Investigation on Molecular Aggregates of Alkylammonium Perfluorocarboxylates in Aqueous Solutions

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Abstract: The aggregation behavior of three alkylammonium perfluorocarboxylates \((C_{n}H_{2n+1}NH_{3}^{+}C_{m}F_{2m+1}COO^{-}; n+m=15, n=2,4,6)\) were investigated by rheology and polarization microscopy. The amphiphiles with \(n=8,10\) were quite stable and hardly soluble in water and could not be studied by the method. The above three amphiphiles formed quite large molecular aggregates in diameter of up to \(3 \mu m\) in the solutions at lower concentration of \(1.5 \text{ mmol dm}^{-3}\). At higher concentrations of \(50\text{-}100 \text{ mmol dm}^{-3}\), on the other hand, the first two amphiphiles formed fine crystallites which were strongly connected to one another, resulting in high viscosity of the solutions, while the third formed stable leaflet-like crystals of larger size depending on the concentration and on the temperature. The high complex viscosity over the concentration range \(20\text{-}50 \text{ mmol dm}^{-3}\) decreases with increasing the oscillating frequency applied to the solution for the first amphiphile, which results from loosening of strong connections among the crystallites due to increasing shear rate.


Key words: alkylammonium perfluorocarboxylate, rheology of aggregate solution, crystal shape, catanionic amphiphile

1 Introduction

Micellization in solutions of fluorocarbon and hydrocarbon surfactant mixtures has been the matter of interest for a long time (1,2), where two kinds of micelles, fluorocarbon-dominant micelles and hydrocarbon-rich micelles, were found to be formed in many mixed surfactant systems (3-5). Especially, to draw a phase diagram for three components systems of hydrocarbon surfactant, fluorocarbon surfactant, and water was quite helpful to understand the miscibility of two surfactants in the micellar state (6,7). In connection with the above studies, catanionic surfactants made of hydrocarbon group ion and fluorocarbon group counterion have become a new type amphiphile of another interest in these years (8-11).

In the preceding papers (12,13), solid and solution properties of alkylammonium perfluorocarboxylates were investigated and found much different from those of conventional ionic surfactants. In other words, the molecular aggregates formed in the solutions are quite large in size, and two heterogeneous regions, hydrocarbon and fluorocarbon regions, are formed not only in their solid state but also in their molecular aggregates in the solutions. This cannot be expected from catanionic surfactants made of hydrocarbon group ions only (14).

In this study then, physicochemical properties in aqueous solutions were further investigated for the three of a series of amphiphiles, alkylammonium perfluorocarboxylates \((C_{n}H_{2n+1}NH_{3}^{+}C_{m}F_{2m+1}COO^{-}; n+m=15, n=2,4,6)\), in the preceding study (13) by employing rheology and polarization microscopy techniques. The chemicals with \(n=8,10\) were quite stable and hardly soluble in water, and therefore, they could not be examined further, although a clear solution could be prepared and investigated for \(n=\)
12,14 (13).

2 Experimental

2.1 Materials

Three amphiphiles, \( \text{C}_6\text{H}_{13}\text{NH}_3^+\text{C}_8\text{F}_{17}\text{COO}^- \) (Ch2CF13), \( \text{C}_6\text{H}_{13}\text{NH}_3^+\text{C}_{11}\text{F}_{23}\text{COO}^- \) (Ch4CF11), and \( \text{C}_6\text{H}_{13}\text{NH}_3^+\text{C}_6\text{F}_{19}\text{COO}^- \) (Ch6CF9), were synthesized by neutralization of the corresponding alkylamine with the corresponding perfluorocarboxylic acid, respectively. The procedure for the synthesis is the same as mentioned in the preceding paper (13). Their purity was checked by the elemental analysis and found quite high. The water used was distilled once after deionization through columns of ionic resins.

2.2 Rheological Measurements

The measurements were performed for Ch2CF13 with a Bohlin CS 10 stress-controlled rheometer at 25°C. The viscoelastic properties, i.e., the dynamic moduli and the magnitude of the complex viscosity, were determined by oscillatory measurement from 0.001 to 10 Hz, whereby alternatively the strain amplitude or the stress amplitude could be kept constant.

2.3 Polarization Microscopy

Microcuvettes (50 × 5 mm, microslides from Camlab England) with a capillary thickness of 2 mm were used for observations with Zeiss-Standard polarization microscope. The concentration used was 50 and 100 mmol dm\(^{-3}\) for Ch2CF13, Ch4CF11, and Ch6CF9, respectively. The preparation of the solutions were made by sonication (Bandelin Sonorex, RK 102H) for an hour at 70°C after mixing the amphiphile and water in a volumetric flask. The solutions were left standing for two nights before the observation. The sample preparation for the microscopic observation was carried out by heating the solution again up to 70°C and cooling it down to room temperature at the constant rate of 0.5°C/min., and the above cycle was made five times.

3 Results and Discussion

Micellization was examined for Ch2CF13 by electric conductivity measurement of the solution, and the cmc value was determined to be \( 2 \times 10^{-5} \) mol dm\(^{-3}\) at 25°C. Unfortunately, however, the value drifted much at each measurement due to poor reproducibility of the conductivity values. Dynamic light scattering measurement was also made for Ch2CF13 at 25 and 50°C after filtration of the solution through a membrane filter of pore-size 0.8 μm. The particle diameter increased from 298.3 to 354.1 nm at 25°C over the period of one day and up to 3170 nm at 50°C after another one day. These results indicate that the system is not in thermodynamical equilibrium and that the aggregates in the system grow in size with time. From the observation by phase contrast microscope too, molecular aggregates of ca. 3 μm in length at maximum were found in the solutions even after

![Oscillatory Rheogram of 20 mmol dm\(^{-3}\) Solution for Ch2CF13 at 25°C.](image-url)
filtration through a filter of pore-size 0.2 μm for the present three surfactants. These results strongly suggest an easy formation and deformation of molecular aggregates depending upon conditions applied. In addition, the solution of Ch2C13 and Ch4Cf11 becomes very viscous at relatively high concentrations, which suggests that these two surfactants are a promising candidate for viscoelastic study.

3.1 Viscoelastic Properties
The viscoelastic properties of the systems are demonstrated in Figs. 1, 2, and 3 for Ch2Cf13. In Figs. 1 and 2 the storage modulus ($G'$), the loss modulus ($G''$) and the magnitude of the complex viscosity ($\eta$) are plotted against the oscillating frequency in a double log plot. Both moduli increase rather rapidly at the lower concentration of 20 mmol dm$^{-3}$ (Fig. 1), where the difference between the two is quite small at lower frequencies but grows with increasing frequency. On the other hand, the storage modulus is much larger than the loss modulus over the whole frequency range and the both moduli gradually

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**Fig. 2** Oscillatory Rheogram of 40 mmol dm$^{-3}$ Solution for Ch2Cf13 at 25°C.

**Fig. 3** Concentration Dependence of the Storage Modulus ($G'$), the Loss modulus ($G''$) and the Magnitude of the Complex Viscosity ($\eta$) at 1 Hz.
increase with the frequency at higher concentrations. The $G'$ values do not vanish for low frequencies over the concentrations examined (20-50 mmol dm$^{-3}$). This indicates the presence of a yield stress. The present rheological behaviors are very similar to those of tetradecyltrimethylammonium (15). In addition, a clear difference in the rheological behavior was observed between 20 and 30 mmol dm$^{-3}$, which suggests an abrupt change in structure of the molecular aggregates within small concentration range.

The solution of Ch2Cf13 shows the pseudoplastic behavior over the concentration range from 20 to 50 mmol dm$^{-3}$, indicating the viscosity decrease with increasing frequency of applied oscillating force. This decrease generally suggests the destruction of large molecular aggregates into smaller pieces with increasing shear rate or the alignment of unimeric structure in the shear field. In the present case, however, the destruction or alignment takes place for the aggregates of crystallites, as is evidenced by the following microscopy. The interesting fact is that there exists little difference in slope of the viscosity against the oscillating frequency in a double log plot among the solutions of concentrations from 20 to 50 mmol dm$^{-3}$, indicating that the destruction and alignment rate of crystallite aggregates against shear rate is independent on the amphiphile concentration. In other words, a skeleton structure of the aggregates is the same from the viewpoints of crystallites’ arrangement and of interaction in the aggregation state, regardless of the total amphiphile concentration. The increase in the storage modulus with the frequency, therefore, originates from an increase in the number of pieces of smaller aggregates, which is prominent at lower amphiphile concentrations. Figure 3 indicates the concentration dependence of the above three parameters at 1 Hz. The whole parameters increase steeply and monotonically with increasing amphiphile concentration or concentration of the crystallites, indicating that they are greatly affected by the size and the number of the crystallite aggregates.

The amount of Ch4Cf11 was not enough to measure the viscoelastic behavior of the solution, but the solution behavior was quite the same between Ch4Cf11 and Ch2Cf13 by eye observation at the same concentration. This was substantiated by the polarization microscopy as mentioned in the following section.

3.2 Polarization Microscopy

The solutions of Ch2Cf13 and Ch4Cf11 are not only viscous but also birefringent. This means the presence of organized molecular assemblies in the solutions, which was examined by the polarization microscopy.

Ch2Cf13 After the sonication treatment, plate-like crystals of 20-100 $\mu$m in length and of 10 $\mu$m in width as saponite were observed at room temperature. The particles are quite different from vesicles, which had been expected from previous studies. The crystallites remained the same from room temperature up to 80°C (Figs. 4-a and -b), just keeping the same texture. This is an indication that the crystallites are quite stable against temperature due to stronger interaction among longer fluorocarbon chains. In other words, no difference in the crystal stability was observed between the sonication treatment and the cycle treatment. Judging from the textures of crystallites, it seems quite easy for the aggregates of crystallites to entrap large amounts of water molecules.

Fig. 4-a  Polarization Microscopic Picture of Ch2Cf13 at 25°C after the Sonication Treatment. Magnification is 100.

4-b  Polarization Microscopic picture of Ch2Cf13 at 70°C after the Cycle Treatment. Magnification is 80.
into apertures formed by them. The interaction among the crystallites is the origin of higher viscosity of the solution over wider temperature range.

**Ch4Cf11** After the sonication treatment, plate-like crystals as Ch2Cf13 were observed at room temperature (Fig. 5), too. A phase transition from the crystal to a lamellar phase takes place over the temperature range 54-58°C on heating and another transition from the lamellar phase to the isotropic solution occurs at 60°C, judging from the configuration change of the crystallites by the microscope observation. The first transition temperature moves up slowly but steadily after each cycle. The presence of lamellar phase is demonstrated by many birefringent droplets (16), pseudoisotropic regions coexisting with the crystallites (Fig. 6). It is quite reasonable that this amphiphile with a shorter fluorocarbon chain has lower phase transition temperatures due to smaller interaction among the chains.

**Ch6Cf9** The original sample is the one recrystallized from acetone-water mixed solvent. After the sonication treatment the solution became turbid, and it took more than one day for the turbid solution to separate into upper clear solution and settled crystallites. The crystallites look like plates but are larger in size compared with the above two amphiphiles (Fig. 7). After the cycle treatment, plate-like crystals which look similar to the above two but much more ordered were observed at room temperature. The crystals melt into isotropic liquid at 46.8°C on heating (the phase transition temperature and the melting points are respectively 48 and 57-61°C for the dry sample (13)), and the temperature for the phase separation into two isotropic liquid phases increases up to 70°C on heating (Fig. 8): one phase is the amphiphile phase saturated

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**Fig. 5** Polarization Microscopic Picture of Ch4Cf11 at 25°C after the Sonication Treatment. Magnification is 100.

**Fig. 6** Polarization Microscopic Picture of Ch4Cf11 at 56°C after the Cycle Treatment. Magnification is 80.

**Fig. 7** Polarization Microscopic Picture of Ch6Cf9 at Room Temperature after the Sonication Treatment. Magnification is 100.

**Fig. 8** Polarization Microscopic Picture of Ch6Cf9 at 70°C after the Cycle Treatment. Magnification is 80.
with water and the other is water phase saturated with amphiphile. On cooling, the amphiphiles separate out as crystallites around 44°C and a lamellar phase starts to appear in the aqueous phase at 43.3°C, which is recognized by the presence of birefringent droplets (several crosses around the center of Fig. 9). At lower temperatures around 40°C well-ordered and larger crystals start to form (Fig. 10), where the crystals grow bigger and more ordered after each cycle.

Better understanding can be made by different kinds of observations. This is also the case for the present study on solution properties of molecular aggregates of catanionic amphiphiles. Photographs have turned out to be direct evidences of the rheological behaviors of the molecular crystallites.

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