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^{1}H NMR Self-Diffusion Study for Mixed Micelles of Fluorocarbon and Hydrocarbon Surfactants[†]

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A pulsed-gradient spin-echo ^{1}H NMR measurement has been performed to study the variation of monomer concentration and micellar size in fluorocarbon–hydrocarbon surfactant mixed systems such as lithium perfluorooctanesulfonates (LiFOS)–lithium dodecyl sulfate (LiDS) and sodium perfluorooctanoate (SPFO)–sodium dodecyl sulfate (SDS). Inflection points were obtained by plotting the self-diffusion coefficients against the reciprocal of total surfactant concentrations above the critical micelle concentration of the mixture (mixture cmc). Those that were assigned to second cmc's were caused by the abrupt change in monomer concentration of hydrocarbon surfactant. The self-diffusion coefficients of micelles depended on the micelle composition and the LiCl concentration. An addition of LiCl induced a micellar growth. In the higher LiCl concentration, the micellar size of LiDS was increased with mixing of LiFOS.

Introduction

In an aqueous solution, surfactants are usually associated to form micelles in spherical or rodlike shape etc.[1-3] The size and shape of micelles can be determined by conventional light scattering measurements.[4-6] However, it is difficult to determine the micellar size of fluorocarbon surfactant by a light scattering method, because the difference in refractive index between the fluorocarbon surfactant and water is extremely small. Thus Hoffmann et al. applied a small angle neutron scattering method to this system and revealed the size and shape of micelles of fluorocarbon surfactant.[7,8]

Mixed micelles are in the focus of research from the view point of both practical application and solution theory.[9-15] The size of the mixed micelles provides important information characterizing such a micellization process, but there are only a few works that deal with the size of mixed micelles.

In fluorocarbon–hydrocarbon surfactant mixed systems, nonideal behavior in a micelle was demonstrated by several experiments.[16-22] In such an investigation, especially, much attention has been focused on the coexistence of two kinds of mixed micelles, which consist of different micelle compositions. Burkitt et al. investigated mixed micelles of a fluorocarbon–hydrocarbon surfactant mixed system by a small angle neutron scattering method.[23,24] They indicated that mixed micelles were cylindrical in shape and proposed that the segregation between hydrocarbon and fluorocarbon surfactants in a micelle would occur.

A pulsed-gradient spin-echo (PGSE) Fourier transform (FT) NMR method was used to determine the self-diffusion coefficients of surfactant micelles.[25,26] Since the translational diffusion of a micelle is different by several orders from that of a monomer, the observed self-diffusion coefficients were also analyzed to quantify the populations of these two sites. Indeed, Lindman et al. estimated surfactant monomer concentrations and the degree of counterion binding by the two-site model.[26] On the other hand, Carlfors and Stilbs applied the self-diffusion measurements to the mixed micelles of fluorocarbon–hydrocarbon surfactants.[19] The composition of mixed micelles was elucidated on an assumption of two coexisting micelles.

When the contribution of the monomer is suppressed, the self-diffusion coefficent of micelles can be used to estimate the micellar size: the reciprocal of the self-diffusion coefficient, which is proportional to the frictional coefficient, was used to estimate the micellar size.

In this paper, a detailed investigation of fluorocarbon–hydrocarbon surfactant mixtures was performed by the self-diffusion measurements through the PGSE FT ^{1}H NMR method. Second cmc's were determined by plotting the self-diffusion coefficients against the reciprocal of total

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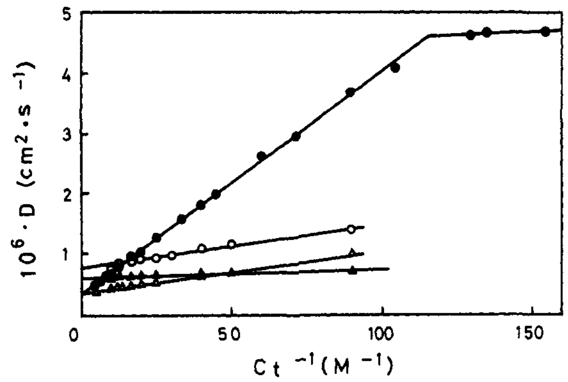

Figure 1. Self-diffusion coefficients as a function of total surfactant concentrations: (●) LiDS, (△) LiTS, (○) LiDS in 0.1 M LiCl, (▲) LiTS in 0.1 M LiCl.

surfactant concentrations. Micellar sizes were evaluated under the addition of LiCl with eliminating the contribution of monomer and intermicellar interactions. The micellar growth was examined by the further addition of LiCl.

Experimental Section

Lithium perfluorooctanesulfonate (LiFOS), sodium perfluorooctanoate (SPFO), lithium dodecyl sulfate (LiDS), lithium tetradecyl sulfate (LiTS), and sodium dodecyl sulfate (SDS) were prepared by the same procedures as reported previously.[20] The PGSE FT ^{1}H NMR measurements for the determination of self-diffusion coefficients were made on protons at 99.6 MHz using an internal D_2O lock on a JEOL FX-100 spectrometer.[27] The duration of the pulsed gradient ranged from 10 to 30 ms. The interval between the two gradient pulses was kept constant at 80 ms. The magnitude of the pulsed gradient was calibrated by the diffusion coefficient of pure water at 25 °C, 2.30×10^{-9} m^2 s^{-1}.[28] D_2O solutions of surfactants were placed in a 5-mm tube with nonspinning at 25 °C. Single exponential decays of the echo amplitude were observed for all samples.

Results and Discussion

Self-diffusion measurements of hydrocarbon surfactants (LiDS, LiTS) in D_2O were performed for each surfactant, their mixtures with fluorocarbon surfactants (LiFOS, SPFO), and the systems containing added LiCl. A fast exchange of surfactants between bulk and micelle exists on the NMR time scales. Therefore, the observed self-diffusion coefficient (D) is obtained by a two-site model.[25]

$$D = \frac{C_s}{C_t} D_S + \frac{C_t - C_s}{C_t} D_M = D_M + \frac{C_s}{C_t}(D_S - D_M) \qquad (1)$$

where D_S and D_M are the self-diffusion coefficients of surfactants in bulk and micelle and C_s and C_t are the monomeric and total surfactant concentrations, respectively. As D_M is generally smaller than D_S, D is expected to increase linearly with the reciprocal of total concentration.

Figure 1 shows self-diffusion coefficients of LiDS and LiTS solutions as a function of total surfactant concentrations. The self-diffusion coefficients were found to be linear against the reciprocal of total concentration above the cmc. The inflection point of LiDS in D_2O gave the cmc, which was in agreement with cms's (8.6 mM) obtained by other experimental methods.[15] Self-diffusion coefficients of LiTS in D_2O were smaller than that of LiDS, because the concentration of monomeric LiTS surfactant was lower than that of LiDS. In 0.1 M LiCl solutions, the self-diffusion coefficients decreased at lower surfactant concentrations. On the other hand, those at higher surfactant concentrations increased in an addition of LiCl. The result suggested that the added LiCl reduced the concentration of monomeric surfactant and suppressed the micelle–micelle interactions rather than induced an increase in micellar size.

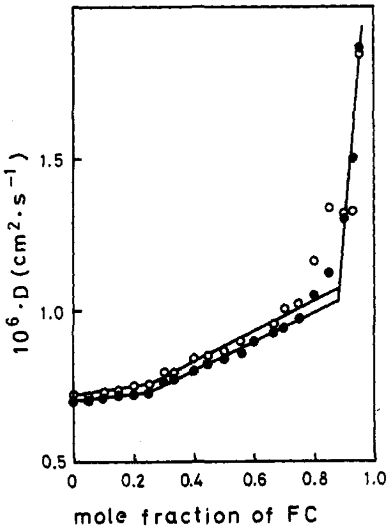

Figure 2. Self-diffusion coefficients as a function of mole fraction of fluorocarbon surfactant (FC): (●) 0.1 M LiFOS–LiDS, (○) 0.1 M SPFO–SDS.

Next, the self-diffusion measurement was applied to the fluorocarbon–hydrocarbon surfactant mixed systems. Figure 2 shows the self-diffusion coefficients for the LiFOS–LiDS and SPFO–SDS mixtures as a function of mole fraction of fluorocarbon surfactant at constant total concentrations of 0.1 M. Three regions were recognized: (1) The self-diffusion coefficient was almost constant when the added amount of fluorocarbon surfactant was few. (2) The self-diffusion coefficient increased linearly with an addition of fluorocarbon surfactant. (3) The self-diffusion coefficient increased abruptly at high mole fraction of fluorocarbon surfactant. The behavior might be attributable mainly to the increase in monomer concentration of hydrocarbon surfactant.

For fluorocarbon–hydrocarbon surfactant mixed systems, the observed self-diffusion coefficient could be expressed as follows, instead of eq 1

$$D = \frac{C_{Hs}}{(1-\alpha)C_t} D_S + \frac{(1-\alpha)C_t - C_{Hs}}{(1-\alpha)C_t} D_M = D_M + \frac{C_{Hs}}{(1-\alpha)C_t}(D_S - D_M) \qquad (2)$$

where α is the mole fraction of fluorocarbon surfactant in the mixture, and C_{Hs} is the monomer concentration of a hydrocarbon surfactant. Since the translational diffusion coefficient of a monomer is different, by 1 order and more, from that of a micelle, the observed self-diffusion coefficients would mainly reflect the change in monomer concentration of hydrocarbon surfactant. Equation 2 indicates that the slope of D vs $1/C_t$ plot above the cmc is proportional to C_{Hs}, when the concentration dependence of D_S and D_M is small at constant composition.

Figure 3 shows the variation of self-diffusion coefficients as a function of total surfactant concentrations at constant composition for LiFOS–LiDS mixed system. Inflection points were observed except in the case of $\alpha = 0.5$. Their values were 55.2, 30.0, and 32.8 mM at $\alpha = 0.25$, 0.3, and 0.75, respectively. The slope on the linear relation of D

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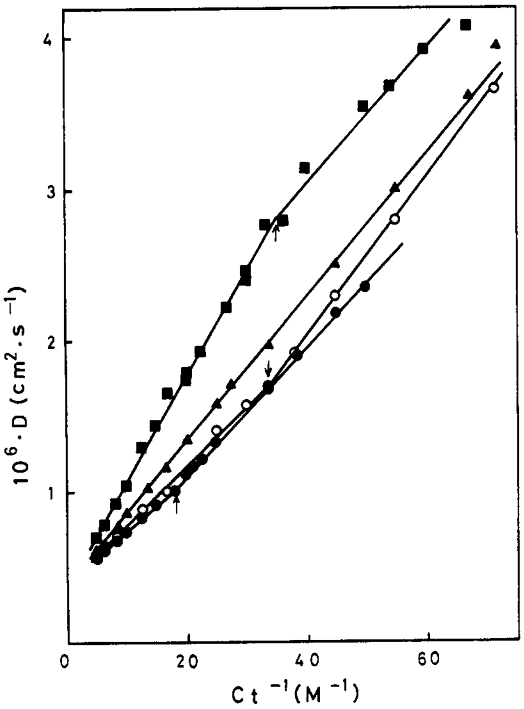

Figure 3. Self-diffusion coefficients as a function of total surfactant concentrations for LiFOS-LiDS mixture: (●) α = 0.25, (○) α = 0.3, (▲) α = 0.5, (■) α = 0.75.

vs $1/C_t$ changed at both sides of this concentration. In the case of α = 0.25 and 0.3, when the slope of a linear relation at higher total concentration was compared with that at lower total concentration, the increase in the latter slope indicated the increase in LiDS monomer concentration, as interpreted from eq 2. On the other hand, in the case of α = 0.75, the decrease in slope at lower total concentration indicated the decrease in LiDS monomer concentration. The LiDS monomer concentration at both sides of the inflection point might coincide in the case of α = 0.5. These inflection points could be assigned to the second cmc's, where it was interpreted that hydrocarbon-rich micelles or fluorocarbon-rich micelles were formed, as described in a previous paper.[29]

For a SPFO-SDS mixture at α = 0.8, Kamrath and Franses calculated the total concentration dependence of monomer and micelle concentrations in detail.[12] They suggested that there were two kinds of mixed micelles present above the second cmc and that the demicellization, i.e., transition from two kinds to one kind of mixed micelles, would occur in higher concentration. Their calculation predicted that the mixture cmc, the second cmc, and the CDC (cricital demicellization concentration) were 21, 34, and 60 mM, respectively.

Figure 4 shows the concentration dependence of self-diffusion coefficients for a SPFO-SDS mixture. The self-diffusion data showed that the inflection points of 33 and 100 mM for α = 0.5 and 33 and 66 mM for α = 0.8 appeared, corresponding to the second cmc and the CDC, respectively. The concentration dependence of self-diffusion coefficient could be considered as follows: above the mixture cmc, the self-diffusion coefficient decreased abruptly due to the decrease in SDS monomer concentration as the total concentration increased, as well as the case of α = 0.25 and 0.3 for the LiFOS-LiDS mixture. Above the second cmc, the decrease of self-diffusion coefficient was suppressed because of the slight decrease in SDS monomer concentration. Above the CDC, the self-diffusion coefficient abruptly decreased owing probably to the transition to one kind of mixed micelles with a large aggregation number.

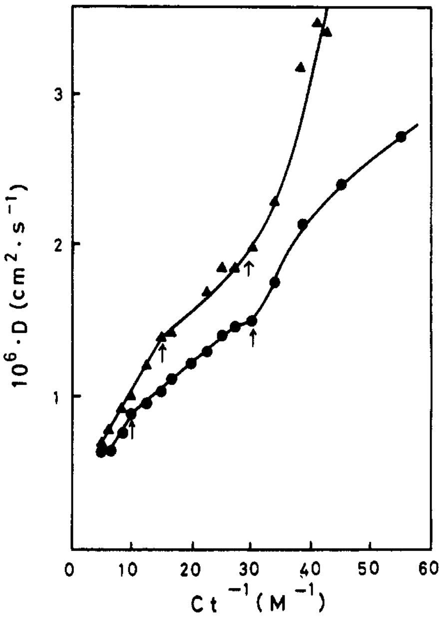

Figure 4. Self-diffusion coefficients as a function of total surfactant concentrations for SPFO-SDS mixture: (●) α = 0.5, (▲) α = 0.8.

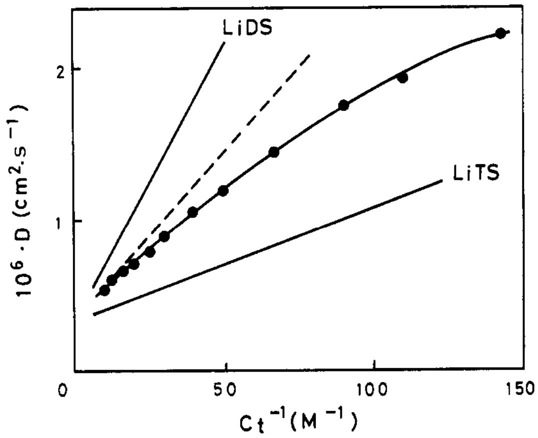

Figure 5. Self-diffusion coefficients as a function of total surfactant concentrations for an equimolar LiDS-LiTS mixture: (- - -) calculated average value of LiDS and LiTS.

Figure 5 shows the self-diffusion coefficients for an equimolar LiDS-LiTS mixture. The observed self-diffusion coefficients deviated from the average value (dotted line in Figure 5) of LiDS and LiTS systems. As the concentration decreased, the observed self-diffusion coefficients approached those of LiTS. This was caused by the decrease in total monomer concentration.

As described above, the variation of monomer concentration of hydrocarbon surfactant can be followed by taking the self-diffusion measurement in D_2O. On the other hand, the self-diffusion coefficient of micelles can be calculated from $D_M = (C_tD - C_sD_S)/(C_t - C_s)$. The self-diffusion coefficients of LiDS and LiTS micelles in D_2O and 0.1 M LiCl were evaluated and plotted in Figure 6. A plot of $1/D_M$ vs micelle concentration was approximately linear. The extrapolated D_M value of LiDS in D_2O at zero micelle concentration was 5.3×10^{-7} cm^2 s^{-1} and the slope was 3.2×10^7 cm^{-2} s mol^{-1} L. On the other hand, in 0.1 M LiCl solution, D_M of LiDS was 8.5×10^{-7} cm^2 s^{-1} and the slope

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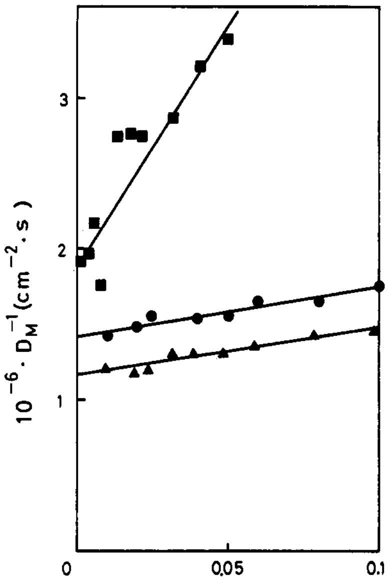

Figure 6. The reciprocal of micellar self-diffusion coefficients as a function of micelle concentrations: (■) LiDS, (▲) LiDS in 0.1 M LiCl, (●) LiTS in 0.1 M LiCl.

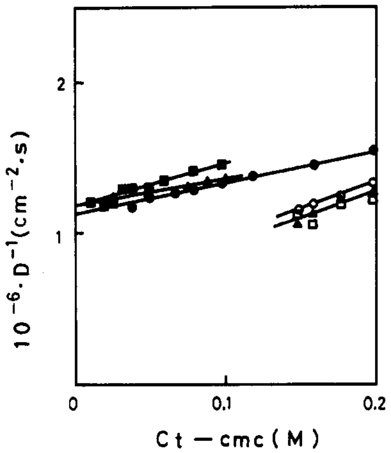

Figure 7. The reciprocal of self-diffusion coefficients as a function of micelle concentrations for LiFOS–LiDS mixture in 0.1 M LiCl: (■) $\alpha = 0$, (△) $\alpha = 0.4$, (●) $\alpha = 0.6$, (○) $\alpha = 0.8$, (▲) $\alpha = 0.9$, (□) $\alpha = 0.95$.

was 3.1×10^6 cm^{-2} s mol^{-1} L. D_M of LiTS in 0.1 M LiCl was 7.1×10^{-7} cm^2 s^{-1} and the slope was 3.3×10^6 cm^{-2} s mol^{-1} L.

A theoretical explanation of the micelle concentration dependence of self-diffusion coefficient has been given by Mazo.[30] The observed concentration dependence of $1/D_M$ was approximately similar in tendency to the theoretical prediction, which takes account of the intermicellar interaction. The hydrodynamic radius of LiDS micelles in 0.1 M LiCl, which was calculated from D_M at zero micelle concentration by the use of the Stokes–Einstein equation, was 2.2 nm. Therefore, the LiDS micelles in 0.1 M LiCl can be considered to remain approximately spherical with a radius corresponding to the length of the extended hydrocarbon chain. The radius of LiTS micelles in 0.1 M LiCl was 2.6 nm, which was larger than that of LiDS micelles.

Figure 7 shows the plots of $1/D$ vs micelle concentration for a LiFOS–LiDS mixture in 0.1 M LiCl. The $1/D$ decreased with the increase in mole fraction of LiFOS. In this case, since the monomer concentration in solutions was low, the $1/D$ value could be approximated as the $1/D_M$ value. Therefore, it could be suggested that the apparent micellar radius decreased with an addition of LiFOS. The behavior was reasonable when taking into account the small aggregation number of LiFOS micelles. The micelle composition could be considered to be equal to the mole fraction of LiFOS, when the monomer concentration lowered by the addition of LiCl. Then the composition dependence of micelle size was similar to the tendency observed by a fluorescence quenching method.[31]

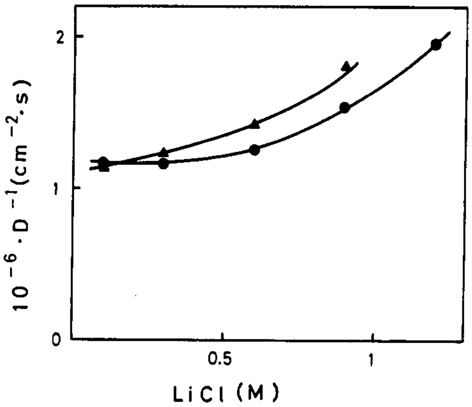

Figure 8. Reciprocal of self-diffusion coefficients as a function of added LiCl concentrations: (●) 30 mM LiDS, (▲) 30 mM LiFOS–LiDS at $\alpha = 0.3$.

Table I. Micellar Growth Induced by LiCl

	[LiCl], M	10^7D, cm^2 s^{-1}	r,[a] nm	a, nm	a/b[b]	n[c]
LiDS	0.1	8.47 ± 0.06	2.2_0	2.6_1	1.3_1	100
	0.3	8.47 ± 0.09	2.1_5	2.4_5	1.2_3	100
	0.6	7.82 ± 0.11	2.2_3	2.7_0	1.3_5	110
	0.9	6.39 ± 0.09	2.6_2	3.9_6	1.9_8	160
	1.2	5.05 ± 0.08	3.1_8	5.8_8	2.9_4	230
LiFOS–LiDS at $\alpha = 0.3$	0.1	8.70 ± 0.03	2.1_4	2.4_2	1.2_1	100
	0.3	8.05 ± 0.09	2.2_6	2.8_0	1.4_0	110
	0.6	6.98 ± 0.09	2.5_0	3.5_7	1.7_9	140
	0.9	5.45 ± 0.15	3.0_7	5.5_5	2.7_8	220

[a] $r = kT/6\pi\eta D$, apparent hydrodynamic micellar radius. [b] a/b, axial ratio of micelles (assuming a prolate ellipsoid, minor axis $b = 2.0$ nm). [c] $n = V_m N_A/\bar{v}$, aggregation number. $\bar{v}$, partial molar volume (LiDS 257.3 cm^3/mol, LiFOS 258.3 cm^3/mol). The $\bar{v}$ values were determined by the density measurement; N_A, Avogadro's number; $V_m = (4/3)\pi b^2 a$.

The micellar growth was examined by the further addition of LiCl. Figure 8 shows the salt-induced increase in apparent micelle size of LiDS in comparison with the LiFOS–LiDS mixture. In 0.1 M LiCl, the apparent micelle radius of LiDS was close to that of LiFOS–LiDS at $\alpha = 0.3$. However, at higher LiCl concentration, the increase in apparent micelle size of LiFOS–LiDS mixture was larger than that of LiDS. The apparent hydrodynamic radii of micelles (r) are summarized in Table I.

The salt-induced increase in micelle size would be attended by the variation from sphere to ellipsoid. Bendedouch and Chen[32] indicated that the LiDS micelle in aqueous LiCl solution could be represented as a prolate ellipsoid according to their small angle neutron scattering experiments. Thus we assumed the shape of micelle was a prolate ellipsoid. The axial ratio (a/b) of micelle was calculated by Perrin's equation assuming a prolate ellipsoid. Then the length of the minor axis (b) was assumed to be 2.0 nm, taking into account of the dodecyl chain with

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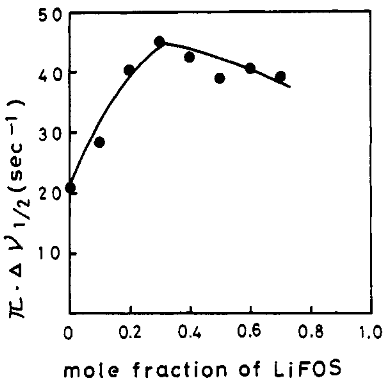

Figure 9. Line width ($\Delta\nu_{1/2}$) of methylene signal as a function of mole fraction of LiFOS for 30 mM LiFOS–LiDS mixture in 1.2 M LiCl.

a hydrated hydrophilic group. As shown in Table I, the axial ratio (a/b) of the LiDS micelle increased up to about 3 with a LiCl concentration up to 1.2 M, whereas the axial ratio of LiFOS–LiDS micelles at $\alpha = 0.3$ already reached about 3 in 0.9 M LiCl. In other words, relatively large mixed micelles were observed at higher LiCl concentration of 0.9 M: $n = 220$ and $a/b = 2.8$ for LiFOS–LiDS of $\alpha = 0.3$ while $n = 160$ and $a/b = 2.0$ for LiDS, where n is an apparent micelle aggregation number calculated by a use of the value of partial molar volume.

In general, the factors in determining the micellar size are mainly the hydrophobic interaction and the electrostatic repulsion between hydrophilic groups. When LiCl was added in order to suppress the electrostatic repulsion between hydrophilic groups, the micellar size increased. Moreover, the incorporation of a rigid fluorocarbon chain might afford the ordered packing of hydrocarbon chains in micelles, which result in increasing the micellar size in a LiFOS–LiDS mixture. Such an increase would allow the segregation between fluorocarbon and hydrocarbon surfactants in micelles to occur.

Burkitt et al. observed micellar growth by mixing perfluorooctanoate and decanoate.[24] They suggested that segregation between hydrocarbon and fluorocarbon surfactants would occur with minimizing the interfacial area between the two hydrophobic chains. On the other hand, our result indicated that the micellar growth and segregation by the addition of a fluorocarbon surfactant were observed only at considerably excess LiCl concentration.

The presence of large micelles has been known to give broad NMR signals owing to the decrease in magnetic relaxation of surfactant.[33-35] It is well established that a sphere–rod transition of micellar shape produces very marked signal broading. Thus the changes in NMR line widths correspond to the changes in micellar size and shape. Figure 9 shows the proton NMR line width at half height ($\Delta\nu_{1/2}$) of the main methylene signal for 30 mM LiFOS–LiDS in 1.2 M LiCl. The line width increased with an addition of LiFOS and showed a maximum at $\alpha = 0.3$. In Figure 10, the line widths were plotted against the added LiCl concentration for a LiDS solution and LiFOS–LiDS mixture at $\alpha = 0.3$. A sharp increase in line width was observed above 1.2 M LiCl for a LiDS solution, while it was observed above 1.0 M LiCl for the mixed solution. Abrupt signal broading could be appreciated by the sphere–rod transition.

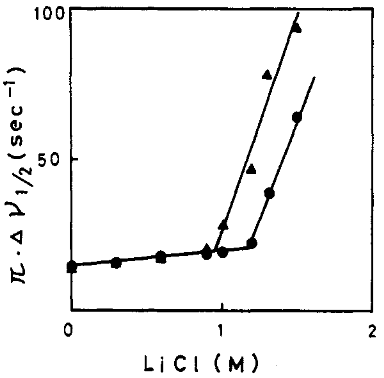

Figure 10. Line width ($\Delta\nu_{1/2}$) of methylene signal as a function of added LiCl concentrations: (●) 30 mM LiDS, (▲) 30 mM LiFOS–LiDS at $\alpha = 0.3$.

We measured the relative viscosity of aqueous micellar solutions in the presence of LiCl. The abrupt increase in relative viscosity of each LiDS and LiFOS solution was observed at 1.2 M LiCl, while that in LiFOS–LiDS mixed solution at $\alpha = 0.3$ was observed at 1.0 M LiCl. Thus the threshold salt concentration of sphere–rod transition was considered to be decreased by mixing of fluorocarbon and hydrocarbon surfactants. In addition, our viscosity data also indicated the maximum micellar size at $\alpha = 0.3$ for a LiFOS–LiDS mixture.

The ordered packing of surfactant in micelles was induced by the incorporation of rigid fluorocarbon chains. The increased packing would give rise to growth in micellar size. When the mole fraction of LiFOS in 1.2 M LiCl increased, the micellar growth would reach the limit due to the immiscibility of fluorocarbon and hydrocarbon surfactants.

Conclusions

The concentration dependence of self-diffusion coefficient could be interpreted by the variation of monomer concentration of hydrocarbon surfactant. The second cmc can be determined from the plot of self-diffusion coefficient against the reciprocal of the total surfactant concentration. The variation of micellar size with an addition of LiCl was evaluated. At higher LiCl concentration, the micellar growth of LiDS was strengthened by the incorporation of LiFOS. Under such a condition, segregation in a micelle would be promoted with minimizing the interfacial area between fluorocarbon and hydrocarbon chains in a large aggregate.

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