



Polyhedral vesicles with crystalline bilayers formed from catanionic surfactant mixtures of fluorocarbon and hydrocarbon amphiphiles

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ABSTRACT

Salt-free catanionic mixtures of perfluorononanoic acid ($C_8F_{17}COOH$) and tetradecyltrimethylammonium hydroxide (TTAOH) in aqueous solution show rich and interesting self-assembly properties. With the addition of TTAOH to a $C_8F_{17}COOH$ solution, a structural transition from polyhedral vesicles with crystalline bilayers to spherical vesicles with fluid bilayers was observed at room temperature, which was demonstrated by cryo- and FF-TEM observations, DSC and WAXS measurements. It is interesting that both uni-lamellar and multi-lamellar polyhedral vesicles were formed in these fluoro- and hydrocarbon catanionic surfactant mixtures. SAXS measurements were performed to determine the interlamellar spacing of the multi-lamellar polyhedral vesicles. The driving force for the formation of the polyhedral vesicles was the crystallization of the $C_8F_{17}COO^- - TTA^+$ ion pairs in the bilayers, which induced the excess anionic surfactants to be segregated and concentrated to produce the vertices of the polyhedral vesicles. Besides, the rheological results show that the rheological properties of the $C_8F_{17}COOH/TTAOH$ system are greatly affected by the fluorocarbon chains due to their high rigidity and Krafft point. The solutions consisting of polyhedral vesicles have high viscoelasticity and high yield stress values while spherical vesicle solutions are not viscoelastic.

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1. Introduction

Vesicles, which exist in numerous biological processes, are very interesting and important self-assembled structures both for scientific research and industrial applications because they are excellent candidates for drug delivery and mimicking biological membranes [1–4]. In surfactant sciences, the so-called “catanionic” vesicles observed in cationic and anionic (catanionic) surfactant mixtures at suitable conditions have attracted much attention. They can form spontaneously and be obtained from a great variety of surfactants [5–11]. In particular, vesicles with unique properties were obtained from salt-free catanionic surfactant systems [10,12,13]. Theoretical models and molecular dynamic simulation have been developed to explain interesting self-assembly phenomena in some salt-free catanionic surfactant systems [14–16]. Among the surfactants used to construct self-assembled aggregates, fluorosurfactants have unique physicochemical properties due to the dual oleophobic/hydrophobic character of perfluorocarbon chains [17–19]. Fluorocarbon/hydrocarbon catanionic mixtures can form a variety of aggregates, such as bilayer cylinders, flat disks and vesicles [20–23].

Catanionic vesicles previously reported were generally spherical with polydisperse sizes [10–13]. Comparatively, nonspherical vesicles, such as polyhedral vesicles, although they have already been found in some lipids or non-ionic surfactant systems [24–28], have been reported in numbered catanionic surfactant mixtures until now [29]. Dubois et al. observed regular icosahedral vesicles with crystalline bilayers in myristic acid/cetyltrimethylammonium hydroxide mixtures (MA/CTAOH) in dilute aqueous solutions with excess of MA [30,31]. Then, Vautrin et al. investigated the influences of pH and ionic strength on the chain melting transition of MA/CTAOH icosahedral vesicles [32]. And later, Carrière et al. found the osmotic deformation of micron-size catanionic vesicles with icosahedral symmetry upon incubation in small solutes (NaCl, glucose) in the similar system of MA/CTACI [33]. Another different case of catanionic polyhedral vesicles was reported by Krafft in the dilute solution of a “true” hydrocarbon–fluorocarbon ion-pair amphiphile octyltrimethylammonium perfluorooctanoate which were formed through a transbilayer flip–flop transfer [34]. Haselwandter and Phillips pointed out that the polyhedral bilayer membranes can actually be energetically favorable compared to spherical vesicles based on simulations [35]. Recently, faceted catanionic vesicles have been successfully used in the synthesis of large faceted hollow silica nanoparticles by Lootens et al. [36].

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In this paper, two amphiphiles with asymmetric alkyl chains, one perfluorocarbon surfactant perfluorononanoic acid ($C_8F_{17}COOH$) and one hydrocarbon surfactant tetradecyltrimethylammonium hydroxide ($C_{14}H_{29}(CH_3)_3NOH$, TTAOH), were mixed in aqueous solutions. The phase behavior was determined in detail. Polyhedral vesicles were formed in $C_8F_{17}COOH$ -rich solutions and a transition from polyhedral vesicles to spherical vesicles was observed with TTAOH concentration increasing. Besides, multi-lamellar polyhedral vesicles were found in the present system, which have rarely been reported in other cationic fluorocarbon/hydrocarbon mixtures, to our knowledge. Differential scanning calorimetry (DSC) and wide angle X-ray scattering (WAXS) measurements showed that the surfactant chains of these polyhedral vesicles were in the crystalline state with a local in-plane orthorhombic packing spatially averaged into a hexagonal packing at room temperature.

2. Experimental

2.1. Materials

Perfluorononanoic acid ($C_8F_{17}COOH$, >98%) was purchased from Fluorochem Company (England) and used without further purification. The Krafft point of $C_8F_{17}COOH$ is $48.3\text{ }^\circ\text{C}$ [18]. The $C_{14}H_{29}(CH_3)_3NOH$ (TTAOH) stock solution was prepared from TTABr (Amresco Company) using a strong base anion exchanger (Ion exchanger III, Merck) as the reported paper [23]. Water was distilled three times with the resistivity of $18.25\text{ M}\Omega\text{ cm}$.

2.2. Methods

2.2.1. Phase behavior study

Phase behavior was studied by visual inspection with the help of crossed polarizers. Samples were prepared by adding different amount of $C_8F_{17}COOH$ into a series of TTAOH stock solutions. All samples were heated to $60\text{ }^\circ\text{C}$ and gently shaken to accelerate the dissolution of $C_8F_{17}COOH$. Then, they were stored for at least 4 weeks at $T = 25.0 \pm 0.1\text{ }^\circ\text{C}$ to reach equilibrium.

2.2.2. pH Measurements

The pH measurements were performed on a PHS-3C precision pH meter (China) at $25.0 \pm 0.1\text{ }^\circ\text{C}$. Two-phase samples were equally stirred during the measurements.

2.2.3. Conductivity measurements

The conductivity data were obtained on a DDSJ-308A conductivity meter (China) at $25.0 \pm 0.1\text{ }^\circ\text{C}$. Samples in the L_1/L_α phase region were equally stirred during the conductivity measurements. The conductivity value for each sample is the average of three measurements.

2.2.4. Differential scanning calorimetry measurements (DSC)

DSC measurements were performed on a DSC-Q10, TA instrument (USA). Each sample was analyzed in an aluminum pan under a flow of nitrogen (20 mL/min) and heated from 10 to $80\text{ }^\circ\text{C}$ at a velocity of $5\text{ }^\circ\text{C/min}$. An empty aluminum pan was used as a reference.

2.2.5. Freeze-fracture transmission electron microscope observations (FF-TEM)

The microstructures of L_α phase samples with high viscosity were determined by FF-TEM measurements. First, a small amount of solution was loaded onto a specimen holder. Then, the specimen holder with the sample was quickly plunged into liquid ethane which was cooled by liquid nitrogen to freeze the sample. Fracture

and replication were carried out on the freeze-fracture equipment (EM BAF 060, Leica, Germany) at $-150\text{ }^\circ\text{C}$. Pt/C was deposited at an angle of 45° to shadow the replicas and C was deposited at 90° to consolidate the replicas. Next, the replicas were transferred onto a copper grid and examined in a JEOL JEM-1400 electron microscope operated at 120 kV . The images were recorded by a Gatan multiscan CCD.

2.2.6. Cryo-transmission electron microscope observations (Cryo-TEM)

The microstructures of L_α phase samples with low viscosity were determined by cryo-TEM measurements. First, about $5\text{ }\mu\text{L}$ sample solution was loaded onto a TEM copper grid which was blotted with two pieces of filter paper, and thin films suspended on the mesh holes were formed. After about 4 s to relax any stress induced by the blotting, the samples were instantly frozen by plunging them into liquid ethane (cooled by the liquid nitrogen) at $-165\text{ }^\circ\text{C}$. Then, the vitrified specimens were inserted into liquid nitrogen and transferred to a cryogenic sample holder (Gatan 626). The observations were carried out on a JEOL JEM-1400 electron microscope (120 kV). The images were recorded by a Gatan multiscan CCD.

2.2.7. Small angle X-ray scattering (SAXS)

The SAXS measurements were performed on the Beamline 4B9A synchrotron radiation X-ray small angle system (Beijing Synchrotron Radiation Facility) at $25.0 \pm 0.1\text{ }^\circ\text{C}$. The imaging plate used was Mar 345 with the resolution factor of 3450×3450 . The distance from the sample to the detector was 173 cm and the data accumulation time was 600 s for each sample.

2.2.8. Wide angle X-ray scattering (WAXS)

The WAXS measurements were performed using a SAXSess Anton-Paar (Austria) with a $\text{Cu K}\alpha$ radiation (0.154 nm) operating at 50 kV and 40 mA . The distance from samples to detector was 261 mm and the temperature was kept at $25.0 \pm 0.1\text{ }^\circ\text{C}$.

2.2.9. Rheological measurements

Steady and dynamic rheological experiments were performed on a HAAKE RheoStress 6000 rheometer with a coaxial cylinder sensor system ($Z41^\circ\text{Ti}$) for low viscous samples and cone-plate system ($C35/1^\circ\text{Ti L07116}$) for samples with high viscosity. In oscillatory measurements, an amplitude sweep at 1.0 Hz was performed prior to the following frequency sweep to ensure that the selected stress was in linear viscoelastic region. In steady shear experiments, the shear rate was gradually increased from 0.001 to 1000 s^{-1} . To achieve equilibrium as far as possible, the gradient was set to be less than $0.5 (\Delta\tau/\tau)/\Delta t\%$ at each shear rate step, and the maximum waiting time was 30 s . All samples were measured by using a cyclic water bath at $25.0 \pm 0.1\text{ }^\circ\text{C}$.

3. Results and discussion

3.1. Phase behavior of $C_8F_{17}COOH$ and TTAOH mixtures

To obtain detailed knowledge about the assembly properties, the phase diagram of perfluorononanoic acid ($C_8F_{17}COOH$) mixed with tetradecyltrimethylammonium hydroxide (TTAOH) at various concentrations was first studied. Fig. 1 presents the phase diagram of $C_8F_{17}COOH/TTAOH/H_2O$ system at $25\text{ }^\circ\text{C}$. The concentration ranges of $C_8F_{17}COOH$ and TTAOH are both $0\text{--}100\text{ mmol L}^{-1}$. Samples out of this range are in the extended nearby phase region. As shown in Fig. 1, the $C_8F_{17}COOH/TTAOH$ system in aqueous solution exhibits rich phase behavior at room temperature. The phase diagram is divided into four regions. On the $C_8F_{17}COOH$ -rich side, one can see a gel phase demarcated by tube inversion experiments which are frequently used in studying gels [37]. The solutions in

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