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ORIGINAL CONTRIBUTION

Micellar size, shape and counterion binding of *N*-(1,1-Dihydroperfluoroalkyl)-*N*,*N*, *N*-trimethylammonium chloride in aqueous solutions

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Abstract Under the limiting conditions, light-scattering method was applied to determine the size and shape of fluorinated micellar structure in aqueous solution. The hydrodynamic radii (r_h) of molecular aggregates were investigated for four amphiphiles with different alkyl chain length: *N*-(1,1-dihydroperfluorooctyl)-, *N*-(1,1-dihydroperfluorodecyl)-, *N*-(1,1-dihydroperfluorododecyl)-, and *N*-(1,1-dihydroperfluorotetradecyl)-*N*,*N*,*N*-trimethylammonium chloride by dynamic light scattering. Size of these molecular aggregates drastically increased with increasing carbon number of alkyl chain and the concentration. For example, the r_h values were 35, 63, 95, and 136 nm for C8, C10, C12, and C14 of the alkyl chain, respectively, at the concentration of 15× critical micelle concentration (cmc) and at 298.2 K. On the other hand, the mean radius of gyration (r_g) and the apparent molecular weight of these aggregates were measured using static light scattering. The r_g value was found to be 34, 73, and 125 nm for C8, C10, and C12 of the alkyl chain, respectively, at the same condition above. The shape of aggregate was analyzed by comparing the dependence of r_g/r_h with theoretical values. The plots of r_g against r_h almost corresponded with the theoretical line of oblate ellipsoid (disk-like), and which was also expected from calculation of packing parameter value. The measurement for chloride ion activity was made by a chloride ion selective electrode to know the degree of counterion binding to the aggregates, whose values increased with increasing total concentration and with the carbon number of alkyl chain. The chloride ion binding to aggregates neutralized cationic head groups under their electrostatic repulsion and partly promoted the growth of aggregates.

Keywords Fluorinated surfactant · Micelle · Light scattering · Counterion binding

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Introduction

Useful and characteristic properties of fluorinated amphiphiles are their oleophobicity, biological inertness, thermal and chemical stability, and high gas capacity [1, 2]. Fluorocarbon chain is stiffer than hydrocarbon chain because of bulky fluorine atoms [1]. Generally, the rigid structure of fluorocarbon chain leads to aggregate formation of less curvature or elongation, i.e., vesicles, lamellar and threadlike micelles [3, 4]. The size and shape analysis of the fluorinated aggregates has been performed mainly by small-angle neutron and X-rays scattering [5, 6] and by the recent technique of cryogenic transmission electron microscopy (Cryo-TEM) [7, 8]. Conventional light-scattering method cannot be easily applied to the very small aggregates of fluorinated amphiphiles system, because their refractive indices are very close to that of water. However, light-scattering apparatus with high-power laser source has

enough ability to measure diffusion coefficient and molecular weight of fluorinated aggregates [9].

Fluorinated ionic surfactants investigated up to now have been mostly ionic ones with chain length of less than 11 carbon atoms [1, 2]. Reports on longer chain fluorinated surfactants have been quite rare. In addition, cationic surfactants are fewer in number and in variety than anionic ones primarily because of their synthetic difficulties [2, 10, 11]. In this study, four cationic homologs of novel fluorinated surfactants were used; *N*-(1,1-dihydroperfluorooctyl)-*N,N,N*-trimethylammonium chloride (C8-TAC), *N*-(1,1-dihydroperfluorodecyl)-*N,N,N*-trimethylammonium chloride (C10-TAC), *N*-(1,1-dihydroperfluorododecyl)- *N,N,N*-trimethylammonium chloride (C12-TAC), and *N*-(1,1-dihydroperfluorotetradecyl)-*N,N,N*-trimethylammonium chloride (C14-TAC).

Surface tension [10], cmc [10, 11], and thermodynamic analysis [12] for the above surfactants were reported in the previous papers. The aim of the present study is: 1) to estimate the size and shape of aggregates from light-scattering measurement [13, 14] and 2) to know the systematic change of aggregates with alkyl-chain length of the above cationic surfactants. In addition, the present authors determined the free counterion concentration [Cl^-] and the degree of counterion binding to the aggregates on the basis of the mass balance, where the amphiphile concentration and the carbon number of alkyl chain were changed. It is quite useful to be able to presume the solution properties of one surfactant from those of the other surfactants. For this purpose, systematic solution properties have to be investigated using homologous surfactants beforehand. In this sense, this study surely works for the above purpose.

Experimental section

Materials The preparations of $C_7F_{15}CH_2N^+(CH_3)_3Cl^-$ (C8-TAC), $C_9F_{19}CH_2N^+(CH_3)_3Cl^-$ (C10-TAC), $C_{11}F_{23}CH_2N^+(CH_3)_3Cl^-$ (C12-TAC), and $C_{13}F_{27}CH_2N^+(CH_3)_3Cl^-$ (C14-TAC) were performed as reported previously [10, 11]. The fluorinated surfactants were purified by repeated recrystallizations from several mixed solvents as before [11]. The purities were checked by elemental analysis and NMR measurement. The observed and calculated values (in parentheses) for elemental analysis were in sufficient agreement within experimental error by weight percentage: C 27.32 (27.66), H 2.32 (2.34), N 3.01(2.93) for C8-TAC; C 26.93 (27.03), H 1.96 (1.92), N 2.35 (2.42) for C10-TAC; C 26.68 (26.59), H 1.64 (1.64), N 1.95 (2.07) for C12-TAC; C 26.35 (26.26), H 1.43 (1.43), N 1.72 (1.80) for C14-TAC. There was no impurity peak for the above amphiphiles in their NMR spectra.

The hydrogenated surfactants of octhyltrimethylammonium chloride (OTAC), decyltrimethylammonium chloride (DeTAC), dodecyltrimethylammonium chloride (DTAC), and tetradecyltrimethylammonium chloride (TTAC) were obtained from Tokyo Kasei Kogyo, and then purified three times by recrystallization from acetone–ethanol mixtures.

Preparation of solutions The water used for preparation of all the aqueous solutions was distilled once from ion-exchange treatment water. The solution was kept under agitation by magnetic stirrer and incubated above 338 K for more than 1 day. The time duration for aggregation equilibrium can be shortened by the above operation [11].

Light scattering The light-scattering measurement was made by a laser light-scattering photometer (ALV-5000, Germany). The light source was a 200-mW Nd:YAG laser, and the wavelength was 532 nm. All sample solutions were filtrated through a membrane filter with a pore size of 0.8 μm (Millipore, MILLEX-AA). The filtrated solution was poured into a cylindrical cell of 15 mm diameter contacted with circulating thermostated water at 298.2± 0.3 K. The sample solutions of more than 3–5 duplications were repeatedly measured 3–10 times within a week after preparation of the solutions. The measurement angle defined a scattering vector q in the light scattered:

$$q = 4\pi n/\lambda \sin(\theta/2), \tag{1}$$

where λ was the wavelength in vacuum, the medium had refractive index n, and the measurement was performed at angle θ. The scattering angle was fixed at 90° for dynamic light scattering and changed between 45 and 135° every 15° for static light scattering.

Dynamic light scattering (DLS) [15, 16]. The experimental normalized intensity–intensity correlation function, $g_2(t)$ is an exponentially decaying function, from which the manual diffusion coefficient is derived through the Siegrel relation with electric field correlation function, $g_1(t)$:

$$g_2(t) = 1 + \beta|g_1(t)|^2, \tag{2}$$

where β takes into account deviations from ideal correlation. $g_1(t)$ is the single-exponential function:

$$g_1(t) = \exp(-\Gamma t) = \exp\left(-Dq^2 t\right), \tag{3}$$

where Γ is the measured relaxation rate and D is the diffusion coefficient. From Eq. 3, the diffusion coefficient can be calculated from the relaxation rate Γ and square scattering vector q^2.

$$\Gamma = Dq^2 \tag{4}$$

The hydrodynamic radius (Stokes radius), r_h, can be evaluated from the diffusion coefficient using the Stokes–Einstein relation:

$$r_h = k_B T/6\pi\eta_0 D \tag{5}$$

where k_B is the Boltzmann constant and η_0 is viscosity coefficient of water.

Static light scattering (SLS) [16]. In SLS measurements of micellar solutions, the concentration c−cmc (g/ml) and q dependencies of $K(c-cmc)/(R_\theta - R_\theta^\circ)$, when measured at sufficiently small q, may be related as

$$\frac{K(c-cmc)}{(R_\theta - R_\theta^\circ)} = \frac{1}{M_w P(q)} + 2A_2(c-cmc), \quad (6)$$

where R_θ and R_θ° are the reduced light intensity of micellar and monomer solution, respectively, M_w is the molecular weight of micelles, and A_2 is the second virial coefficient.

Here, optical constant, K, is given by

$$K = 4\pi^2 \tilde{n}_0^2 \left(\partial \tilde{n}/\partial c\right)^2 \Big/ \left(N_A \lambda^4\right) \quad (7)$$

for polarized incident light of wavelength λ, where $\tilde{n}_0$ is the solvent refractive index, $\partial \tilde{n}/\partial c$ is the refractive index increment of solution, and N_A is Avogadro's number.

Here the particle-scattering factor, $P(q)$ is expanded in the form

$$\frac{1}{P(q)} = 1 + \frac{16\pi^2 \tilde{n}_0^2}{3\lambda^2} r_g^2 \sin^2\frac{\theta}{2} + \cdots, \quad (8)$$

where r_g is the radius of gyration of micelles.

As $c \to 0$, Eq. 6 becomes

$$\frac{K(c-cmc)}{(R_\theta - R_\theta^\circ)} = \frac{1}{M_w}\left(1 + \frac{16\pi^2 \tilde{n}_0^2}{3\lambda^2} r_g^2 \sin^2\frac{\theta}{2}\right) \quad (9)$$

Hence, the mean-square radius of gyration, r_g^2 can be evaluated from the slope of the plotting $K(c-cmc)/(R_\theta - R_\theta^\circ)$ against $\sin^2\frac{\theta}{2}$ at sufficiently small values of $r_g^2 q^2$, and the intercept values ($\theta \to 0$) give apparent molar weight of micelles ($^{ap}M_w$). Finally, the molar mass of micelles M_w at the cmc have been calculated by fitting the curves of $1/^{ap}M_w$ vs (c-cmc) by second-order least-square fit.

The specific refractive index increments of the solutions $(\partial \tilde{n}/\partial c)$ were measured using a differential refractometer (Otsuka Electronics, DRM-1020) at 298.2 K. The 20-W iodine lamp was used for the light source, the wavelength being adjusted at 532 nm using an interference filter. From the measurements, the slope of $(\partial \tilde{n}/\partial c)$ was found to be 0.037 for C8-TAC, 0.032 for C10-TAC, and 0.052 for C12-TAC.

Electrode potential measurement The measurements were made for the counterion (Cl^-) with a voltmeter (TOA-DKK, HM-30 V), where an ion selective electrode (Cl-125B) and a reference electrode were indirectly connected to the sample solutions by a 5% agar bridge with 10% NH_4NO_3. The electromotive force (ΔE) of the cell was measured after each stepwise introduction of an aliquot of the concentrated stock solutions of the surfactants into the sample solution, where the temperature was kept constant within 298.2 K± 0.1 K and the reference was 10% NH_4NO_3 solution. The Nernst equation held good for this cell over the concentration range from 10^{-5} to 10^{-1} M as far as NaCl was used as a solute, where the activity coefficient was determined by the Debye–Hückel equation [17].

Results and discussion

The fluorinated surfactants have a tendency to form aggregates with less curvature, and the aggregates are very sensitive to surfactant concentration and to the alkyl chain length [2]. To gain enough scattered light intensity, the DLS apparatus was controlled with variable 200 mW of high laser power (532-nm light source). The change of r_h for the aggregates with logarithms of the concentration at 298.2 K are illustrated in Fig. 1, where the each sample plot was measured five times and the average values are shown with standard deviations from three to five samples. The four kinds of amphiphiles formed large aggregates above the cmc, and the sizes of aggregates rapidly increased with increasing concentration over wide concentration range.

Figure 2 illustrates changes of r_h with carbon number of alkyl chain for the fluorinated amphiphiles and corresponding hydrogenated ones at 298.2 K. The former concentrations were adjusted to be 15×cmc in the aqueous solution, while the latter ones were adjusted to be 5×cmc for OTAC and 15×cmc for the other hydrogenated

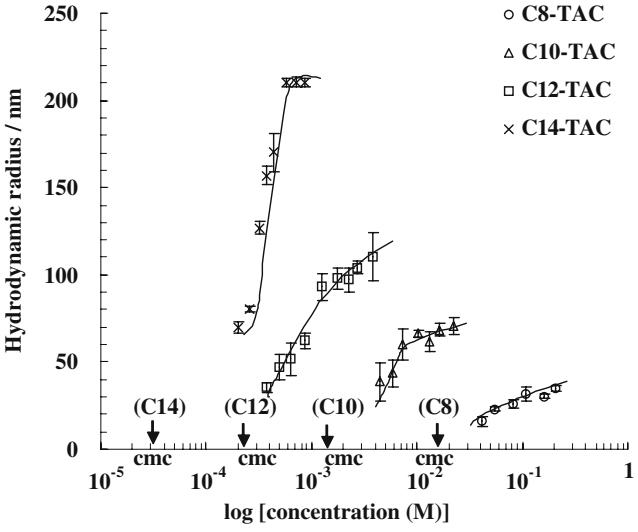

Fig. 1 Change of hydrodynamic radii (r_h) with logarithmic concentration for C8-, C10-, C12-, C14-TAC at 298.2 K. *Arrows* indicate the cmc of each amphiphiles

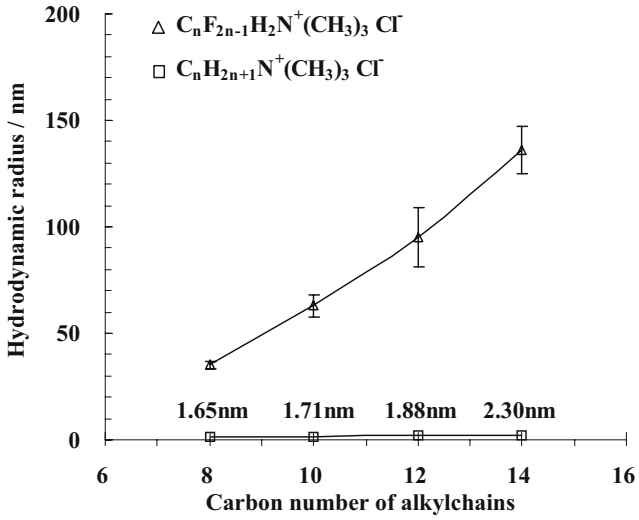

Fig. 2 Change of hydrodynamic radii (r_h) with the carbon number for *n*-alkyltrimethylammonium chlorides at 298.2 K. The concentration of the fluorinated amphiphile solutions are adjusted to be 15×cmc in the solution. Those of the hydrogenated amphiphile solutions are adjusted to be 5×cmc for OTAC and 15×cmc for the others using 1 M NaCl solution

surfactants in 1 M NaCl solution. The reason for adding NaCl into hydrogenated surfactants solution was that the size of hydrogenated micelle could not be determined in aqueous solution due to extremely small aggregation number of micelle [18, 19]. The authors dare to take this step because they want to confirm with change of numerical values. As Fig. 2 shows, the r_h values of the fluorinated surfactants drastically increased with increasing carbon number of alkyl chain, which indicates that the rigid and hydrophobic fluorocarbon chains lead to larger aggregate formation and have greater sensitivity to the chain length for the aggregate growth.

On the other hand, the hydrogenated surfactants formed small micelles of radii ranging from 1.6 to 2.3 nm with increasing alkyl chain length, although the increasing rate is quite small. In addition, according to the works by Ikeda et al., $C_nH_{2n+1}N^+(CH_3)_3Cl^-$ formed small micelles whose aggregation number was kept to be monodisperse over the wide concentration range [18, 19]. It is clear from these results that the morphological behavior of the fluorinated amphiphiles is remarkably different from those of hydrogenated ones. However, it should also be mentioned that cationic fluorinated surfactants of C_nF_{2n+1} $(CH_2)_2Pyr^+Cl^-$ (*n*:6, 8, and 10) formed spherical micelles in the aqueous solution regardless of alkyl chain length [7].

Reduced light-scattering intensity from various concentration solutions for C*n*-TAC (*n*=8, 10, 12, and 14) at 298.2 K were measured over the angle range of 45–135°. However, the data of C14-TAC could not be taken as analysis object due to extremely low scattering intensity. The plots of $K(c-cmc)/(R_\theta - R_\theta^\circ)$ vs $\sin^2(\theta/2)$ are shown in Fig. 3a C8-TAC, b C10-TAC, and c C12-TAC. According to the Eq. 9, the intercept values of vertical axis gives an apparent average molecular weight of aggregate ($^{ap}M_w$) and the slope is related with r_g [16]. The linearity for the plots roughly holds well over the measuring angle range in Fig. 3, i.e., the micellar interactions, including electrostatic and hydrodynamic ones, did not largely influence the present system. Therefore, the linear regression of Eq. 9 does apply to the present analysis for the plots directly.

Dependence of r_g values on various concentrations is summarized in Table 1, where r_h, $^{ap}M_w$, and the aggregation number (n) at the extrapolated cmc are given together. The light-scattering method is useful for large micellar aggregates or relatively high concentration due to scattering detection limit. The r_g and r_h values for C*n*-TAC (*n*=8,10, and 12) are held mostly constant at higher concentrations, showing that the micellar size and shape do not change

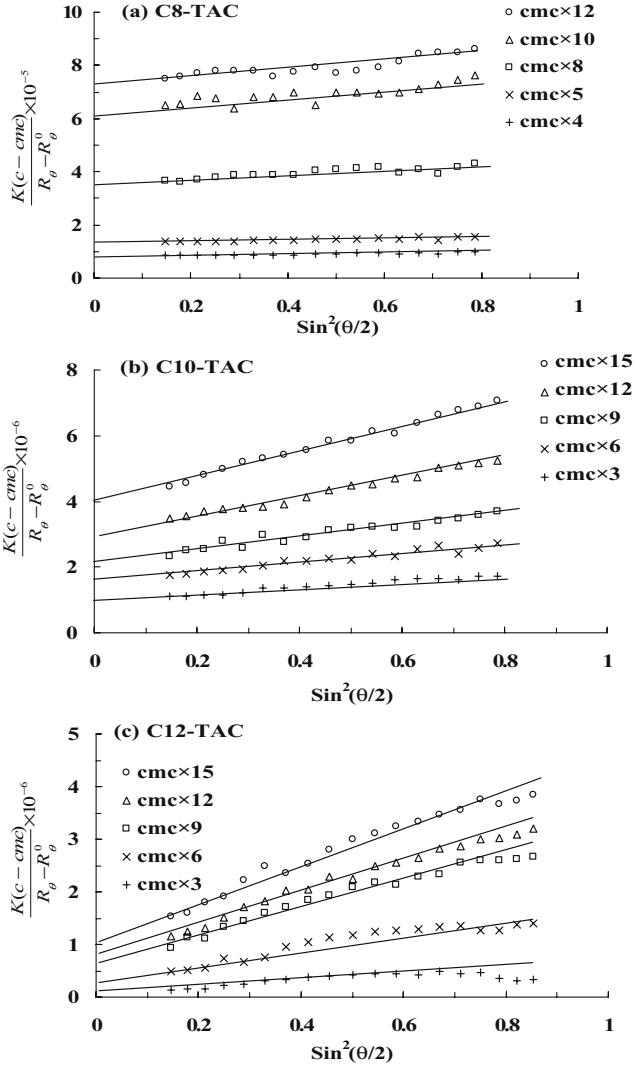

Fig. 3 Angular dependence of reduced light scattering intensity for (**a**) C8-, (**b**) C10-, and (**c**) C12-TAC solutions at 298.2 K. The plots are corresponding to Eq. 9

Table 1 Experimental data of the hydrodynamic radius (r_h) and radius of gyration (r_g), apparent micellar molecular weight ($^{ap}M_w$), aggregation number (n_{cmc}) at the cmc, and packing parameter for C8-, C10-, and C12-TAC

Amphiphiles	Concentration (mM)	r_h (nm)	r_g (nm)	$^{ap}M_w \times 10^3$	n_{cmc}	Packing parameter
C8-TAC	13.6 (cmc)			(146)	(306)	0.7
	54.4 (cmc×4)	23	35	123		
	68.0 (cmc×5)	26	33	75		
	109 (cmc×8)	32	35	28		
	136 (cmc×10)	32	34	16		
C10-TAC	1.48 (cmc)			(1,402)	(2,428)	0.8
	8.88 (cmc×6)	63	70	641		
	13.3 (cmc×9)	67	68	463		
	17.8 (cmc×10) (cmc×12)	68	72	333		
	22.2 (cmc×15)	70	73	253		
C12-TAC	0.25 (cmc)			(3,292)	(4,857)	–
	1.50 (cmc×6)	95	138	2,667		
	2.25 (cmc×9)	97	135	1,351		
	3.00 (cmc×12)	106	139	1,209		
	3.75 (cmc×15)	110	125	847		

much with the concentration. Comparing the experimental data of r_g vs r_h plots with the theoretical prediction lines based upon different shapes (Table 2), we can examine the shape of aggregates: sphere, oblate ellipsoid, prolate ellipsoid, and rigid rod [13, 14].

Several investigators have used light-scattering method and its theoretical prediction to study molecular aggregates in actual system, which has shown many useful and validity results [13–16, 20–22]. The geometrical formulas are summarized in Table 2, with accompanying essential parameter given below. The minor semi-axis b was assumed to be the C10-TAC length of the surfactant molecule from computer software (Chemical Draw), 1.9 nm, which is supposed to an extended conformation (in reality, small b value has almost no effect on theoretical curves). In the same way, the radius r was assumed to be 1.9 nm in rod model. The experimental plots of r_g/r_h and theoretical lines are shown together in Fig. 4.

The r_g and r_h values for Cn-TAC (n=8,10, and 12) are very near the theoretical line of oblate ellipsoid (disk-like), although a slight difference is observed for C12-TAC. The r_g/r_h was almost a constant value in spite of changing from low to high concentration and alkyl-chain length in the present system, which facts totally supported experimental assumption and result. The results strongly suggest that oblate ellipsoid of aggregates are formed in Cn-TAC solutions. Another theoretical approach has been used to evaluate the shape of molecular aggregates, where the approach was based upon the self-organization model by Israelachvili et al. [23].

Recently, the useful index of packing parameter of their model was applied to single-chain fluorinated amphiphiles by F. Giulieri [3], where the packing parameter was calculated to be 0.69 for C8-TAC and 0.79 for C10-TAC (Table 1) using optimal surface area per polar head[11] and other molecular geometrical information [3]. The aggregates of Cn-TAC were suggested to be disk-like, vesicular, or lamellar structure, judging from relatively larger packing parameter (0.5~1). In addition, fluorinated amphiphiles have the property that even single-chain amphiphiles can form bilayer aggregates or vesicles, although this is usually unfavorable for single-chain hydrogenated amphiphiles [8].

Table 2 Geometric equations for the hydrodynamic radius (r_h) and radius of gyration (r_g) for the typical shapes [13, 14]

Shape	r_h	r_g
Sphere	R	$\sqrt{\frac{3}{5}} \times R$
Oblate ellipsoid: (major semiaxis a, major semiaxis b)	$\frac{\sqrt{a^2-b^2}}{\arctan\left(\sqrt{a^2-b^2}/b\right)}$	$\sqrt{\frac{2a^2+b^2}{5}}$
Problate ellipsoid: (major semiaxis a, major semiaxis b)	$\frac{\sqrt{a^2-b^2}}{\ln\left[\left(a+\sqrt{a^2-b^2}\right)/b\right]}$	$\sqrt{\frac{a^2+2b^2}{5}}$
Rigid rod: (length L, radius r, and $\sigma = \ln(L/r)$)	$\frac{L}{2\sigma-0.19-\frac{8.24}{\sigma}+\frac{12}{\sigma^2}}$	$\sqrt{\frac{L^2}{12}+\frac{r^2}{2}}$

The b is supposed to be 1.9 nm in the present case.

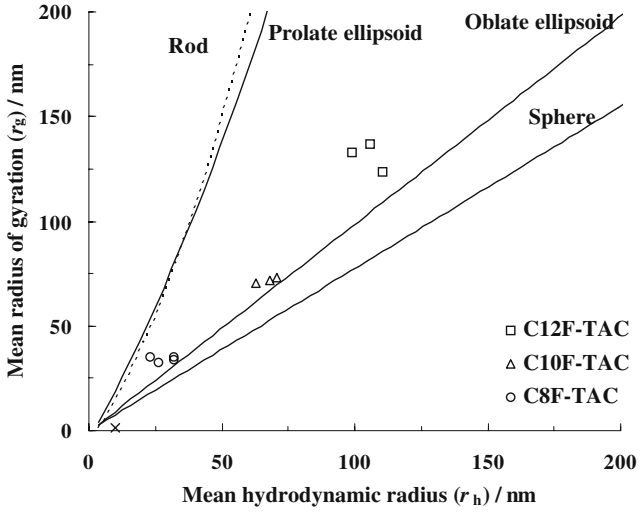

Fig. 4 Mean radii of gyration (r_g) vs corresponding mean hydrodynamic radii (r_h). The experimental data are plotted at various concentrations and the *solid lines* indicate the theoretical predictions for *sphere*, *oblate ellipsoid*, *prolate ellipsoid*, and *rigid rod*

It is common knowledge that corresponding hydrogenated amphiphile ($C_nH_{2n+1}N^+(CH_3)_3Cl^-$) forms sphere micelle with small aggregation numbers: 43.6 (n=12) [21], 62.3 (n=14) [22], and 112 (n=16) [24].

On the other hand, C8-, C10-, and C12-TAC form an oblate ellipsoid aggregate of larger aggregation number (Table 1). As a matter of course, a factor affecting the change in shape of aggregate is the potential difference between the two kinds of surfactant. A fluorocarbon chain is stiffer than a hydrocarbon chain because of the bulky fluorine atoms. Furthermore, well-balanced volume combination of head group and fluorocarbon chain leads to a cylindrical molecule, which makes the aggregates much larger.

Indeed, the present study is not perfect from the viewpoint of the presence of electrostatic interaction

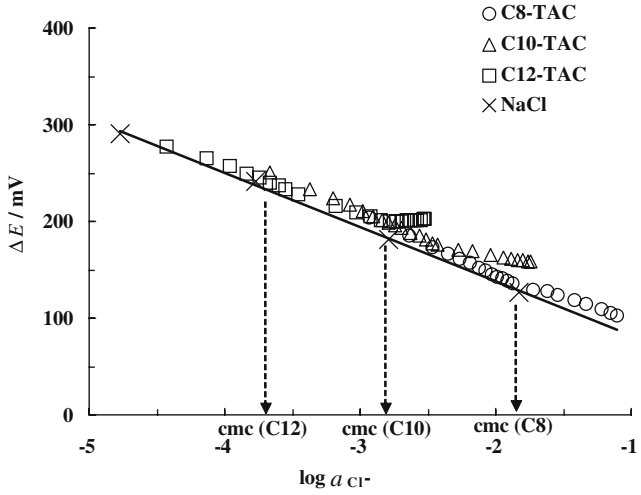

Fig. 5 Change of electrode potential (ΔE) with Cl^- activity for NaCl, C8-, C10-, C12-TAC solutions at 298.2 K. The Nernst slope for NaCl solutions was 56 mV equiv^{-1}

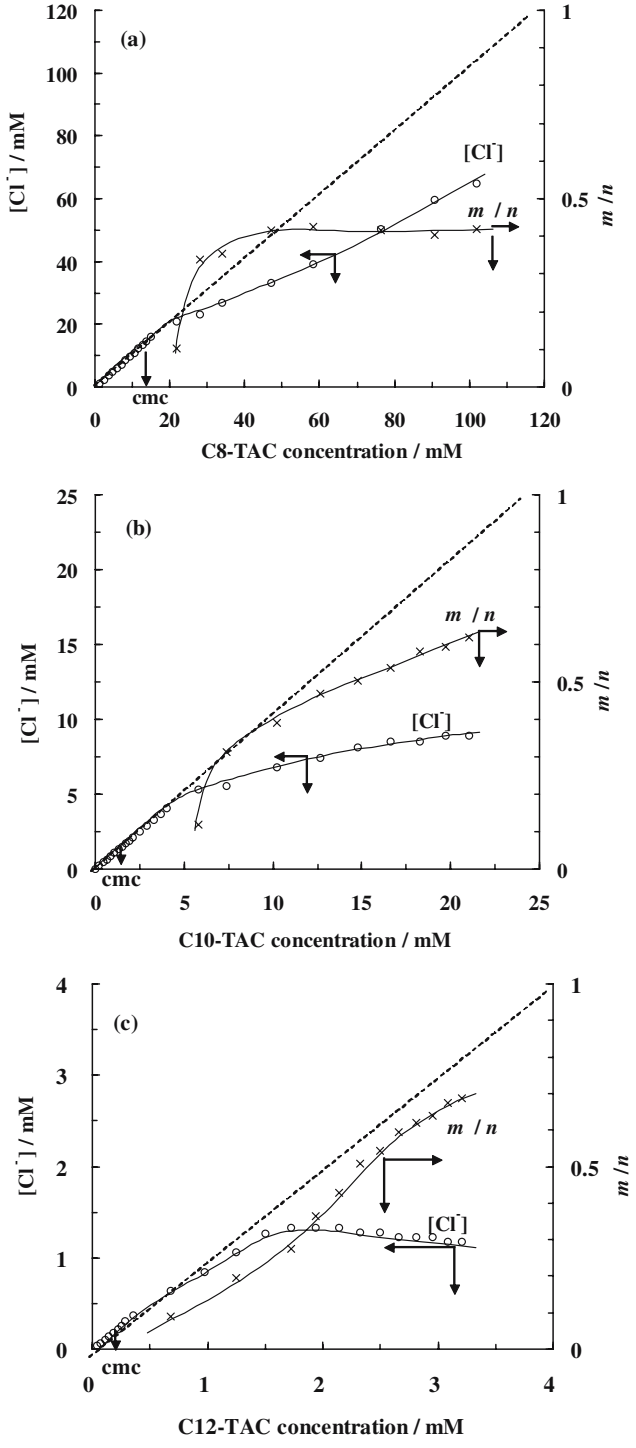

Fig. 6 Change of Cl^- concentration (*left vertical axis*) and of the degree of counterion binding to aggregates (m/n) (*right vertical axis*) with total Cn-TAC concentration at 298.2 K. The *dashed line* indicates the total concentration: (**a**) C8-, (**b**) C10-, and (**c**) C12-TAC

between charged aggregates, but the present data certainly support the main result of this paper, i.e., the aggregates are oblate ellipsoids. Any systematic work on homologous perfluorinated cationic surfactants like the present case has never been published, as far as the authors know, and therefore, the present experimental facts work quite well for further study on perfluorinated surfactants.

An electromotive force created by using an ion selective electrode is well suited for activity measurement of ionic species. The relation between electrode potential ΔE and activity of chloride ion (a_{Cl^-}) obeys the Nernst equation [17]

$$\Delta E = -\frac{RT}{F} \ln (a_{Cl^-}) + \text{constant}, \quad (10)$$

where F is the Faraday constant and the ideal slope (RT/F) is 59.2 mV equiv.$^{-1}$ at 298.2 K. The linearity was checked first by NaCl solution, and the Nernst slope was confirmed to hold well over the measurement concentration range (Fig. 5); 56 mV equiv.$^{-1}$ over detectable concentration range. Figure 5 illustrates the relationship between the electromotive force (ΔE) and the activity of chloride ion for C8-, C10-, and C12-TAC solutions, from which the Cl^- concentration is calculated from the elongated linearity of ΔE against logarithm of the activity below the cmc.

However, the Cl^- concentration could not be obtained for C14-TAC due to the cut-side detection limit at the lower concentrations. As the result, a good linearity was observed for fluorinated amphiphile solution below the cmc, and the Nernst slopes were 61 for C8-TAC, 59 for C10-TAC, and 54 mV equiv.$^{-1}$ for C12-TAC. As Fig. 5 shows, the linear relationship between the ΔE and $\ln a_{Cl^-}$ holds up to two–four times the cmc for the above solutions, and then the plots remarkably deviated from the linearity. The linearity can be used to estimate $[Cl^-]$ using a gap from linearity. The obtained $[Cl^-]$ is plotted as a function of the fluorinated amphiphiles concentration in Fig. 6a C8-TAC, b C10-TAC, and c C12-TAC.

Moreover, the degree of counterion binding to aggregates (m/n; m is the number of bound counterions per micelle, n is the aggregation number) can be given by the mass balance as:

$$m/n = (C_t - [Cl^-])/(C_t - [S^+]) = (C_t - [Cl^-])/(C_t - \text{cmc}) \quad (11)$$

The degree can be evaluated from $[Cl^-]$ and $[S^+]$ (monomer concentration) at any C_t (total concentration) [25]. Here, the monomer concentration of $[S^+]$ is assumed to be the cmc.

Now that both $[Cl^-]$ and the cmcs [10, 11] are available, the m/n values can be evaluated by using Eq. 11. As for C8-TAC, the m/n values increase with the total concentration from cmc up to three times cmc and then remain constant as ca. 0.43. On the other hand, the m/n values rapidly increase with increasing total concentration for C10-TAC and C12-TAC (Fig. 6), which contributes more to growth of their aggregates due to decrease in the electrostatic repulsion among head groups. A series of the present observations are consistent with an increase in the size of aggregation with concentration, as Fig. 1 shows.

When the present results are compared with those of the corresponding hydrogenated amphiphiles ($C_nH_{2n+1}N^+(CH_3)_3Cl^-$), the fluorinated amphiphiles have larger m/n values [26]. The m/n value for DTAC was reported to be 0.53, from fluorescence probe method. Moreover, the m/n values increase with increasing carbon number of alkyl chain in the present case. Asakawa et al. also determined the m/n values for micelles of $C_nH_{2n+1}N^+(CH_3)_3Br^-$ and cationic fluorinated surfactants of $C_nF_{2n+1}(CH_2)_2Pyr^+Cl^-$ with different alkyl chain lengths, and the values were almost equal to 1 for long alkyl chain surfactant [26]. The Cl^- bindings to head groups neutralized cationic head groups under electrostatic repulsion, consequently promoting the growth of aggregates to a certain extent.

Conclusion

Light-scattering method was applied not only to hydrogenated carbon systems but also to fluorinated ones under certain conditions. The present experimental plots r_h vs r_g were in pretty good agreement with a theoretical line, supporting oblate ellipsoid of the aggregates. The size of fluorinated amphiphiles in water was much larger than that of the corresponding hydrogenated amphiphiles. The morphological behaviors of the aggregates depend on the concentration, the carbon number of alkyl chain, and the counterion binding. In conclusion, the shape of the present fluorinated aggregates at appreciably high concentration above the cmc was found to be large oblate ellipsoid.

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