

Discovery of a Structural Transition by Small-Angle Scattering in a Macroscopic and Spontaneous Interfacial Motion

Interfacial deformation is observed when an oil droplet having cosurfactant is in contact with an aqueous phase that contains cationic surfactant. Such oil droplets can even walk spontaneously at the bottom of a container. Although the generation of aggregates at an interface during deformation is repeatedly observed, the detailed mechanism of the interfacial motion associated with the aggregate formation is still unclear. In this study, we conducted small-angle neutron and X-ray scattering experiments, which confirmed a transition of aggregate structures immediately after the initially-formed aggregates detached from the interface. This drastic change in the mesoscopic structure could be a key to resolving the underlying physics of the interfacial motion.

Living organisms today have fully evolved through the long history of Earth. In the early stages of the beginning of life, simple mixtures of some chemicals were presumably a starting point. Metabolism, among other essential factors, is required to make a chemical mixture being a living system, that is a transduction of energy from microscopic chemical energy to macroscopic coherent motions. One example of energy transduction is amoeboid motion, which is highly sophisticated and hierarchical in structure and dynamics. However, primitive forms of life should not have been as complex. Therefore, significant attention has focused on mimicking such energy transductions in a simple chemical system. Here we demonstrate a system which shows such energy transduction: a droplet that walks spontaneously by consuming chemical energy. In order to make a droplet sink in an aqueous phase, the oil phase has slightly larger relative density than water, which is controlled by adding 1,1,2,2-tetrabromoethane. Upon placing this heavy oil droplet inside an aqueous phase, the oil droplet walked around by undergoing bleb-like deformation at the bottom surface (Fig. 1 a) [1, 2].

The walking motion of a droplet is essentially a re-

sult of interfacial deformation, so-called blebbing motion, which can be observed with various geometries such as a floating oil droplet or an oil-water interface in a Hele-Shaw cell [3, 4]. One of such systems is composed of an organic phase, a tetradecane solution of palmitic acid (PA), and an aqueous phase containing octadecyltrimethyl ammonium chloride (OTAC). Mixing PA with OTAC in water leads to the formation of a surfactant aggregate, so-called alpha gel [5], which is stable and has finite elasticity in water. The structure of alpha gel in submicrometer scales was confirmed to be a lamellar structure as shown in Fig. 1 b by small-angle X-ray scattering (SAXS) where surfactant bilayers are repeated with a periodic distance d of 40 nm [3]. Since PA itself is not well soluble in water but diffuses inside the aqueous phase when associated with OTAC, the following processes are likely happening when our system composed of organic and aqueous phases is set. First, both PA inside the organic phase and OTAC in the aqueous phase diffuse and adsorb onto the oil-water interface. Secondly, PA and OTAC make an aggregate and desorb from the interface. The elastic aggregate, therefore, is continuously generated at the oil-water interface.

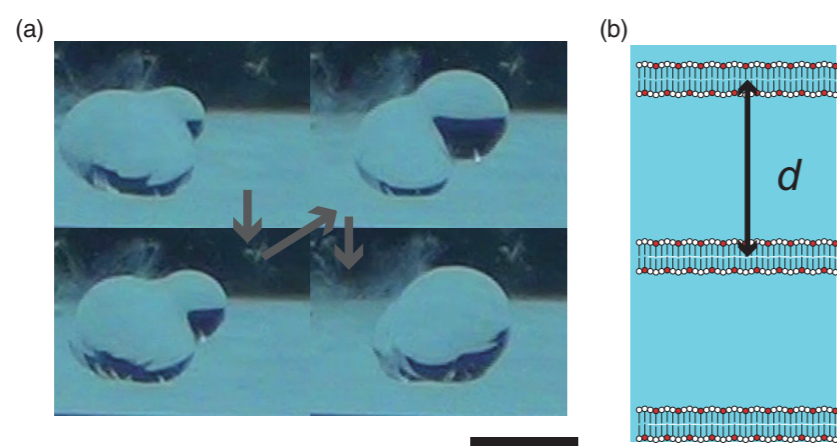


Figure 1: (a) A walking droplet on a substrate. Snapshots were taken every 1 s. Scale bar: 1 mm. A video image can be found at [2]. (b) Typical structure of the aggregate. A bilayer structure was separated by water whose periodic distance is denoted by d .

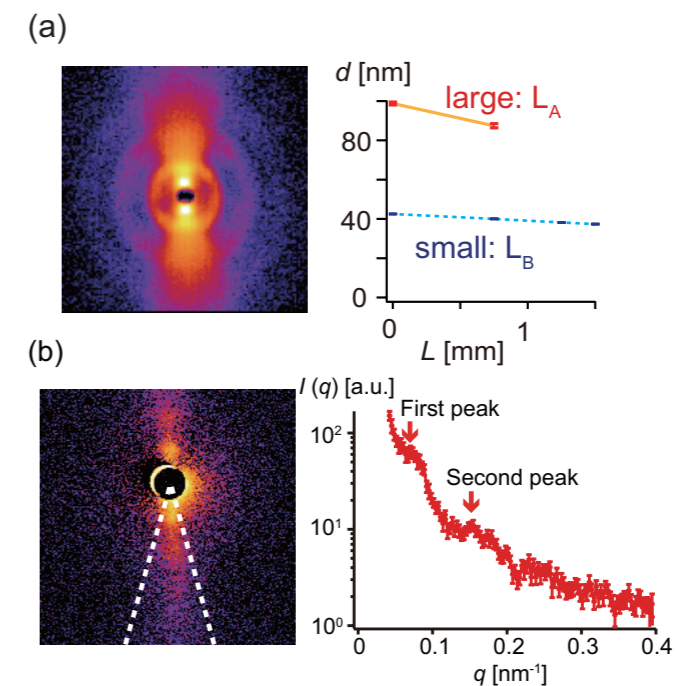


Figure 2: (a) (left) SANS image taken at the oil-water interface ($L = 0$ mm), where L denotes the distance from the oil-water interface in an aqueous phase. (right) Obtained repeat distance of the aggregate. Aggregate with small d (L_B) was confirmed everywhere, but aggregate with large d (L_A) was confirmed only when the beam spot was at the interface. The extension of L_A was at $L < 1$ mm. The error bars represent \pm one standard deviation. (b) (left) SAXS image taken at the oil-water interface. (right) Sector average of the image, where $q = 4\pi\lambda^{-1} \sin \theta$ (λ : X-ray wave length, 2θ : scattering angle), shows a first peak at $(0.071 \pm 0.003) \text{ nm}^{-1}$ which corresponds to $d = (89 \pm 4) \text{ nm}$. The error bars represent \pm one standard deviation.

We have ascribed the continuous formation of such elastic aggregates to the origin of interfacial motion [4]. However, the estimated pressure caused by the aggregate formation was too small to explain the induction of interfacial motion. In order to fully understand the mechanism of such deformation, we conducted more detailed analysis on the aggregate structure, focusing on the structural change upon a formation of aggregates at the oil-water interface. In the past SAXS measurements [3], the aggregate structure was measured at several mm away from the interface to avoid possible interference of the interfacial motion on the SAXS observations. However, in this study, we used small-angle neutron scattering (SANS) and SAXS, focusing on the spontaneously moving interface [6]. The SANS results showed that an aggregate with approximately twice larger d (≈ 80 nm) exists only in the proximity of the interface as shown in Fig. 2a. In attempting to confirm that this newly found aggregate exists at the oil-water interface, SANS measurements were limited in spatial and temporal resolution due to a large diameter of the neutron beam (2 mm) and long exposure time (10 min). Therefore, SAXS measurements were conducted on BL-6A and BL-10C, which have smaller beam size (0.25 mm \times 0.5 mm) and shorter exposure time (5 s). It was confirmed that the same aggregate with a larger repeat distance d (≈ 80

nm) exists only near the interface (Fig. 2b). Therefore, our observation showed that the aggregate undergoes a drastic transition from L_A whose typical d was 80 nm to L_B whose d was 40 nm as the aggregate detaches from the oil-water interface. Such drastic transition of the aggregate structure possibly induces elastic force within the aggregate. We believe these findings are the first clue to fully understanding the interfacial deformation [6].

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BEAMLINES

BL-6A and BL-10C

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