Structure formation of cationic and anionic surfactants at oil/water interfaces

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Introduction
Spontaneous formation of spatio-temporal orders in nonequilibrium systems is one of the most important topics in recent physics and a lot of studies have been performed. However, almost all of these studies focused only macroscopic orders but not microscopic structures. It would be more interesting if we can discuss the macroscopic spatio-temporal order formation based on microscopic structure formation.

We have studied blebbing at a periphery of an oil droplet including anionic surfactant (palmitic acid; PA) which floats on cationic surfactant (trimethyl-stearylammonium chloride; STAC) aqueous solution [1]. The blebbing seems to be induced by repetitive formation and removal of aggregates made of PA and STAC at an oil/water interface. To investigate the structure of the aggregates, we measured the microscopic structure of the aggregates by small angle X-ray scattering (SAXS) at BL-15A in PF, KEK, and it was suggested the aggregates have lamellar structures with an interval of around 40 nm [2]. Although we could confirm the aggregates have such microscopic structures, the previous measurement was performed over the whole sample, which have mesoscopic order at a submillimeter scale. In the present study, thus, we made SAXS measurement using a microbeam of X-ray at BL-4A in PF, KEK. Through the present measurements, we could achieve the more detailed spatial difference in microscopic structures around the oil/water interface [3].

Experimental Setup
STAC and PA were purchased from Tokyo Chemical Industry Co., Ltd. Tetradecane for an organic phase was available from Wako Pure Chemical Industries, Ltd. The chemicals were used without further purification. Water was purified by a Millipore milli-Q system. Firstly, we prepared 50 mM of STAC aqueous solution and 20 mM PA tetradecane solution. A 500-µL portion of an organic phase was placed on a 700-µL aqueous phase. The cell was made of acrylic plate and the window for the X-rays was covered with a Kapton film as shown in Fig 1a. The oil-water interface started to bleb immediately after the organic phase had been poured on the aqueous phase. For SAXS measurements by microbeam X-ray, we used the SAXS apparatus installed at BL-4A in PF, KEK. We moved the system horizontally at a constant velocity, and measured the local structures of aggregates.

Experimental Results and Discussion
At the oil/water interface, the spatially-periodic distribution of aggregates were seen. The typical size of such structures was around 3 mm. The aggregates were formed at the interface and they were pushed downward, i.e. toward the aqueous phase. By microbeam SAXS measurements, we achieved the scattering pattern as shown in Fig. 1b, which obviously shows that the aggregates have an anisotropic structure, i.e. a lamellar structure, at a micrometer scale. Noteworthy enough, the scattering pattern was isotropic by the measurement at BL-15A, at which the diameter of X-ray beam was at submillimeter scale [2]. By horizontally scanning the location, the amplitude of scattering signals were periodically changed. Figure 1c shows the P(k, x), which is the maximum value of the scattering intensities along a circle corresponding to k, and Σ(0, x), which is the standard deviation of scattering intensity with respect to angle, θ. The direction in which strong scattering signals were detected also changed periodically. We could deduce the direction of lamellar is dependent on the location; at the edge of the aggregation, there exists tilted lamellar structure, while at the center part of the aggregation, the horizontal lamellar structures were formed.

Figure 1: (a) Experimental setup. (b) Spatial distribution of scattering data obtained 5400 s after the contact of organic and aqueous phase. x in the figure correspond to that in (c) (c) Plots of P(k, x) and lnΣ(0, x).

References

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