Aggregate Structure of *N*-(Perfluoroalkylmethyl)-*N*,*N*,*N*-trimethylammonium Chloride by Transmission Electron Microscopy

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The size and shape of aggregates were investigated for four fluorinated amphiphiles with different alkyl chain lengths: $C_{n-1}F_{2n-1}CH_2N^+(CH_3)_3Cl^-$ (C*n*-TAC; $n = 8$, 10, 12, and 14) by TEM. The micrographs showed that C*n*-TACs were mostly disc-like or ellipsoid-shaped lamella, which exponentially grew up their size from 10 nm (C8-TAC) to 500 nm (C14-TAC).

The unique properties and rigid structure of a fluorocarbon chain leads to aggregate formations of less curvature or elongation above cmc.[1–3] The fluorocarbon chain can make it possible even for single chain surfactants to form large aggregates in aqueous solution.[4–7] As example of effect of alkyl chain length on micellar structure, $C_nF_{2n+1}(CH_2)_2Pyr^+Cl^-$ ($n = 6$, 8, and 10) formed small globular micelles in aqueous solution regardless of alkyl chain length.[8] However, their shapes change from spherical micelles to larger thread-like or bilayer structures with increasing salt concentration. The reports on the relation with alkyl chain length and aggregate structure for fluorinated surfactants are rarely to be found in comparison to hydrocarbon surfactants. Fluorinated ionic surfactants investigated up to now have mostly been ionic ones with a chain length of less than 11 carbon atoms.[1–3] Reports of fluorinated surfactants with longer chains have been quite rare. In addition, cationic surfactants are fewer in number and variety than anionic ones primarily due to difficulties in their synthesis.[1–3] In this study, four cationic homologues of novel fluorinated surfactants were used; *N*-(perfluoroheptylmethyl)-*N*,*N*,*N*-trimethylammonium chloride (C8-TAC), *N*-(perfluorononylmethyl)-*N*,*N*,*N*-trimethylammonium chloride (C10-TAC), *N*-(perfluoroundecylmethyl)-*N*,*N*,*N*-trimethylammonium chloride (C12-TAC), and *N*-(perfluorotridecylmethyl)-*N*,*N*,*N*-trimethylammonium chloride (C14-TAC). The surface tension,[9] cmc,[9,10] and thermodynamic analysis[11] for these surfactants were reported in the previous papers. Moreover, the shape of the present fluorinated aggregates was found to be a large oblate ellipsoid by a combination of light scattering and theoretical predictions.[7]

In the present study, the authors attempted to visualize the micellar size and shape of the above four-fluorinated amphiphiles using the transmission electron microscopy (TEM) method. This systematic study of different fluorinated alkyl chains will be helpful for further studies on the fluorinated surfactants.

The plots of hydrodynamic radius vs gyration one for the present fluorinated surfactants were in pretty good agreement with a geometrical prospective line for micellar structure,[12] supporting oblate ellipsoid of the aggregates in our previous report.[7] The micellar diameters were 60, 126, 190, and 272 nm for C8, C10, C12, and C14 of the alkyl chain, respectively, at a concentration of 15 × cmc (298.2 K).[7] The fluorinated surfactant concentrations have little influence on the micellar size over the several times of cmc.[7] Therefore, their concentrations were adjusted to fit the experimental conditions for the TEM observations, but within the above range. The TEM images for the fluorinated surfactant solutions are shown in Fig. 1 (a) C8-, (b) C10-, (c) C12-, and (d) C14-TAC.

C8-TAC aggregates at a 54.4 mM surfactant concentration (cmc × 5) are shown in Fig. 1a. The aggregates are formed in a poly-disperse state, which can be clearly classified into two groups according to their size. The diameter of the relatively larger aggregates is approximately 10–30 nm and that of the small ones is less than ca. 5 nm. The light scattering method shows that the C8-TAC aggregates had an angular dependence on the measurement angles and poly disperse state with including a distribution of small aggregates (ca. 2 nm) at 298.2 K,[10] as described in a previous paper.[7] Judging from the relatively larger diameters in Fig. 1, it seems reasonable to assume that the large aggregates are disc-shaped of lamellas, because the diameters are too large to assume a spherical structure. On the other hand, spherical micelles constitute a majority of the solution, and the few spherical micelles form string-like geometrical arrays in Fig. 1a. It is quite unusual for a single component surfactant to exist clearly with two different sizes in an aqueous solution. In addition, a few reports on fluorinated surfactant systems have been shown to coexistence of different aggregates in using TEM method.[13,14]

C10-TAC forms two types of aggregates at 13.3 mM (cmc × 9); as shown in Fig. 1b. The white color of the ellipsoid indicates extremely large disc-shaped lamellas, whose diameters are less than approximately 30 nm. On the other hand, a characteristic contour is seen in the micrograph, which is unilamellar vesicle with hydrodynamic diameter of approximately 100 nm. There is a possibility that the vesicles involve water phase inside them, as indicated by the black area of the circle. The diameters and geometrical structures in the TEM observations are consistent the predictions from the light scattering data, as previously discussed.[7] Moreover, the packing parameter was calculated to be 0.79 for C10-TAC, which suggested a

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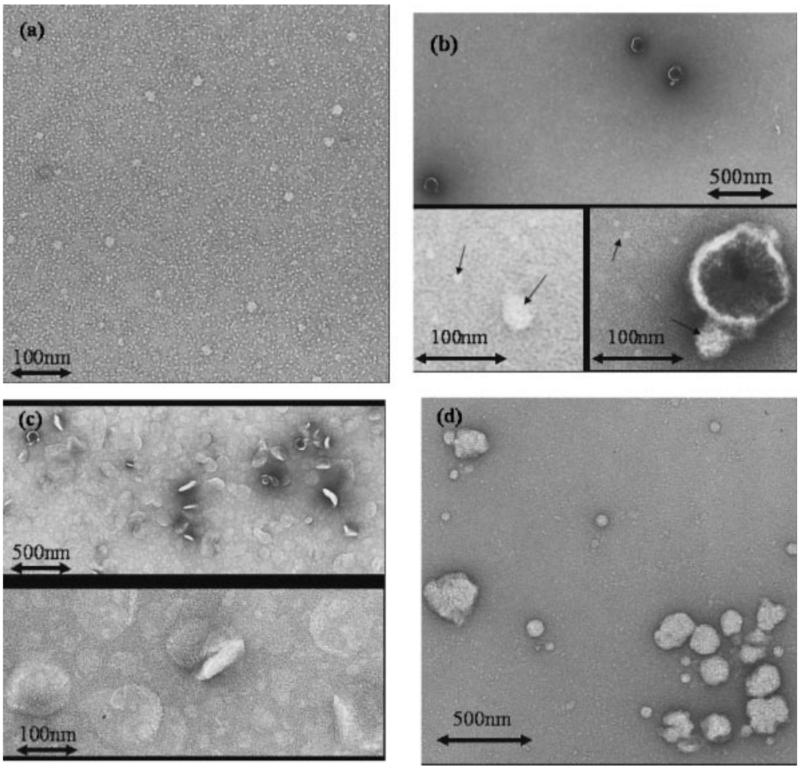

Fig. 1. TEM image of C*n*-TAC aggregates: (a) C8-TAC at 54.4 mM, (b) C10-TAC at 13.3 mM, (c) C12-TAC at 2.25 mM, and (d) C14-TAC at 0.87 mM. The arrows in (b) micrograph indicate the ellipsoidal aggregates.

vesicle or lamellar structure.[7]

C12-TAC solution was adjusted to 2.25 mM (cmc × 9) for TEM observations. The aggregates of C12-TAC are of a typical oblate ellipsoidal shape as shown in the micrograph of Fig. 1c. Moreover, a few unilamellar vesicles with closed bilayer aggregates were rarely observed in Fig. 1c, which was also observed for the C10-TAC solution (Fig. 1b). Recent research shows that a similar partial fluorinated surfactant $C_8F_{17}C_4H_8N^+(CH_3)_3Br^-$ forms narrow ribbons (4 nm × 3 nm) with a relatively narrow width; further, it has networks of multi-connected micelles in salt-free solutions as well as in the presence of salts, at a surfactant concentration of 24.4 mM (ca. cmc × 25), according to a TEM micrograph.[5] In this study, the molecular differences between $C_{11}F_{23}CH_2N^+(CH_3)_3Cl^-$ and $C_8F_{17}C_4H_8N^+(CH_3)_3Br^-$ are the number of fluorines and the types of halogen counter ions; additionally, the former has a cmc of 0.25 mM[10] whereas the latter has a cmc in the range of 0.8–1.3 mM[15] at 298.2 K. The larger aggregates of $C_{11}F_{23}CH_2N^+(CH_3)_3Cl^-$ mainly originated from their rigid and non-flexible molecular structures. This result indicates that the rigid and the hydrophobic fluorocarbon chains lead to larger aggregate formations.

C14-TAC solution is a clear transparent at 0.87 mM (cmc × 30). According to the previous paper, the aggregates maintained their hydrodynamic diameters above cmc × 20.[7] The C14-TAC forms extremely large aggregates that grow over 500 nm in diameter as observed in the TEM image (Fig. 1d). It is reasonable for a large distorted circle or a bumpy contour shape to be a stacking lamellar structure, by judging from coexistence of large and small units of the aggregates.

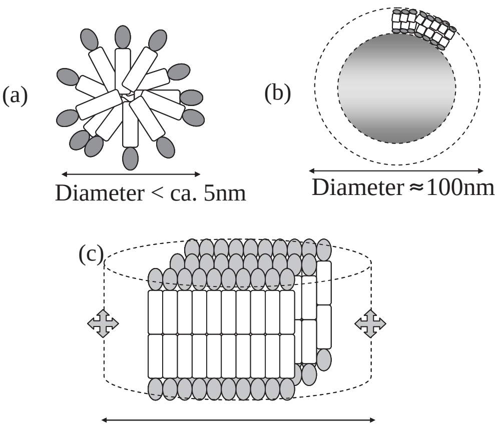

Fig. 2. Schematic structure of C*n*-TAC aggregates from TEM micrographs: (a) spherical micelle, (b) unilamellar vesicle, and (c) oblate ellipsoidal lamella. The size diameters are approximately estimated from their micrographs.

From the above TEM analysis, we can draw the following image structures for the C*n*-TAC solutions. Many circular small spots shown in Fig. 1a correspond to the normal spherical micelles (Fig. 2a), which are observed mainly for the C8- and C10-TAC solutions. Moreover, a few number of unilamellar structures with a diameter of 100 nm (Fig. 1b) are shown in the micrographs of C10- and C12-TAC. The aggregates involving water had a characteristic structure (Fig. 2b), but their existence was rare in the total distribution. The four fluorinated surfactants mainly formed disc or oblate ellipsoidal shapes, which were composed of large and small stacking lamellar aggregates (shown in Fig. 2c). The cause of poly-disepersity in size originated from the stacking of several lamellar aggregates. The lamella block parts may be suitable to build and release from the macroscopic structures. The combinations of the small and large aggregates (i.e., two distributions) may work for the advantage of decreasing total energy of the aggregates in the present fluorinated surfactant systems. On the other hand, the fluorinated surfactants of $C_nF_{2n+1}(CH_2)_2Pyr^+Cl^-$ ($n = 6$, 8, and 10) formed spherical micelles in a dilute aqueous solution regardless of the alkyl chain lengths.[8] Moreover, $C_8F_{17}SO_3Li$ formed large number of uniform spherical micelles (ca. 3–4 nm). It is quite a rare case for a single chain and a single component surfactant to form large aggregates of different size in salt-free solutions.

The size of the C*n*-TAC aggregates drastically increased with increasing carbon number in the alkyl chain. On the other hand, the hydrogenated surfactants of $C_nH_{2n+1}N^+(CH_3)_3Cl^-$ ($n = 8$, 10, 12, and 14) formed smaller micelles having a radii ranging from 1.6 to 2.3 nm with an increasing alkyl chain length. They formed smaller micelles whose aggregation number maintained as mono-disperse over wide range of concentrations.[16,17] It is clear from the above results that the morphological behavior of the fluorinated amphiphiles is remarkably different from that of hydrogenated ones.

Experimental

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.[9,10] The fluorinated surfactants were purified by repeated recrystallizations from several mixed solvents as described previously.[10] The purities were checked by elemental analysis and NMR measurements. The observed and calculated values (in parentheses) for the elemental analysis were in sufficient agreement within experimental errors in weight percentage: C 27.32 (27.66), H 2.32 (2.34), and N 3.01 (2.93) for C8-TAC; C 26.93 (27.03), H 1.96 (1.92), and N 2.35 (2.42) for C10-TAC; C 26.68 (26.59), H 1.64 (1.64), and N 1.95 (2.07) for C12-TAC; and C 26.35 (26.26), H 1.43 (1.43), and N 1.72 (1.80) for C14-TAC. No impurity peaks were observed in the NMR spectra of the above amphiphiles. The water used for preparation of all the aqueous solutions was distilled once from ion-exchange treatment water. The solution was agitated by a magnetic stirrer and incubated above 338 K for more than one day. The time duration for the aggregation equilibrium can be reduced by this operation.[10]

TEM observation; a droplet of the surfactant solution was placed on a carbon-firm grid for two minutes. The excess liquid was removed by touching one end of the grid with a filter paper. After the grid was partially dried, a drop of a staining solution (2% uranyl acetate) was placed on the grid for two minutes. The excess liquid was removed by a filter paper and the grid was dried at room temperature. All micrographs were taken by the JEOL JEM-1200EX operated at 100 kV.

The TEM work was performed at the "Hanaichi Ultrastructure Research Institute" in Okazaki (Japan).

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