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Short haired wormlike micelles in mixed nonionic fluorocarbon surfactants

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Abstract

We have studied the rheological behavior of viscoelastic wormlike micellar solution in a mixed system of nonionic fluorinated surfactants, perfluoroalkyl sulfonamide ethoxylate, $C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_nH$ abbreviated as $C_8F_{17}EO_n$ ($n = 10$ and 20). Above critical micelle concentration, the surfactant, $C_8F_{17}EO_{20}$ forms small spherical micelles in water and the viscosity of the solution remains constant regardless of the shear rate, i.e., the solutions exhibit Newtonian behavior. However, upon successive addition of the $C_8F_{17}EO_{10}$ the viscosity of the solution increases and at certain $C_8F_{17}EO_{10}$ concentration, shear-thinning behavior is observed indicating the formation wormlike micelles. Contrary to what is expected, there is a viscosity increase with the addition of the hydrophilic $C_8F_{17}EO_{20}$ to $C_8F_{17}EO_{10}$ aqueous solutions at certain temperature and concentration, which could be attributed to an increase in rigidity of the surfactant layer and to the shifting of micellar branching to higher temperatures. The oscillatory-shear rheological behavior of the viscoelastic solution can be described by Maxwell model at low frequency. Small-angle X-ray scattering (SAXS) measurements confirmed the formation of small spherical micellar aggregates in the dilute aqueous $C_8F_{17}EO_{20}$ solution. The SAXS data shows the one-dimensional growth on the micellar size with increase in the $C_8F_{17}EO_{10}$ concentration. Thus, the present SAXS data supports the rheological data.

Keywords: Fluorocarbon surfactants; Oligomers; Wormlike micelles; Rheological behavior; Small-angle X-ray scattering

1. Introduction

It is well known that surfactants can self-assemble in very long aggregates, so called wormlike micelles that can entangle to form viscoelastic solutions [1], which find possible applications in many fields [2]. Although most studies have been done in cationic systems, there are also some recent reports on nonionic mixed surfactant systems [3–7]. Ligoure and co-workers [8] studied the rheology of the hairy wormlike micelles decorated with amphiphilic block copolymer to address the role of polydispersity on viscoelasticity.

Contrary to polymers, wormlike micelles continuously break and recombine; hence, there is the chance of a synergistic effect if both (polymers and wormlike micelles) are mixed in solution. Still, there are few studies on the effect of adding polymers to viscoelastic solutions. It has been reported that this effect depends on the structure of the polymer. Water-soluble or highly hydrophobic polymers induces a loss of viscoelasticity either by adsorbing in the micellar surface or solubilizing in the micellar core, due to changes in the curvature [9]. On the other hand, a viscosity enhancing effect has been found when a hydrophobically modified polymer is added [10], which was attributed to the formation of a common network.

Recently, we presented a study on a binary fluorocarbon surfactant/water system in which wormlike micelles were found [11]. Fluorocarbon surfactants are a particular class of surfactants that are more hydrophobic and reduce the surface tension of an aqueous solution to an extent, which is unattainable with hydrocarbon surfactants. They also show a much lower critical micellar concentration (cmc) than hydrocarbon-chain surfactants of same length, have high chemical and thermal stability and therefore are useful in many practical applications where hydrocarbon surfactants would decompose. Moreover, they are

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useful for the preparation of nanomaterials with especial properties [12,13].

It has been found that the viscoelastic properties of the fluorinated micelles are lost when a hydrophobic fluorinated oligomer is added, which was attributed to a rod to sphere transition induced by the solubilization of the hydrophobic compound in the micellar cores [14]. On the other hand, it is known that water-soluble oligomers such as polyols tend to increase the cloud point of hydrocarbon-chain non-ionic surfactants [15], an effect similar to that of some short chain alcohols [16], which has been attributed to a decrease in the solvophobic effect, resulting in smaller cmc and lower aggregation numbers [16]. However, the effect of water-soluble oligomers on the structure of fluorinated wormlike micelles remains to be clarified.

In this context, we present some results on the effect of adding hydrophilic oligomeric fluorosurfactant to a solution of fluorinated wormlike micelles.

2. Experimental

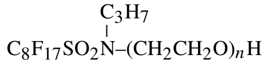
2.1. Materials

Perfluoroalkyl sulfonamide ethoxylate surfactants, C_8F_{17}-$SO_2N(C_3H_7)(C_2H_4O)_nH$, designated as $C_8F_{17}EO_n$ ($n = 10$ and 20) were obtained from Mitsubishi Materials (Japan). Schematic molecular structure of the surfactant is shown in Scheme 1. $C_8F_{17}EO_{20}$ is considered herein as an oligomer. The surfactant $C_8F_{17}EO_{10}$ was purified by placing it under vacuum for several days in order to remove volatile components until weight became constant.

Polyethylene glycol 1000 abbreviated as; PEO_{22} was the product of Wako Chemical Industries, Ltd. (Japan). Millipore water was used throughout the experiment.

2.2. Rheological measurements

Samples for rheological measurements were homogenized and kept in water bath at specified temperature for at least 24 h to ensure equilibration before performing measurements. The rheological measurements were performed in a stress-controlled rheometer, AR-G2 (TA Instrument) using cone-plate geometries (diameters 60 mm for low-viscosity sample and 40 mm for high-viscosity sample, each with a cone angle of 1°) with the plate temperature controlled by peltier unit. A sample cover provided with the instrument was used to minimize the change in sample composition by evaporation during the measurement. Frequency sweep measurements were performed in the linear viscoelastic regime of the samples (10% strain), as determined previously by dynamic strain sweep measurements.



$$C_8F_{17}SO_2\overset{\overset{C_3H_7}{|}}{N}\text{–}(CH_2CH_2O)_nH$$

Scheme 1. Molecular structure of $C_8F_{17}EO_n$ (amphiphiles with $n = 20$ and 10 were used in this study).

2.3. Small angle X-ray scattering (SAXS)

SAXS measurements on fluorinated surfactants solutions were carried out using a SAXSess camera (Anton Paar, PANalytical), which is attached to a PW3830 laboratory X-ray generator with a long fine focus sealed glass X-ray tube (K_α wavelength of 0.1542 nm) (PANalytical) and operated at 40 kV and 50 mA. The SAXSess camera is equipped with a focusing multiplayer optics and a block collimator for an intense and monochromatic primary beam with low background, and a translucent beam stop for the measurement of an attenuated primary beam at $q = 0$. Samples were enclosed into vacuum tight thin quartz capillary with an outer diameter of 1 mm and thickness of 10 µm and the same capillary was used for all measurements to attain the exactly the same scattering volume and background contribution. The sample measurements temperature was controlled with a thermostated sample holder unit (TCS 120, Anton Paar). The scattered intensities were first measured on an imaging plate (IP) detection system Cyclone (Perkin-Elmer, USA), and via SAXSQuant software (Anton Paar) two-dimensional intensity data were transformed to the one-dimensional scattering curves as a function of the magnitude of the scattering vector,

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

where θ is the angle between the incident beam and the scattered radiation. All data were transmission-calibrated by normalizing an attenuated primary intensity at $q = 0$ to unity, and were corrected for the background scattering from the capillary and the solvents. The absolute scale calibration was done using water as a secondary standard.

In general, for concentrated systems, the contribution of the intraparticle scattering are related to the form factor $P(q)$ and the interparticle correlations are related to the structure factor $S(q)$. Therefore, proper choice of structure factor model in the SAXS data analysis is essential in order to account for the interparticle interference scattering. For monodisperse spherical systems the total scattered intensity $I(q)$ involving n particles in unit volume can generally be given by

$$I(q) = nP(q)S(q), \tag{2}$$

where $P(q)$ is the averaged form factor and $S(q)$ is the static structure factor. For dilute system $S(q)$ is equal to one and the $I(q)$ is simply given by $P(q)$. An expression similar to Eq. (2) can be applied to polydisperse spherical and nonspherical system by replacing $S(q)$ by $S^{\mathrm{eff}}(q)$ [17]. $S^{\mathrm{eff}}(q)$ is no longer only a function of the particle distribution in space but depends also on the form amplitudes of the particles. The average form factor, $P(q)$ is given by the Fourier transformation of the pair-distance distribution function (PDDF), $p(r)$, as

$$P(q) = 4\pi \int_0^\infty p(r)\frac{\sin qr}{qr}\,\mathrm{d}r, \tag{3}$$