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M. Matsumoto
C. E. McNamee
D. P. Bossev
M. Nakahara
T. Ogawa

Structure of salted-out, solubilized micelles and microemulsions on the perfluorinated anionic surfactant tetraethylammonium perfluorooctyl sulfonate studied by cryogenic transmission electron microscopy

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M. Matsumoto · C. E. McNamee
D. P. Bossev · M. Nakahara · T. Ogawa
Institute for Chemical Research
Kyoto University
Uji, Kyoto 611-0011, Japan
e-mail: matsumoto@scl.kyoto-u.ac.jp
Tel.: 81-774-383072
Fax: 81-774-383014

Abstract Tetraethylammonium perfluorooctyl sulfonate (TEAFOS; critical micelle concentration, 1 mM), which forms a threadlike micelle in its pure solution, was adopted to study the structure of salted-out, solubilized micelles and microemulsions by cryogenic transmission electron microscopy. The concentration of the surfactant was kept constant at 60 mM. The micelle solution salted out with $LiNO_3$ provided a surfactant phase in the presence of a clear interface. The surfactant phase was studded, being formed of homogeneously dispersed spherical micelles, and had no obvious threadlike forms. The micelles, which solubilized the maximum amount of perfluorinated oil, were spherical and had the same size as isolated spherical micelles in pure TEAFOS solution. The microemulsions were formed in the presence of perfluorinated alcohol as cosurfactant and the particles were rotund even when the concentration of the perfluorinated oil was equivalent to that for solubilization and the sizes increased with increasing oil content. The difference in size between the solubilized micelles and microemulsions with the same amount of oil suggested that the oil molecules had been solubilized between palisades of perfluorinated alkyl chains in the micelles and had dissolved in the cores of the microemulsions.

Key words Perfluorinated anionic surfactant · Cryogenic transmission electron microscopy · Micelle · Solubilization · Microemulsion

Introduction

A great interest in perfluorinated anionic micelles is because of the structural changes affected by their concentration, temperature, the species of the counterions, supporting electrolytes, and cosurfactants or solubilizates.

The micellization of perfluorinated anionic surfactant molecules in water, similar to the case of nonfluorinated anionic surfactants, is entropy-driven by configuration changes of ordered–disordered water molecules around their hydrophobic parts. This positive entropy change acts as a driving force to decrease and minimize the free energy at equilibrium [1]. The configuration changes to disordered–ordered water molecules are induced by hydrophobic counterions bound to hydrophilic surfaces of the micelles of perfluorinated anionic surfactants. The negative entropy change, which increases the free energy, entails the rearrangement of the micelle structure to decrease the overall areas of the micelle surfaces exposed to water. A typical example of such a negative entropy change is tetraethylammonium perfluorooctyl sulfonate (TEAFOS). This surfactant assembles threadlike micelles consisting of strings of beads and is a good contrast to the no-thread-forming surfactant of lithium FOS, which has a hydrophilic counterion [2, 3]. In nonfluorinated cationic surfactants the spherical micelles are also transformed into single-thread micelles and vesicles by a few different types of hydrophobic counterions [4–9].

TEAFOS is a thermally and chemically stable surfactant.[1] The severe solutions of acid and base as supporting electrolytes permit the formation of TEAFOS micelles at very low and high pH [10].

Perfluorinated surfactant micelles solubilize perfluorinated oils, and the solubilized solution is optically isotropic and transparent. Most studies of solubilization have been performed using ternary phase diagrams, but the general rules for the loci of solubilizates and the mechanisms of solubilization are still open issues because of many pertinent parameters such as types, concentrations, the hydrophile–lipophile balance (HLB) of surfactants, salts, pH, and so forth. Hydrophobic counterions are also favorable for oil solubilization in the case of perfluorinated anionic surfactants [11].

Another prominent application of perfluorinated surfactants is microemulsification. Several classes of perfluorinated surfactants permitted the formation of oil-in-water [12–14], water-in-oil [13–15], and oil-in-oil [16] types of microemulsions. Partially fluorinated oligomeric and polymeric lipophiles greatly lowered the interfacial tensions at perfluoropolyether–nonfluorinated oil interfaces. These lipophiles provided the formation of oil-in-oil types of sterically stabilized macroemulsions [17].

Cryogenic transmission electron microscopy (cryo-TEM) is a rather new and powerful technique for structural studies of perfluorinated surfactant micelles, in addition to ordinary methods such as small-angle neutron scattering and birefringence. This method images two-dimensional projections of a specimen and visualizes the shape and size of micelles, whereby the sample is kept in its native state in solution by thermal fixation. The thermal fixation is achieved by plunging a thin liquid film of the sample solution on a microgrid into liquid ethane or propane to cool it fast enough to prevent rearrangement of water molecules into a crystalline form [18]. Another great advantage of cryo-TEM is the low specimen temperature during image recording with an electron microscope. This is connected to a degree of damage to the specimen being inevitable through electron irradiation. The irradiation damage at liquid nitrogen temperatures is reduced to one-quarter compared to the damage at room temperature. At liquid helium temperatures the irradiation damage becomes 1/20 [19]. Such ultralow specimen damage allowed the electron crystallographic reconstruction of major surface amino acid residues of a membrane protein in three dimensions with a resolution of 0.3 nm [20] and the visualization of biosurfactant micelles [21].

To our knowledge, cryo-TEM studies of micelle systems have approached about 100 publications in total; however, most studies have been devoted to a homologous series of non-fluorinated cationic surfactants with different counterions and salt concentration, of nonionic surfactants, and amphiphilic polymers. Regarding cryo-TEM studies of perfluorinated anionic surfactant micelles, we find a rudimentary examination [2].

The important feature of TEAFOS is that the solution viscosity depends on the species of counterion even when a salt is included as a supporting electrolyte in solution. In addition, there are no direct studies of the structure of salted-out, solubilized micelles and microemulsions of TEAFOS by cryo-TEM that are the aims of the present paper.

Materials and methods

TEAFOS [$C_8F_{17}SO_3N(C_2H_5)_4$, 98% purity] was purchased from Aldrich, 1H,1H-perfluoro-1-nonanol [$CF_3(CF_2)_7CH_2OH$, 98% purity], perfluoro-1-methyldecalin [PFMD; $C_{11}F_{20}$, 85% purity] from PCR, and lithium nitrate ($LiNO_3$, 99% purity) were from Fluka. All the chemicals were used without further purification. In all the experiments doubly distilled water that was passed through reverse osmosis membranes and ion-exchange resins was used.

The solubilization of PFMD, which is insoluble in water, into TEAFOS micelles was performed by a batch method; a given weight of PFMD was mixed with 25 g of a solution containing TEAFOS and the mixture was shaken by hand. The solubilization process was rather slow and took several weeks at room temperature.

Microemulsions of TEAFOS with PFMD were obtained in the presence of the cosurfactant perfluorinated alcohol. The size of the surfactant solution was 25 g constant, which included an additional size of PFMD. Several types of perfluorinated alcohol were examined with a different chain length of perfluorinated carbon: 1H,1H-perfluoro-1-butanol [$CF_3(CF)_2CH_2OH$, 97% purity], 1H,1H-perfuoro-1-heptanol [$CF_3(CF_2)_5CH_2OH$, 97% purity], 1H,1H-perfluoro-1-octanol [$CF_3(CF_2)_6CH_2OH$, 97% purity], 1H,1H-perfluoro-1-nonanol [$CF_3(CF_2)_7CH_2OH$, 98% purity], 1H,1H-perfluoro-1-decanol [$CF_3(CF_2)_8CH_2OH$, 98% purity] from PCR. The most effective alcohol as a cosurfactant was 1H,1H-perfluoro-1-nonanol. It was soluble in PFMD, but not in water, and permitted the formation of a microemulsion with gentle shaking by hand over a concentration range from 4 to 10 wt% in PFMD. In all the experiments the concentration of TEAFOS (critical micelle concentration, cmc, 1 mM) was kept constant at 60 mM. TEAFOS had its highest solution viscosity in pure solution.

The relative solution viscosity at room temperature was measured using an Ostwald type of capillary viscometer.

The surface tension of pure TEAFOS solution was measured by a Wilhelmy glass-plate method. The interfacial tensions at the interfaces of TEAFOS micelle–PFMD solutions were measured by the spinning-drop and drop-volume methods.

To identify the solubility of the cosurfactant 1H,1H-perfluoro-1-nonanol in the micelles and microemulsions, the proton chemical shifts of the methylene group from the cosurfactant were measured in D_2O using a multipurpose Fourier transform NMR spectrometer (JEOL, EX-279, wide-bore type, 6.35T) at 30 °C. The chemical shifts of the proton peaks were fixed relative to the external reference of sodium trimethylsilyl propanesulfonate, which is soluble in D_2O.

A few microliters of a sample solution was placed on a microgrid covered with a holey carbon film prior to the cryo-TEM observations. A pair of tweezers held the microgrid, and excess solution, which penetrated into the holes of the carbon film,

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[1] In ^1H NMR and ^{19}F NMR studies there is no decomposition of TEA counterions and FOS anions in D_2O till 250 and 300 °C.

was blotted from both sides of the grid to thin the sample solution. Then, the specimen grid was immediately plunged into a liquid ethane container maintained at about 100 K in a compartment cooled to the temperature of liquid nitrogen using a Reichert-Jung KF-80 cryofixation apparatus. It was subsequently placed in the compartment (liquid nitrogen temperature) of a specially designed cryogenic transfer system [22] attached to a cryogenic transmission electron microscope (JEM 4000SFX). This microscope had an acceleration voltage of 400 kV with an apparent resolution of 0.25 nm. A specimen holder containing the microgrid was transferred to a specimen stage with a top entry system in the cryogenic transmission electron microscope, where the temperature was around 4.5 K. The microgrid transfer led to the elevation of the specimen stage. It was recooled to 4.5 K by providing a superfluid state of liquid helium to the stage. The details of the procedure have been described elsewhere [19, 22]. The images of pure, salted-out, solubilized micelles and microemulsions were recorded at a direct magnification of 30000–50000× and over a temperature range from 4.5 to 9 K with defocus values of 2–4 μm to enhance image contrast. The calculation of a contrast transfer function at the defocus values and acceleration voltage permitted an image resolution limit of about 1 nm. The sizes of the spherical micelles given in the text were taken as an average of distributions of about 100 sample particles.

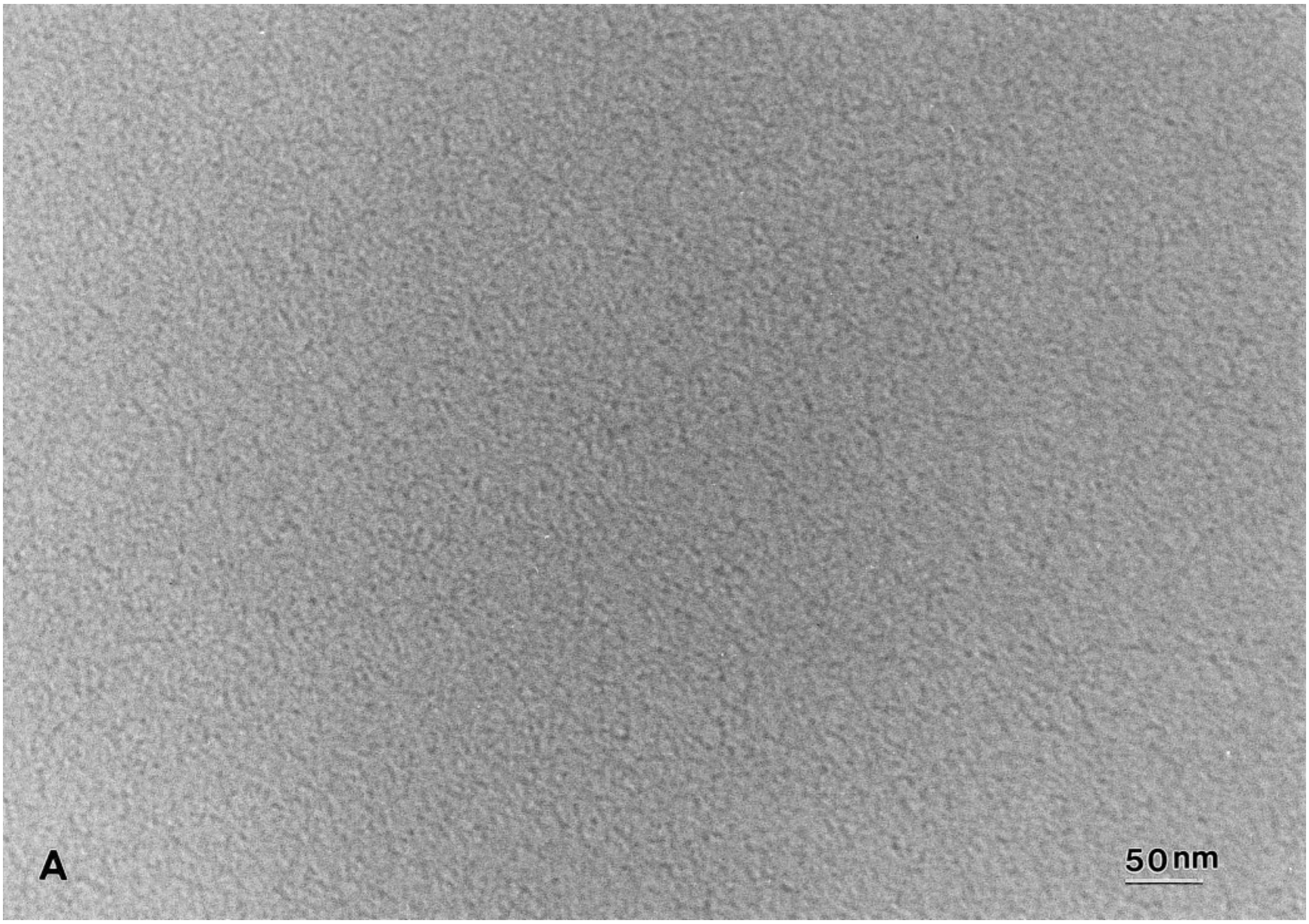
To minimize the electron irradiation dose to the specimen plane for image recording, a new specimen plane was used by shifting the specimen position irradiated with the electron beams for image focusing (minimum dose system). The total electron dose applied to the specimen for image recording was less than 10 electrons/Å^2.

Results and discussion

Transformation of threadlike micelles into spherical micelles of TEAFOS with $LiNO_3$

The TEAFOS micelles form threadlike structures in water, and the micelle solutions have very high viscosities because of network formation [2, 3]. The fine structure of the threadlike micelles is different from a single-thread structure, such as for cetyltrimethylammonium or cetylpyridinium micelles with hydrophobic counterions [4–9], and a string composed of spherical micelles as a basic unit that was confirmed by a high magnification

Fig. 1A, B Cryogenic transmission electron microscopy (*cryo-TEM*) images of tetraethylammonium perfluorooctyl sulfonate (*TEAFOS*) micelles in the absence and presence of $LiNO_3$. The concentration of TEAFOS was kept constant at 60 mM in different concentrations of $LiNO_3$. At 50 mM $LiNO_3$ the surfactant solution separated into two phases with a clear interface. **A** Networks constructed with strings of beads (threadlike micelles) without $LiNO_3$; **B-1** and **B-2**, *upper* and *lower phase images* of TEAFOS micelle solutions at 50 mM $LiNO_3$. The upper phase includes no micelles. The lower phase involves no well-evolved networks constructed with strings of beads and isolated spherical micelles (*arrows*)



cryogenic image [3]. A similar structure has been reported for cationic polyamphiphiles studied by cryo-TEM [23, 24]. This fine structure resembles positively charged alumina and zirconia particles coagulated with hydrophobic IO_3^- and BrO_3^- (structure maker) counterions to form networks, which give rise to high solution viscosities [25]. Cetyltrimethylammonium surfactants, however, form spherical micelles when the counterions are hydrophilic, such as bromide. The same occurs with FOS micelles when the counterion is hydrophilic lithium, and no increase in solution viscosity is found [2]. The mixed micelle solutions of tetraethylammonium and lithium FOS at an overall constant concentration reveal high or low solution viscosity depending on their mixing ratios, which suggests the structural transformation of the micelles [26]. The structural transformation of threadlike micelles of TEAFOS may be obtained in the presence $LiNO_3$ as a supporting electrolyte.

When the TEAFOS micelle solution contains $LiNO_3$ as a supporting electrolyte, the solution viscosity decreases with increasing $LiNO_3$ concentrations at a constant concentration of TEAFOS. The relative viscosity of pure TEAFOS at 60 mM was about 7×10^4 times higher than the viscosity of water at 22 °C and decreased by 14, 50, and 65% in the presence of 1, 10, and 30 mM $LiNO_3$, respectively. At 50 mM $LiNO_3$ the TEAFOS solution separated into two phases and showed a clear interface. The upper and lower phases were optically transparent and translucent, respectively. The upper phase had a viscosity similar to that of water, while the lower phase, which was salted out, had a viscosity 65% of that of the pure TEAFOS solution.

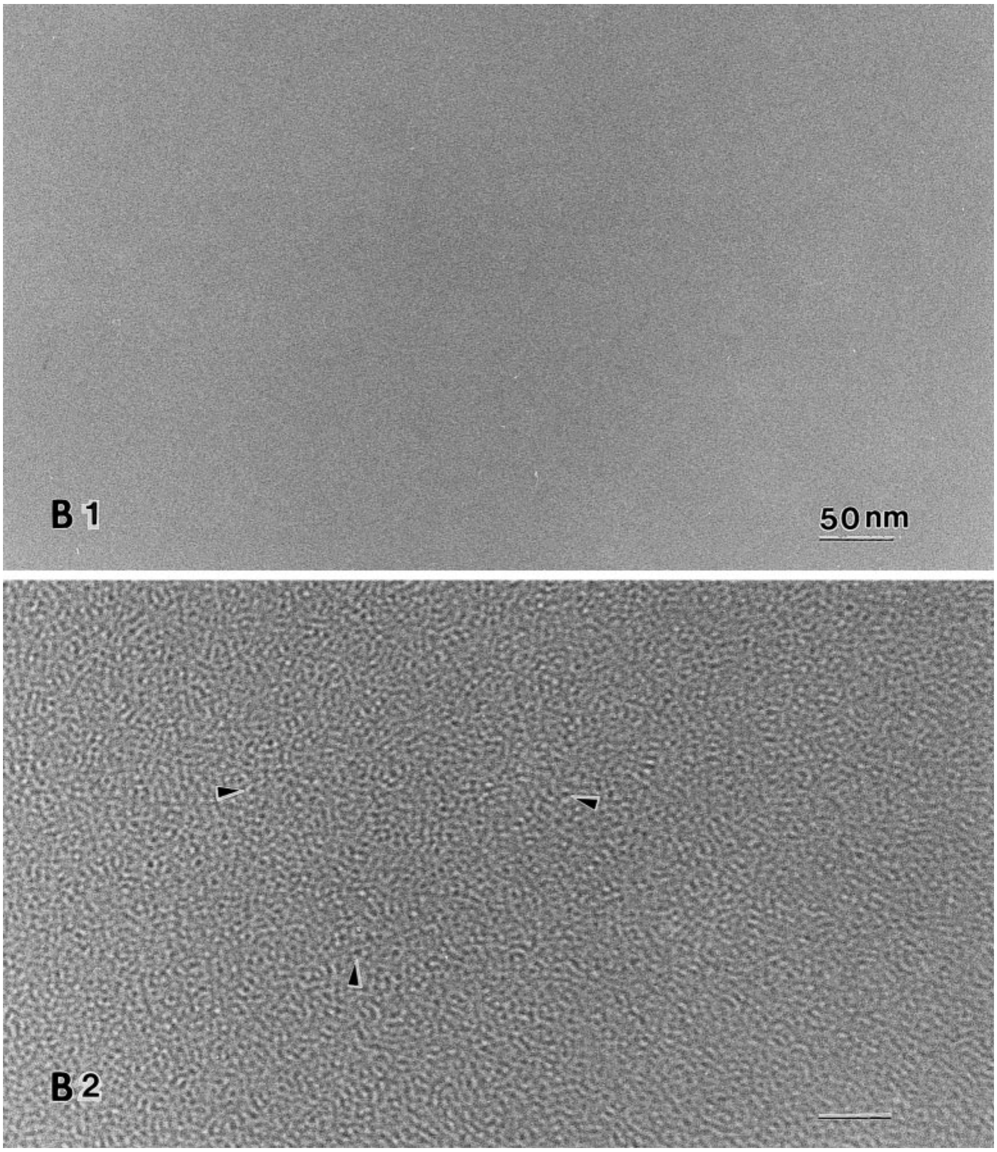


Fig. 1 (*Contd.*)

Images of TEAFOS micelles with no $LiNO_3$ and 50 mM $LiNO_3$ are shown in Fig. 1. In Fig. 1A the pure TEAFOS micelles have networks constructed with strings of beads (threadlike micelles) and isolated spherical ones, where the threadlike micelles are in equilibrium with isolated particles. The threadlike and isolated spherical micelles have widths and diameters of 4 ± 1 nm. At $LiNO_3$ concentrations of 1, 10, and 30 mM, no obvious structural or size changes were observed, even though the solution viscosity decreased. At 50 mM $LiNO_3$ the upper phase was imaged without the appearance of micelles (Fig. 1B1), while the lower phase was imaged with densely dispersed spherical micelles without obvious network formation (Fig. 1B2).

The aggregation number of ionic micelles tends to increase with added salt concentration in general; however, the aggregation number in the presence and absence of salts has little effect when the univalent salt concentration is varied up to 100 mM [27]. The sizes of the micelles at 50 mM $LiNO_3$ in Fig. 1B2 were 4 ± 1 nm, similar to those of pure TEAFOS systems, which reflected the minor influence of the salt.

According to the adsorption experiments of tetraalkylammonium ions onto a dropping mercury electrode at different surface charges, the ions strongly adsorb and act in a similar way to nonionic organic materials [28]. In fact, the TEA ions drastically depress the interfacial tension of mercury to give a zero value at a high polarization and they emulsify spontaneously [29].

TEA ions rather than lithium ions tend to bind competitively strongly to the surfaces of FOS micelles when TEAFOS and lithium FOS micelles are mixed [26]. The binding fraction of TEA counterions studied using the ^1H chemical shifts, which provide direct information on counterion binding onto the micellized FOS head groups, is 0.5 at a concentration of 100 mM of pure TEAFOS. This corresponds to the half neutralization of negatively charged FOS micelles at the Stern layer. The same binding fraction of the TEA ions is maintained even when the mixing ratio of lithium FOS was increased to 0.5 at an overall concentration of

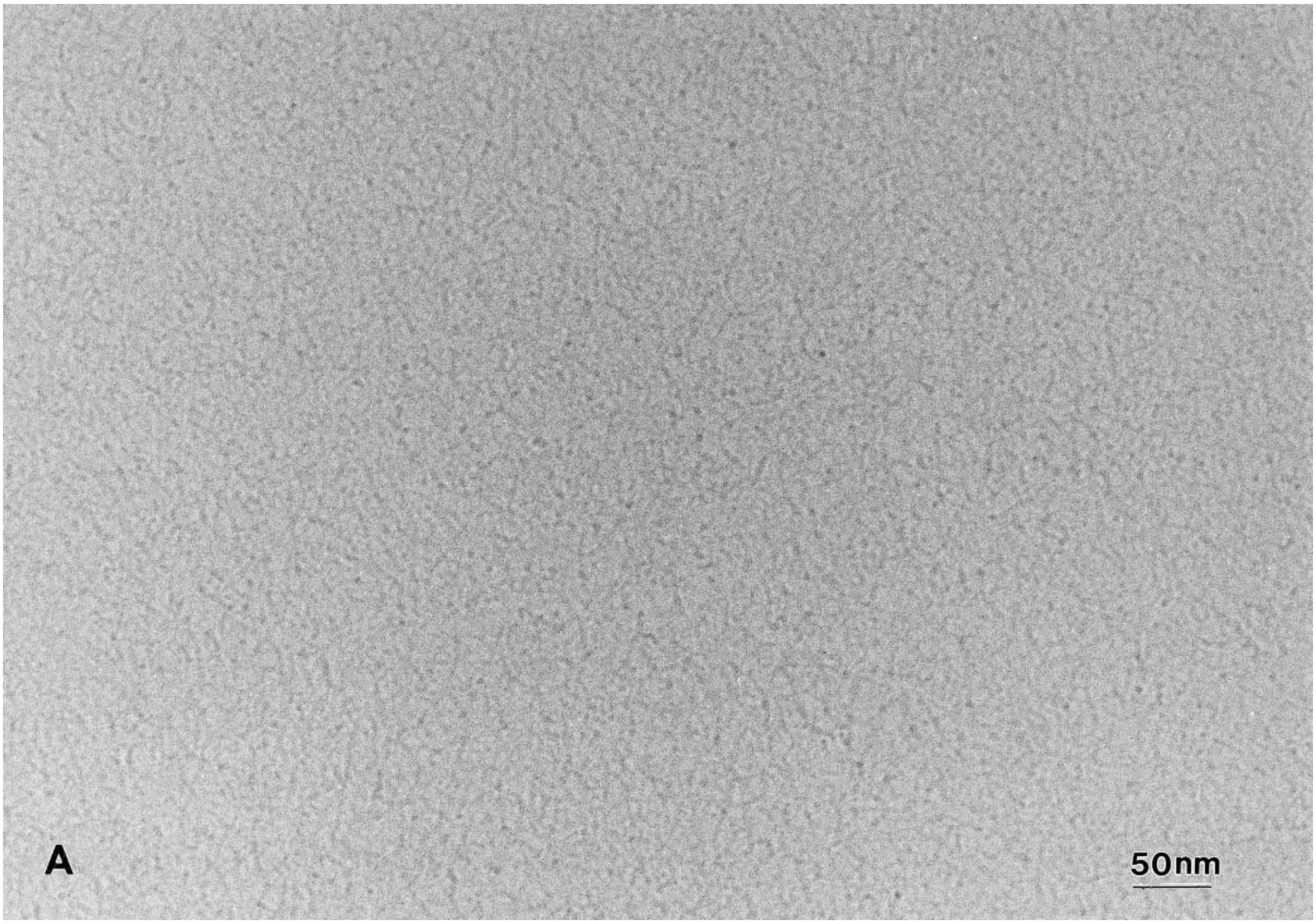


Fig. 2 Cryo-TEM images of TEAFOS micelles that solubilized perfluoro-1-methyldecalin (*PFMD*): **A** 0.2 wt% PFMD; **B** 1 wt% PFMD (maximum solubilization at room temperature). No obvious density changes of threadlike micelles are found between Figs. 1A (pure TEAFOS micelles) and 2A, but an obvious change from a threadlike form to a spherical form is seen between Figs. 1A and 2B

100 mM. A further increase in the lithium FOS mixing ratio gives rise to the participation of binding of lithium ions to the micelle surfaces. Hence, it is considered that the preferential, strong binding of the hydrophobic TEA ions to the FOS micelle surfaces is essential for the formation of threadlike micelles by hydrophobic attraction.

The decrease in the micelle solution viscosities of TEAFOS at the increased concentrations of $LiNO_3$ may be attributed to the insufficient evolution of threads and the increased density of isolated spherical micelles; the hydrophilic lithium ions weaken the hydrophobic attraction between FOS spherical micelles owing to hydrophobic TEA ions in the double layer.

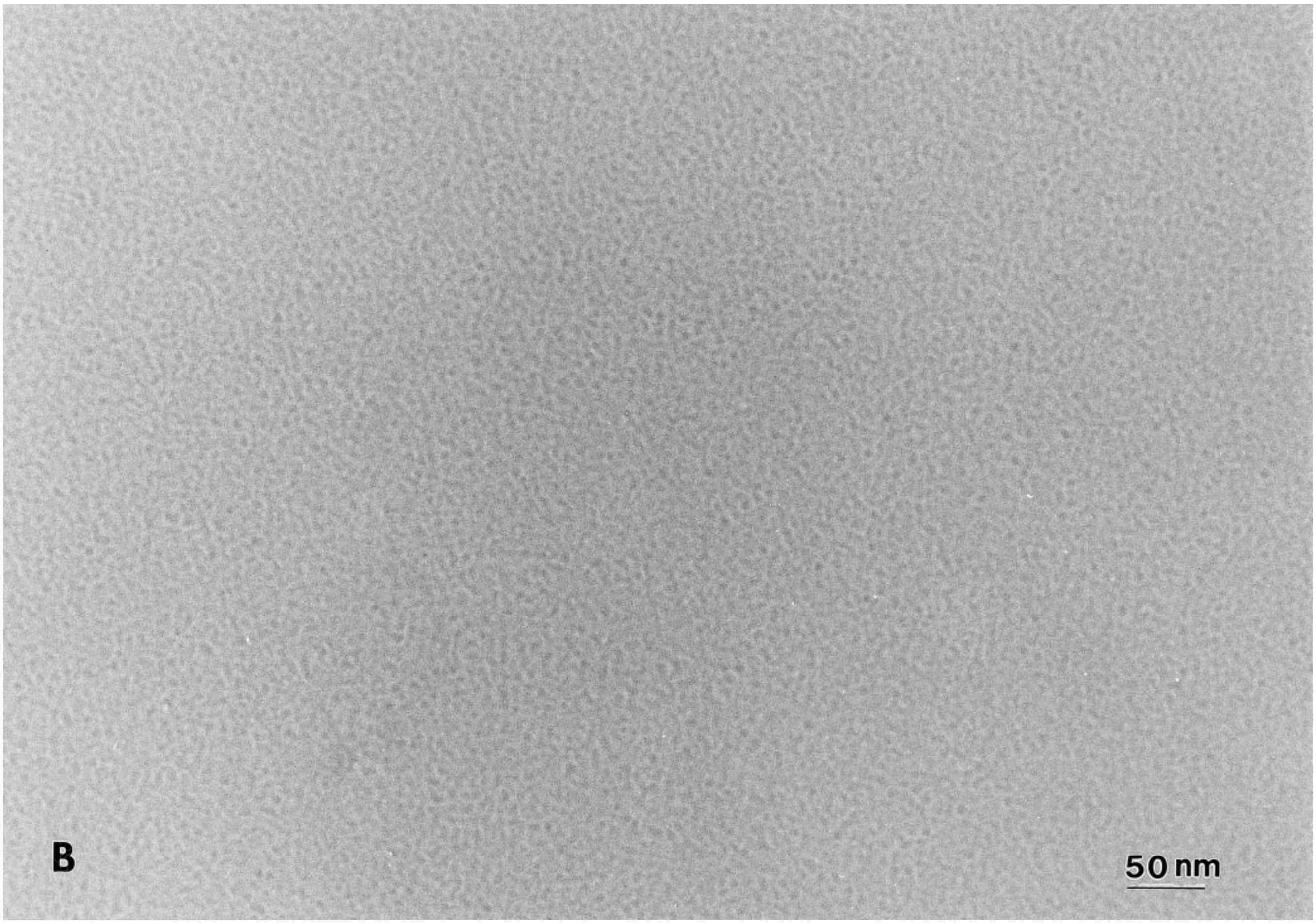
Structure of TEAFOS micelles that solubilized PFMD

The solubilization of fluorinated oils in the micelles of perfluorinated surfactants in water depends on their alkyl chain length, the types of polar groups, and the counterions, similar to the case of nonfluorinated surfactants [30]; however, a general statement of the mechanism of solubilization and of the structure of solubilized micelles is still an open issue, because the HLB, the types and structures of the surfactants, and the polarity of the solubilizates are pertinent to them.

The slow rate of solubilization of PFMD in TEAFOS micelles implies that the adsorption and desorption of FOS molecules to and from PFMD–water interfaces play an important role in the solublilization. The solubilization may be facilitated by the aggregation of rotund FOS molecules, since perfluorinated alkyl chains bereave the PFMD molecules of the interfaces when desorbing occurs.

The maximum solubilization of PFMD in the TEAFOS micelles was 1 wt% (20 mM), which was a modest value. The solution viscosity depended on the solubilizate concentration. At 0.2 wt% of solubilizate it became 86% of the pure TEAFOS system. At the maximum solubilization the viscosity was identical to that of pure water. Images of solubilized micelles at 0.2 and 1.0 wt% PFMD are displayed in Fig. 2A and B, respectively. Figures 1A (pure TEAFOS micelles) and 2A evinced no difference between the micelle structure while keeping

Fig. 2 (*Contd.*)



the threadlike forms, which are no longer seen in Fig. 2B, although the diameters of the spheres in these three micrographs were still in a range of 4 ± 1 nm. The absence of the chained formation of spherical micelles at the maximum solubilization explains why the solution viscosity is low. The small-sized micelles (small volume) in pure TEAFOS solutions also explain why the solubilization occurs in small amounts.

TEAFOS lowered the surface tension to 19 mN/m at the cmc (1 mM). The surface tension isotherm provided a limiting area of 0.54 nm^2 near the cmc using the Gibbs equation. The aggregation number of the spherical micelles for pure TEAFOS was estimated to be 93 molecules using the limiting area and the micelle areas for a 4-nm diameter. The concentration for the micelle formation of TEAFOS is assumed to be 59 mM, and the maximum solubilization of PFMD is 20 mM. We found that one PFMD molecule was solubilized by three FOS molecules in the micelles. It could not be determined whether the loci of the oil molecules solubilized in the micelles are in the palisades of the perfluorinated alkyl chains or in the cores in the micelles from the micrographs; however, the absence of changes in size of the micelles with and without PFMD led to the conclusion that their loci may be the palisades in the light of the size changes of rotund microemulsions at the same concentration of PFMD, as discussed later.

Structure of PFMD in water types of microemulsions

The formation of various types of emulsions is also a study of interest for fluorinated surfactant systems. Several classes of fluorinated surfactants form oil-in-water [12–14], water-in-oil [13–15], and oil-in-oil [16, 17] types of micro- and macroemulsions.

The TEAFOS surfactant is highly surface-active and depresses the interfacial tensions at PFMD–water interfaces. The interfacial tension measured by the drop-volume method was 51.1 mN/m (22–23 °C) at pure water–PFMD interfaces and was minimized and kept constant at 1.2 mN/m above a TEAFOS concentration of 3 mM. This surfactant revealed no practical stabilization and microemulsification of PFMD droplets in water. A homologous series of perfluorinated alcohols with different chain lengths as cosurfactants were tested to determine whether a microemulsion is formed in the presence of TEAFOS. The most effective cosurfactant was 1H,1H-perfluoro-1-nonanol, which has a rather long chain. Regarding our results for the cosurfactants,

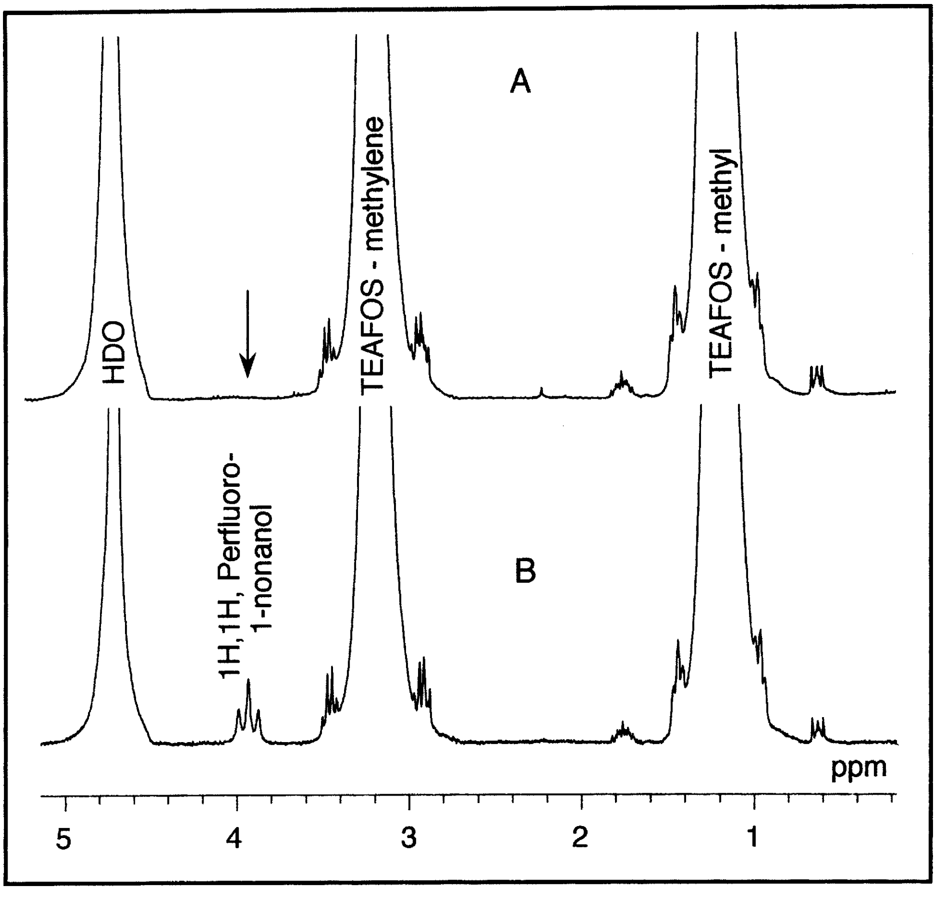


Fig. 3 ^{1}H NMR spectra from the cosurfactant (1H,1H-perfluoro-1-nonanol) and TEAFOS micelles: A 1 wt% of the alcohol in the TEAFOS micelle solution; B 10 wt% of the alcohol in PFMD microemulsions at 30 °C. The *upper spectrum* shows no appearance of the proton peaks from the alcohol. The *lower spectrum* shows the evident proton peak from the cosurfacatant in the microemulsions

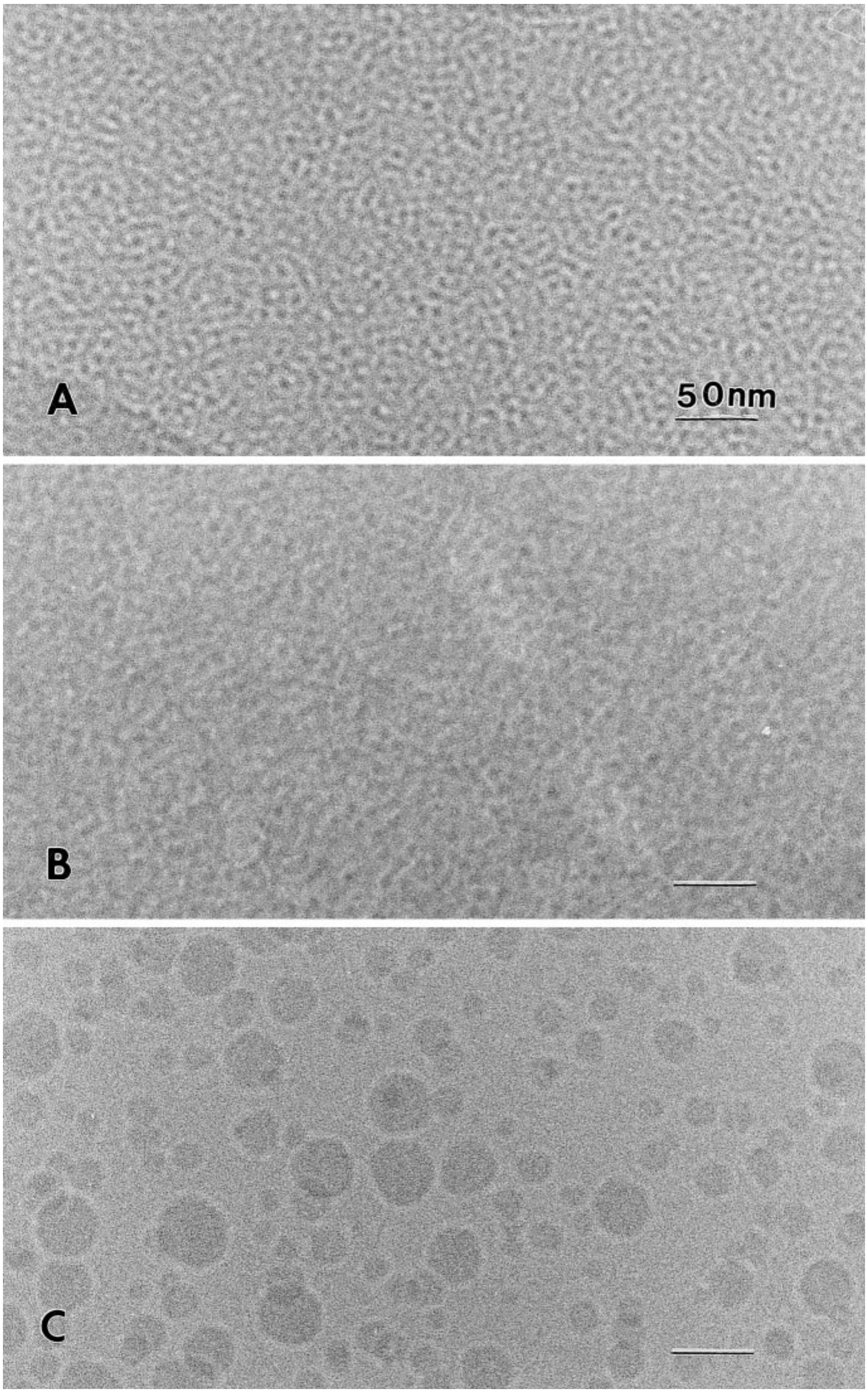


Fig. 4 Cryo-TEM images of PFMD in water types of microemulsions. The concentration of 1H,1H-perfluoro-1-nonanol as the cosurfactant dissolved in PFMD was kept constant at 10 wt%: **A** 1 wt% PFMD (equivalent to the maximum solubilization concentration); **B** 3 wt% PFMD; **C** 12 wt% PFMD. These microemulsions were optically isotropic and transparent below 3–5 wt% and translucent above 6 wt%. All the microemulsions had a viscosity similar to that of water

no effective microemulsification has been reported on a perfluorinated alcohol with a short chain for the system of $C_8F_{17}SO_3Li/C_4F_9C_2H_4OH$/perfluorodecalin/$H_2O$ studied using a pseudoternary phase diagram [31].

1H,1H-perfluoro-1-nonanol is insoluble in water, very lipophilic, and does not solubilize in FOS micelles. The ^{1}H NMR spectrum in the system of the micelle solution of 60 mM TEAFOS including 1 wt% of solid powders of the alcohol is shown in Fig. 3, spectrum A. Here, the solution was kept for 1 week after heating and shaking by hand before the measurement. The registered proton peaks originated from methylene and methyl groups in the TEA counterions, from HDO, and from the side peaks of the external reference at about 0.6 and

1.8 ppm; however, there is no peak from the alcohol at the resolution limit of 0.01–0.02 wt%.

On the other hand, the alcohol is soluble in PFMD up to a concentration of 10 wt% at room temperature. The interfacial tensions measured by the drop-volume method were constant at 14.5 mN/m at the interfaces of water and PFMD solution above an alcohol concentration of 0.055 wt%. The interfacial tension between the PFMD solution that included 10 wt% of the alcohol and the TEAFOS solution was 1.2 mN/m, measured by the spinning-drop and drop-volume methods. This value was unexpectedly high for spontaneous emulsification in the presence of the cosurfactant. However, PFMD in the solution system concerned was immediately microemulsified by gentle shaking by hand. Hence, the alcohol must be acting as cofilms of FOS films to form a dense adsorption film. Figure 3, spectrum B evidently shows proton peaks from the alcohol in the microemulsion, where the alcohol and PFMD concentrations are 10 wt% in PFMD and 1 wt% in the TEAFOS solution.

The microemulsified solution was optically transparent up to 3–5 wt% PFMD; from 6–12 wt% PFMD it became translucent. The stability of these microemulsions was slightly poor in contrast to thermodynamically stable microemulsions, and the life time increased from only a few hours to several hours as the PFMD content decreased. The microemulsified solution transformed the transparent or translucent phases into turbid phases with time and resulted in precipitation. The instability of the microemulsions is not explained properly and is under question at the present stage. Hence, the microemulsification was performed just before the thermal fixation prior to the imaging of microemulsions by cryo-TEM.

Cryo-TEM images of the PFMD-in-water types of microemulsions are shown in Fig. 4. The globular particles in Fig. 4A emerge with discernible diameters of 6 ± 1 nm at 1 wt% PFMD, which is the same concentration as for the maximum solublization. The same size is also found in the case of 3 wt% PFMD (Fig. 4B). A PFMD content over 3 wt% led to the formation of polydispersed, rotund, globular microemulsions. A typical example of the polydispersed particles for 12 wt% PFMD is shown in Fig. 4C; the size distribution being several nanometers to 50 nm. In all the systems of microemulsions, the solution viscosity was as low as that of pure water. Hence, the absence of thread formations, as shown in the micrographs of Fig. 4, is acceptable.

The larger-sized particles of the microemulsions at the same PFMD content (1 wt%) as the solubilization explain the fact that PFMD molecules are dissolved in the cores of FOS micelles in an early stage of the microemulsification, reflecting no time-consuming process in contrast to the solubilization.

In conclusion, a high concentration of $LiNO_3$ as a supporting electrolyte transformed the TEAFOS thread-like micelles into a homogeneous dispersion of spherical micelles. The solubilization of PFMD into the TEAFOS micelles was modest because of the small volume of the unit spherical micelle. The absence of size changes of the pure micelles and the solubilized micelles explained the allocation of the PFMD molecules to be in the palisades of the alkyl chains of spherical micelles. The rotund microemulsions obtained at the same concentration as the PFMD solubilization supported the fact that the oil molecules had dissolved in the cores of the spherical micelles.

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