometer at 84.26 MHz and some on a Bruker FX-250 F-T form NMR spectrometer at 234 MHz using $C_6H_5F/CDCl_3$ solution as an external standard. ^{133}Cs NMR spectra were obtained with a JEOL FX-90Q spectrometer at 11.70 MHz using $CsCl/D_2O$ as an external standard. The change in the ^{19}F chemical shift, namely, the difference between the observable chemical shift at total concentration for the surfactant and at low concentrations (the monomeric state), is denoted by $\Delta\delta = \delta_{\text{obsd}} - \delta_{\text{mon}}$. Positive values of $\Delta\delta$ represent a downfield shift, whereas negative $\Delta\delta$ values indicate an upfield shift from the monomeric state. ^{19}F–T_1 measurements were also made with an FX-90Q spectrometer. T_1 values were obtained by the inversion-recovery method, using a 180°–τ–90° pulse sequence. The deuterium signal from solvent D_2O was used as an internal lock signal.

Results and Discussion

Cesium Salts of Perfluoroalkanoic Acid: The representative ^{19}F NMR spectra in a CsPFO solution below and above cmc at 30 °C are shown in Fig. 1. The assignments for fluorine atoms have been given previously.[19] Only the ω-CF_3 and the α-CF_2 groups were resolved adequately enough for accurate chemical shifts to be measured. For the λ-CF_2 group that is adjacent to ω-CF_3, it was difficult to specify an inherent peak because of fine splitting due to the coupling with the other fluorine atoms. Other CF_2 groups near the center of the chain were insufficient to obtain a complete resolution of the spectrum, as shown in the figure. In this study, we observed two separate sets of the ^{19}F signals for the fluorocarbon surfactant molecules. At 30 and 50 °C, the changes in the ^{19}F chemical shifts ($\Delta\delta$) of the ω-CF_3 and α-CF_2 groups for CsPFO and CsPFH in D_2O as a function of reciprocal surfactant concentration (m^{-1}/kg mol^{-1}) are shown in Figs. 2 and 3a, respectively. It can be seen that the chemical shifts were almost constant at low concentration. With increasing surfactant concentration, the signals shifted to upfield. The change in the slope of the plot shows the formation of the micelles. The surfactant concentration at which this

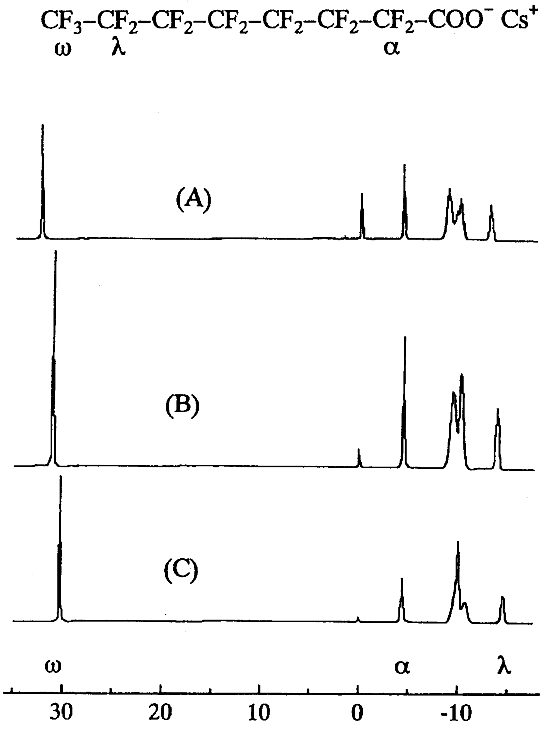
$$\underset{\omega}{CF_3}\text{-}\underset{\lambda}{CF_2}\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}\underset{\alpha}{CF_2}\text{-}COO^-\ Cs^+$$

Fig. 1. Variation of ^{19}F NMR spectra of CsPFO in D_2O as a function of the concentration: (A) below cmc, (B) above cmc, and (C) at higher concentration.

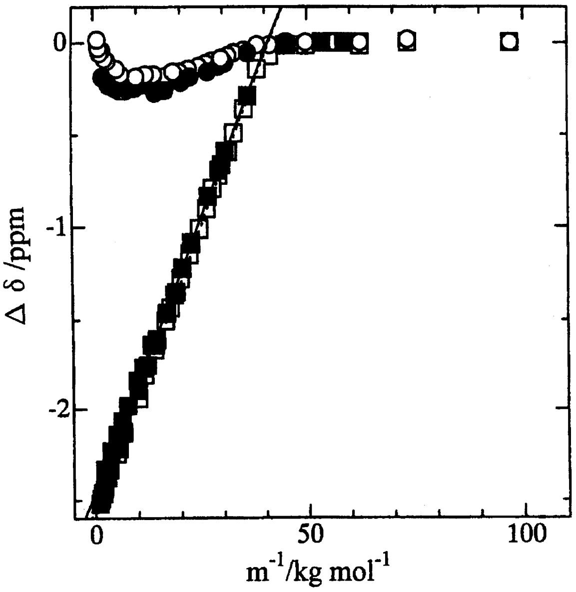

Fig. 2. ^{19}F chemical shift difference $\Delta\delta$ with inverse concentration of CsPFO in D_2O at 30 (open symbols) and 50 °C (closed symbols): α-CF_2 (○, ●); ω-CF_3 (□, ■).

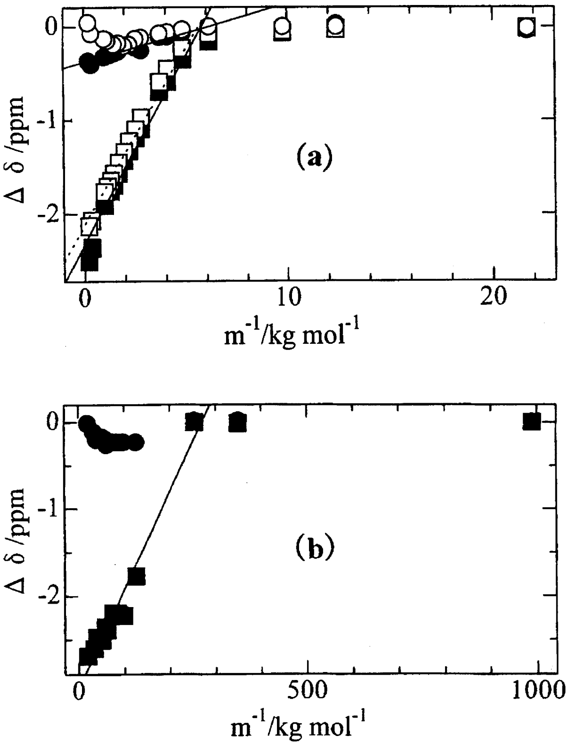

Fig. 3. ^{19}F chemical shift difference $\Delta\delta$ with inverse concentration of CsPFH and CsPFD in D_2O at 30 and 50 °C: (a) CsPFH, (b) CsPFD. The symbols are the same as those in Fig. 2.

discontinuity occurs is taken as the cmc. Especially, the ω-CF_3 group shifted largely to upfield at concentrations above the cmc, whereas the α-CF_2 group near the polar head group shifted slightly to upfield at first, this is then followed by a lowfield shift at higher concentrations, except CsPFH at 50 °C. This difference may be explained by assuming that the α-CF_2 group is attached closer to the micellar surface, as compared with the ω-CF_3 group situated inside of the micelle. The lowfield shift of the α-CF_2 group at higher concentrations is probably related with the counterion. This difference can be interpreted if the electrostatic environment of the micellar surface is changed by increasing the degree of counterion attachment above the cmc (II) (see later). Similar behavior to that for CsPFO in Fig. 2 was also observed at 50 °C for CsPFD with a longer carbon chain length, as shown in Fig. 3b. All these data of the ω-CF_3 group were fitted to pairs of straight lines by a linear least-squares method, and the resulting three cmc values are given in Table 1, with APFO, SPFO, and RbPFO (see later). The cmc value for CsPFD at 30 °C could not be determined because of the low solubility of the surfactant in D_2O. The cmc value for CsPFO was in good agreement with literature values[8] obtained by the conductance method. As far as we know, for both CsPFH and CsPFD, not much is known about the cmc values. As can be inferred from Table 1, the cmc value decreases as the number of carbon atoms in the hydrophobic group increases, but the value is practically independent of the temperature in the range 30 to 50 °C.

Table 1. Critical Micellar Concentration Estimated by ^{19}F Chemical Shift Data for Some Salts of Perfluorocarboxylic Acids in D_2O

Surfactant	cmc/mol kg^{-1} at 50 °C	cmc/mol kg^{-1} at 30 °C
CsPFH	2.0×10^{-1}	2.0×10^{-1}
CsPFO	2.4×10^{-2}	2.4×10^{-2}
CsPFD	2.9×10^{-3}	—[a]
APFO	2.6×10^{-2}	2.8×10^{-2}
SPFO	3.0×10^{-2}	3.1×10^{-2}
RbPFO	2.4×10^{-2}	—[a]

a) Insoluble in D_2O.

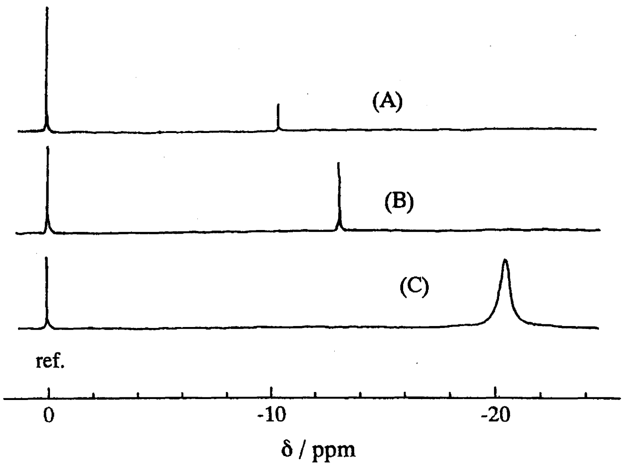

Fig. 4. Variation of ^{133}Cs NMR spectra of CsPFO in D_2O as a function of the concentration: (A) below cmc, (B) above cmc, and (C) at higher concentration.

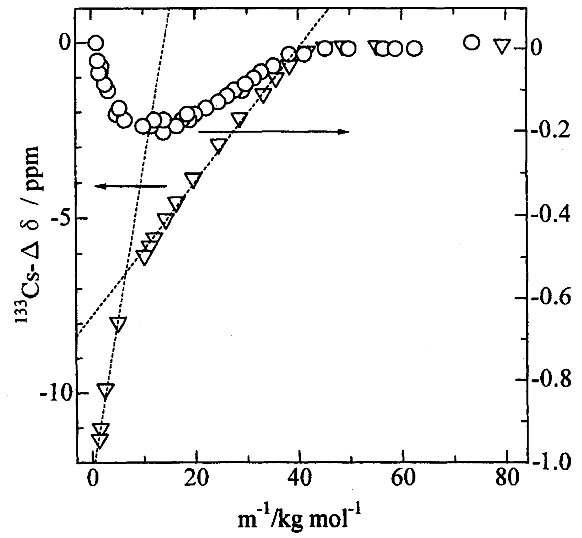

Fig. 5. Comparison of ^{133}Cs with ^{19}F chemical shift differences of CsPFO in D_2O at 30 °C: ^{133}Cs (▽); ^{19}F α-CF_2 (○).

^{133}Cs NMR spectra were recorded for CsPFO/D_2O solutions with surfactant concentration. As illustrated by some typical ^{133}Cs NMR spectra displayed in Fig. 4, the most notable change in the ^{133}Cs spectra is a line broadening of the Cs signal at higher concentrations. In Figs. 5 and 6, ^{133}Cs chemical shifts of CsPFO and CsPFH at 30 °C are given as a function of the reciprocal surfactant concentration. For a comparison, the results of ^{19}F chemical shift for α-CF_2 groups are also included in the figures. The plot of the ^{133}Cs chemical shift seems to be linear below and above cmc. At low concentrations below cmc, the ^{133}Cs shift is independent of concentration. In the region of cmc, the shift changes to upfield, and further, a break off point appears in each curve at high concentrations. It is worth noting that the breaks in the ^{133}Cs curve above cmc define two straight lines intersecting at $m = 0.14$ mol kg^{-1} for CsPFO and 0.83 mol kg^{-1} for CsPFH, corresponding to a sharp break seen in the plot of the α-CF_2 group described already. Consequently, two different breaks were observed in each plot. The same trends were shown by Zhao and Fung[14,20] in studies of sodium dodecyl sulfate and sodium *cis*-7-dodecenyl sulfate using proton chemical shift measurements. They also termed the two break points the cmc and so-called cmc (II), suggesting the larger micelles. As can be seen from Fig. 5, the break point of ^{19}F was different from ^{133}Cs. Although the cause of the difference is unknown to us, in this study we decided cmc (II) from the break point of ^{133}Cs. The values of the cmc and the cmc (II) thus obtained are 2.4×10^{-2} and 1.4×10^{-1} mol kg^{-1} for CsPFO, and 2.0×10^{-1} and 8.3×10^{-1} mol kg^{-1} for CsPFH, respectively. These values of the latter surfactant are higher than the corresponding values of the former, because of a less hydrophobic character. Further, the values

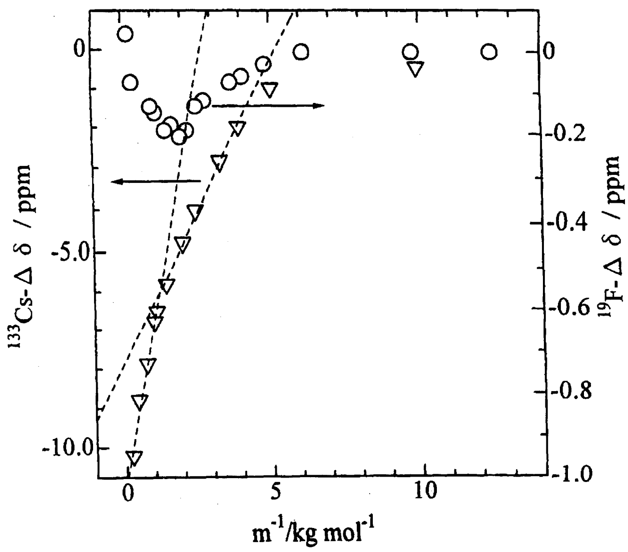

Fig. 6. Comparison of ^{133}Cs and ^{19}F chemical shift difference for CsPFH in D_2O at 30 °C. The symbols are the same as those in Fig. 5.

at the so-called cmc (II) are estimated at about 4—6 times the values at the cmc. These changes are most likely due to the transformation of spherical micelles into the larger micelles, most likely ellipsoidal micelles. Because the chemical environment of the chain in the ellipsoidal micelle is different from that of the spherical micelle to cause a break in the chemical shift plots, it may be caused by different conformation in the molecular packing in the micelle interior. Generally, coulombic repulsions between head groups are largely responsible for preventing both the onset of the micellization at low concentration and the formation of large micelles at higher concentrations. Because fluorinated alkanoates carry less charge, the head groups can pack closer to one another, resulting in a smaller cmc and the existence of large micelles. This decrease in surface charge promotes micelle growth as well as an increase of the intermicellar interaction. In addition, particular attention should be given to the electrostatic effect due to the interaction with counter ions.

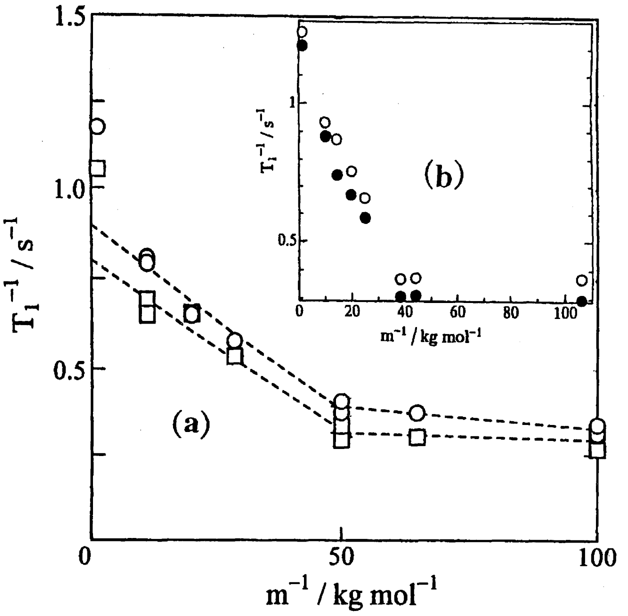

Fig. 7. (a) ^{19}F spin-lattice relaxation rate $T_1{}^{-1}$ with inverse concentration of CsPFO in D_2O at 30 °C: α-CF_2 (○); ω-CF_3 (□). Insert (b): APFO in D_2O at 30 °C: α-CF_2 (○); ω-CF_3 (●).

^{19}F Spin-Lattice Relaxation Rates: In an aqueous solution, the motional behavior of the surfactant molecules depends on whether they exist as monomers or in micelles, and on the size of the micelles. The ^{19}F spin-lattice relaxation rates $T_1{}^{-1}$ of α-CF_2 and ω-CF_3 groups in CsPFO solution are plotted in Fig. 7a as a function of the inverse of surfactant concentration, with the result of APFO solution in Fig. 7b. Following the phase separation model,[21] the observed relaxation rate $T_1{}^{-1}$ is assumed to be a weighted average of the relaxation rates in the micelles and the monomers: $T_1{}^{-1} = \mathrm{cmc}/c(T_1{}^{-1})_{\mathrm{mon}} + (c-\mathrm{cmc})/c(T_1{}^{-1})_{\mathrm{mic}}$, where c is the total surfactant concentration. In the figure, one expects to obtain two lines intersecting at the cmc in $T_1{}^{-1}$ vs. m^{-1} plots for both groups. At low concentrations, there is little change in $T_1{}^{-1}$ within experimental error, whereas the $T_1{}^{-1}$ increases with surfactant concentration in the limited range of concentration above the cmc (ca. 1.4—2.5×10^{-1} mol kg^{-1} for CsPFO, for example), and an approximately linear relationship exists. The decrease in T_1 with micelle formation is generally regarded as the restraint placed upon the molecules when aggregated into micelles. It is expected that internal chain motions would be hindered in the micellar state relative to the corresponding motions in the monomeric state. Another factor to be considered is the change in environment that a molecule undergoes during micelle formation. This behavior results in severe immobilization at the polar head because surfactant molecules interact strongly with neighboring molecules, counter ions and solvent molecules at the micellar surface. For ^{19}F nuclei, as well as proton nuclei in alkyl chain, Henriksson and Odberg[21] previously demonstrated that the observed relaxation rate was the sum of the relative contribution due to both intermolecular and intramolecular processes. In D_2O solutions, the intermolecular relaxation would be mainly caused by fluorine–deuterium interaction for the monomer, whereas fluorine–fluorine interaction in different molecules would occur mainly for the micelle, and this would lead to a relative decrease in T_1 for the micellar state. The deuterium nucleus has a rather small magnetic moment as compared with that of the proton and the contribution from the solvent to the intermolecular relaxation rate may be ignored in D_2O solution. In the solutions of unaggregated molecules, it is suggested that overall reorientation of the molecule will be rapid, with a slight degree of segmental motions along the chain in a molecule, indicating that the relaxation behavior in this dilute concentration range is mainly governed by the overall motion of the monomer against the resistance of solvent. When the concentration of $C_7F_{15}COOCs$ increases, we get for the D_2O solutions an increase of the fluorine–fluorine contribution. The transfer from the unaggregated to the micellar state results in a further increase in the relaxation rate. The increase can be caused by two different factors. First, as stated already, there is an increase in the fluorine–fluorine contribution to the intermolecular relaxation rate due to the higher fluorine concentration in the micelles. Secondly, the intramolecular relaxation rate might increase due to slowing down of the rotational motion of the molecules in the micelles compared with the unassociated surfactant molecules. However, it is not clear to us which is the dominant factor for the present results. In this regard, ^{19}F NMR results were compared with previous ^{13}C–T_1 study for octyltrimethylamonium bromide (OTAB),[22] with equal carbon number. In the latter case, the freedom of motion was found to increase with distance from the surfactant head group for the OTAB micellized surfactants. As for the ω-carbon group occupying the interior of micelles, it has a prominent segmental motion almost independent of the surfactant concentration, and hence the micellar interior has properties that approach these of a liquid hydrocarbon. Thus, the hydrocarbon core was found to be fluid state. On the contrary, for the CsPFO solution, it is seen that the relative difference in relaxation rate between α-CF_2 and ω-CF_3 groups is markedly smaller than that between the α-methylene and the ω-methyl groups for OTAB above the cmc. In APFO solution, a similar tendency was noticeable between α-CF_2 and ω-CF_3 groups, as shown in Fig. 7b. For the present limited scope, the previous results with normal hydrocarbon surfactant might have some implications for perfluorinated surfactants also. It seems to be a general finding that there is no significant difference between α- and ω-groups along the fluorocarbon chain. Moreover, we may expect the solvent contact effect within the micelle on the relaxation to be considerably smaller for both groups, for example. Then, the present results will be explained based on the internal conformation of the micelle rather than the interaction between micelles. As for the conformational state upon the formation of micelles, the relative population of *trans* and *gauche*-conformers needs to be considered. In the case of fluorocarbon chain, there are an increased proportion of *trans*-conformers, because the F-groups of the fluorocarbon chain are bulkier than the alkyl carbon groups. This means that the *trans* conformations of the fluorocarbon chains are energetically more favorable situations than unstable *gauche* ones.[23] In view of the present results, it is likely that fluorocarbon chains as units are far less flexible than their hydrocarbon chains and it seems reasonable to expect perfluorinated surfactants to assemble as rigid micelles. Further, it might be necessary to have a detailed knowledge of the local environment for different positions of both ^{19}F and ^{13}C nuclei along the fluorocarbon chains in the micelles. These T_1 measurements would serve to provide some information about each contribution to the relaxation from intermolecular and intramolecular interactions mentioned above.

Chain Length Dependence to the cmc: It follows that the cmc values are an exponentially decreasing function of the number of carbon atoms (n) in the nonpolar side chain. From the resulting cmc values for the $C_nF_{2n+1}COO^-Cs^+$ system with n = 5—9, the plot of $\log m_{\mathrm{cmc}}$ against n gives a straight line with a slope of -0.46 ± 0.01, as shown in Fig. 8a. Accordingly, the straight line obeys the relation: $\log m_{\mathrm{cmc}} = 1.60 - 0.46n$. Combining this with the results for alkyltrimethylammonium bromides (C_nTAB) and alkylpyridinium bromides (C_nPyB) in a previous study (Fig. 8b),[24] we find that the negative linear relationship between the logarithm of the cmc and the number of carbon atoms is seen to satisfy a similar relationship for a given homologous series of ionic surfactants according to the equation: $\log \mathrm{cmc} = a_0 - a_1 n$, where a_0 and a_1 are constants. Because the value of a_0 is approximately constant for a particular head group, a_1 values are more informative. The a_1 values of $C_nF_{2n+1}COO^-Cs^+$ are -0.46, this means that the values of cmc decrease by the factor of about 2.9 for each CF_2 group added to the perfluoroalkyl chain. For C_nTAB and C_nPyB, the a_1 values are -0.30 and -0.32, as pointed out already by Lin and Somasundaran[25] for ionic hydrocarbon surfactants. Thus, the cmc values decrease by the factor of about 2.0 or 2.1 for each CH_2 group to the alkyl chain. The larger value of a_1 for the fluorocarbon surfactants suggests that hydrophobic interactions between fluorocarbon chains might be stronger than those between hydrocarbon surfactants in aqueous solutions. Because of the electronic character of the carbon–fluorine bond, a fluorocarbon chain is more "rigid" than a hydrocarbon chain. The effect of each CF_2 group on micelle formation is roughly equivalent to that of 1.5 CH_2 groups. This conforms to the general rule[26] that the cmc of fluorocarbon solutions will be the same as for aqueous hydrocarbon solutions with a chain length about 1.5 times larger than for the fluorinated compound.

Various Salts of Perfluorooctanoic Acid: Three typ-

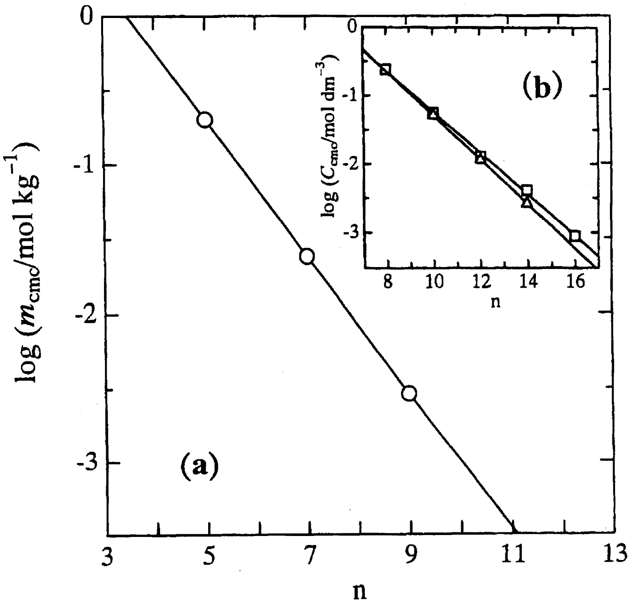

Fig. 8. (a) Relation between $\log m_{\mathrm{cmc}}$ and the carbon numbers in the chain of $C_nF_{2n+1}COO^-Cs^+$ in D_2O at 50 °C. Insert (b): C_nTAB (□) and C_nPyB (△) in H_2O at 30 °C, by surface tension method.[25] (a), slope = -0.46; (b), slope = -0.30 and -0.32. Their correlation coefficients r are all 0.999.

ical plots of $\Delta\delta$ against m^{-1} of the ω-CF_3 and the α-CF_2 groups for the SPFO, APFO, and RbPFO in D_2O solutions at 30 and 50 °C, except RbPFO at 30 °C, are shown in Figs. 9 and 10. Different from the results obtained for the CsPFO solution, two different breaks for the α-CF_2 group were not observed in each plot. In these figures, there are two linear segments that intersect at $m^{-1} = m_{\mathrm{cmc}}{}^{-1}$ as well as for Cs salts described above. The cmc values obtained are listed together in Table 1. Na, NH_4, and Rb salts had cmc values close to the literature values[27—30] within ±0.01 mol dm^{-3} at most in the temperature range 25—50 °C. As shown in Table 1, one of the more remarkable things about micellization for the perfluorinated surfactants is the very weak temperature dependence of the cmc. For various ions having the same valency, the lyotropic series may have a role to play in the explanation of smaller cmc variations, if the hydrophobic groups are the same. Thus, the cmc values decrease in the order of SPFO > APFO > CsPFO≒RbPFO. Our cmc values might contribute little new information because the properties of these aqueous solutions have been studied by earlier workers, except CsPFH and CsPFD. In present study, we have reconfirmed that ^{19}F NMR technique provided an excellent way of determines cmc values, although multinuclear NMR study of perfluorinated surfactants is rather scarce. To our knowledge, abrupt changes in physical properties of surfactant solutions above the cmc, discussed in terms of a second and third cmc, are not fully explored at present. Such changes in the physical properties above the "normal" cmc are likely manifested as alterations in micellar sizes or shapes, counter ion binding, extent of hydration, or a combination of changes in these parameters. In particular, the counter ion binding to the micelle in D_2O solution appears to decrease with the increase in the hydrated radius of the ion and to increase with increase in its polarizability and charge. Thus, the order of decreasing binding is $Cs^+ > Rb^+ > Na^+ > Li^+$, as shown for alkyl sulfate micelles.[31] Changing the counter ion from sodium, ammonium, and rubidium to cesium means that more counter ions bind to the head group region, allowing larger aggregate structures. The interaggregate electrostatic interaction is weaker because more head group charge is balanced by bound counter ions. At the present time, we are not sure of the nature of larger micelles, accompanied by the shape, stability and so on. The major technique used in this investigation was ^{19}F NMR. Recently, an alternative technique for examining micellar systems is provided by SANS and/or SAXS. A combination of these techniques enables us to gain a rather comprehensive understanding of the nature of large micelles of these systems. Details of this are beyond the scope of the present work and await further investigation.

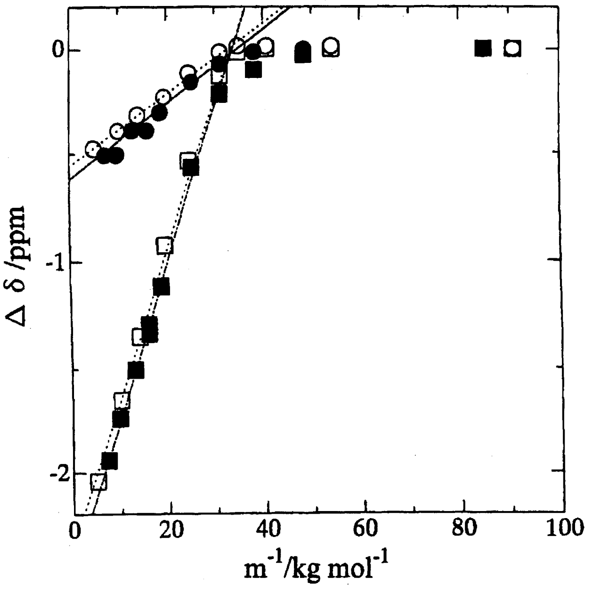

Fig. 9. ^{19}F chemical shift difference $\Delta\delta$ with inverse concentration of SPFO in D_2O at 30 and 50 °C. The symbols are the same as those in Fig. 2.

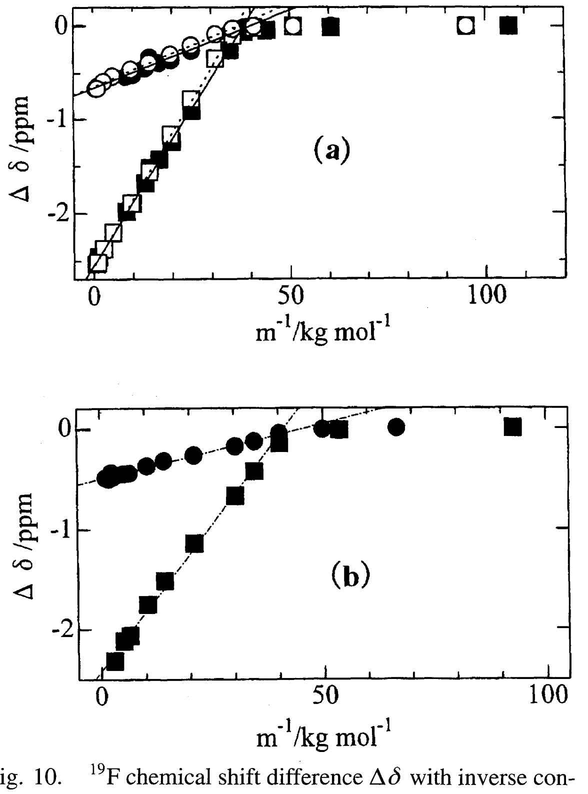

Fig. 10. ^{19}F chemical shift difference $\Delta\delta$ with inverse concentration of APFO and RbPFO in D_2O at 30 and 50 °C: (a) APFO, (b) RbPFO. The symbols are the same as those in Fig. 2.

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