A Marangoni-Driven Molecular Automaton

We have succeeded in observing the dynamic structure of a water surface under Marangoni flow using a simultaneous multiple angle-wavelength dispersive X-ray reflectometer developed at AR-NE7A. We have repeatedly observed that lipid molecules at the air-water interface become regularly oriented normal to the surface at every onset of the Marangoni convective flow. In this phenomenon, cyclic chemical-mechanical energy conversion causes the water surface to flow intermittently and periodically. It should be regarded as a self-driven engine, and may assist understanding of the mechanism of rhythm generation that controls life activities such as heart beats.

Oscillatory behaviors are very common under non-equilibrium conditions. Imagine a weight hanging by a string. If no force acts on the weight, it remains stationary. If we pull it slightly away from the equilibrium position, it starts swinging, and the period and amplitude are very stable. Such oscillatory behavior is ubiquitous in biological systems, such as with breathing, heart beats, brain rhythm and circadian rhythm. The study of simple nonbiological systems provides clues for the understanding of biological rhythms.

Here, we focus on the spontaneous oscillation of surface tension caused by the Marangoni effect [1, 2]. Marangoni convection is a flow on a water surface due to a gradient of surface tension. When a surfactant droplet is suspended under the water surface [Fig. 1(a)], the surfactant molecules that diffuse to the water surface induce a continuous Marangoni flow. If a small amount of insoluble surfactant is spread on the water surface in advance, then spontaneous oscillations of the surface tension are observed. Regular oscillations have been observed for a couple of days [Fig. 1(b)]. If small particles are placed on the water surface, the particles will move quickly in the direction away from the capillary, in synchronization with the decrease in surface tension, and then slowly return to their original state. That is, Marangoni convection occurs intermittently and periodically. For convenience, we call the surfactant suspended under the water surface as "donor" and the surfactant spread on the water surface as "acceptor". The donor surfactant is partially soluble in water, whereas the acceptor surfactant is insoluble. We used long-chained alcohol as a donor surfactant and a lipid as an acceptor surfactant.

X-ray reflectometry of the water surface was performed to examine the structure of the surfactant monolayer at the atomic level during the spontaneous oscillation of surface tension. X-ray reflectivity measurements under dynamic conditions were performed with an acquisition time of 0.1 s using our recently developed simultaneous multiple-angle wavelength dispersive X-ray reflectometer [Fig. 1(c)] [3, 4]. In this system, a convergent X-ray beam which has continuously varying energy and glancing angle is reflected in the vertical direction by the liquid surface.
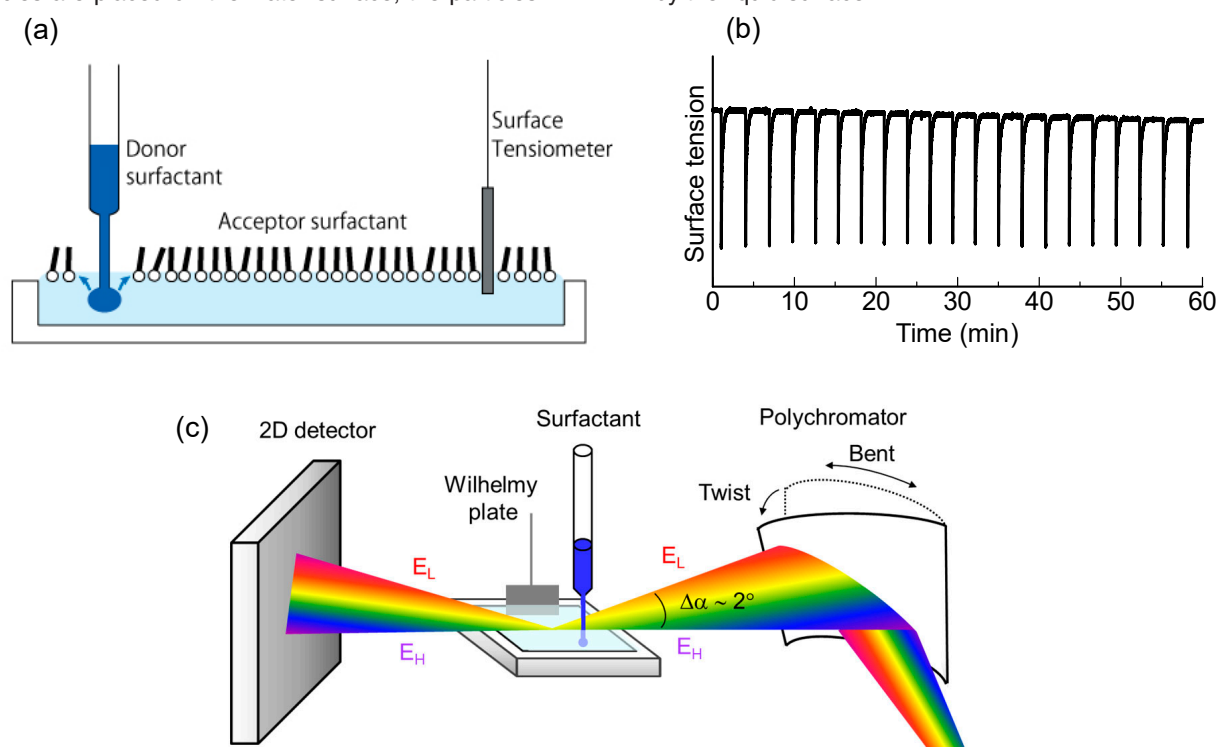

(a)
(b)
(c)

Figure 1: **(a)** Experimental setup. The surface tension is measured using a Wilhelmy plate. **(b)** Oscillations of surface tension produced by 1-octanol in the presence of a spread monolayer of DSPC. **(c)** Simultaneous multiple-angle wavelength dispersive X-ray reflectometer at AR-NE7A.
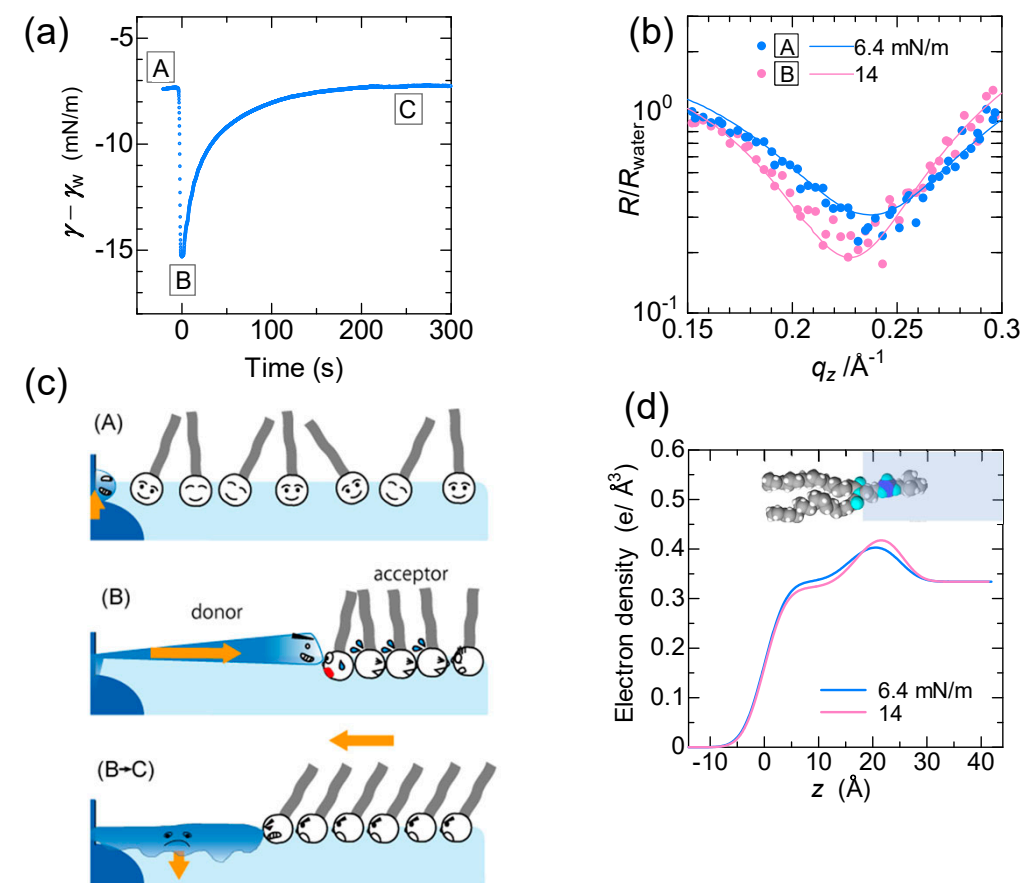

Figure 2: **(a)** Surface tension for DSPC/1-octanol. **(b)** X-ray reflectivity curves of DSPC films taken in states A (blue) and B (pink) divided by that of water. **(c)** Schematic illustration of the behavior of the donor and acceptor surfactants during the spontaneous oscillation of surface tension. **(d)** Electron density profiles corresponding to the fits of the reflectivity curves under the conditions of A and B. The z-axis is taken normal to the water surface. The peaks originate from the phosphor group of DSPC penetrated in the water.

We divided the oscillation of surface tension into three states [Fig. 2(a)]. The X-ray reflectometry curves taken under dynamic conditions for states A and B are shown in Fig. 2(b). The solid curves are the X-ray reflectivities of the 1,2-dioctadecanoyl-sn-glycero-3-phosphocholine (DSPC) monolayer at certain surface pressures. These curves coincide with those for the monolayers with Marangoni flow, which indicates that the monolayer was compressed to give a higher surface pressure in state B. We obtained the electron density profiles along the direction normal to the water surface by fitting the reflectivity data [Fig. 2(d)]. The peaks originated from the phosphor group that had penetrated the water. The difference in the electron density between the head and the tail groups for state B became larger than that in state A. The acceptor molecules in the monolayer became regularly oriented normal to the surface at a higher surface pressure. In the B → C process, the reflectivity curve gradually returned to that obtained in state A. These processes are illustrated in the cartoon [Fig. 2(c)]. A Marangoni flow pushes away molecules on the water surface in state B, then pushes back until they return to their original position.

In conclusion, we have determined the dynamic structure of self-assembled monolayers under sponta-neous oscillation of surface tension induced by the Marangoni effect at the molecular level. The molecules in the monolayer become regularly oriented normal to the surface at every onset of the decrease in surface tension. In this system, the collective motions of two surfactants interact with each other in a systematic manner to control a stable periodic motion: the donor molecules produce a Marangoni flow, and the acceptor molecules push the flow back. These could be fundamental units that produce biological rhythms.

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