Induced-current-generated System Using the Chemomechanical Transduction at a Nitrobenzene/Water Interface

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An induced-current-generated system using the nonequilibrium phenomena of water, nitrobenzene, and trimethylstearylammonium chloride is proposed. A nitrobenzene droplet spontaneously carried a small magnet around a coil, resulting in the induced current. Incidentally, we observed that the spontaneous rotation occurred without any contact with a glass substrate.

Spontaneous oscillation at liquid/liquid interfaces under isothermal conditions has been actively studied for the understanding of nonequilibrium systems and the construction of new chemomechanical transductions.[1–3] Spontaneous oscillations by alcohol transfer through water/alkane interface[4,5] and at water/nitrobenzene interfaces have much in common.[6–8] Sha et al. have reported that those spontaneous oscillation stably continued for 120 h and that the period was controllable by the interface area.[9] Those results are considered to initiate an artificial chemomechanical engine that originally existed in living organisms.[1] However, the concrete engineering application of such nonequilibrium systems has not been suggested. In this letter, we first report an engineering application of the spontaneous oscillation: an induced-current-generated system.

The schematic image of our system is shown in Figure 1a. Forty-five milliliters of 1 mM trimethyloctadecylammonium chloride in pure water was poured into a Petri dish with a diameter of 90 mm. A fan-shaped gap (35°) and a hole (40-mm diameter) were prepared in a transparent blue plastic rotor (75-mm diameter and 0.1-mm thickness). A plastic square blade (35 mm × 15 mm × 0.1 mm thickness) was hung on the side of the fan-shaped gap. Total volume of the rotor was 337 mm^3. A small magnet (Neodymium, 3-mm diameter, 3-mm thickness, 3100 G, N-005, Create Co., Japan) was attached to the rotor using epoxy. Neodymium is a light magnet (7.3 g/cm^3 density). The total weight of the rotor including the magnet was 0.579 g. The rotor was floated on the water phase. A commercially available coil (4-mH inductance, 8-mm diameter, and 3-cm length) was set in the rotor hole. The distance from the coil to the magnet was ca. 2 cm. A 4.7 Ω resistor was connected to the circuit.

A 3 mM iodine solution (0.5 mL) in nitrobenzene saturated with potassium iodide was poured into the fan-shaped gap of the rotor. The induced current was measured using a picoammeter (Model 6487, Keithley) every 0.07 s. The total circuit resistance was 140 Ω (including the internal resistance of the picoammeter, 80 Ω). The movement of the nitrobenzene droplet was successively monitored using a digital video camera (NTSC DC40, Canon). All the measurements were carried out at room temperature (ca. 21 °C). The movies of the digital video camera were analyzed by editing software (Power Director, Cyber Link).

When the rotor was floated on the water phase, the magnet on the rotor faced north and functioned as an azimuth compass

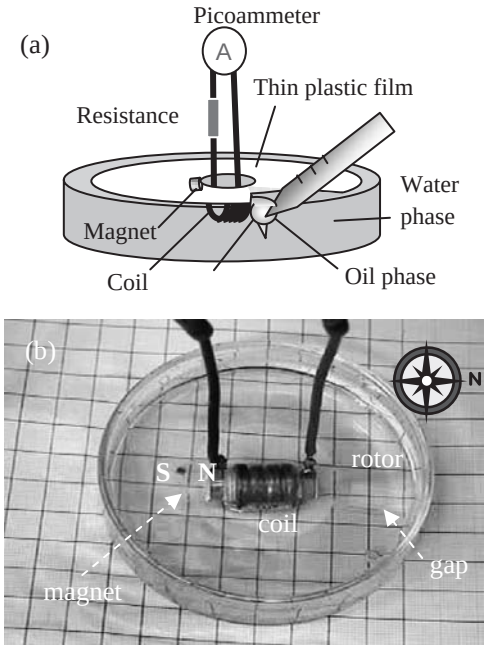

Figure 1. Schematic image (a) of our induced-current-generating system using interface-tension change. The digital camera image was obtained before pouring the nitrobenzene droplet was shown in (b). The black lines on the sheet are at intervals of 1 cm.

(Figure 1b). The value of the geomagnetic force was not uniform because it strongly depends on a solar wind. We used values obtained in Kakioka city, Ibaraki prefecture, Japan, in June, 2007: the horizontal component of the geomagnetic force B_h, 30023 nT.[10] The magnetic charge of our magnet Q_m was calculated as 2.5×10^{-5} Wb from multiplying the magnetic flux density by the cross-sectional area of the magnet. Thus, the horizontal geomagnetic force on our magnet F_H is ca. $Q_m \times B_h = 0.75$ [nN].

The rotor began to rotate when a nitrobenzene droplet was poured in the fan-shaped gap (see also the movie in Supporting Information).[15] In consequence, the horizontal component of the spontaneous movement F_m was larger than $F_H/r = 20$ nN, here r is the radius of our rotor (37.5 mm). The maximum value of the interface-tension change was reported as 15 mN m^{-1}.[11] Sweepingly, the length of the interface that contributed to the spontaneous movement is considered as larger than 20 nN/15 mN m^{-1} = 1.3 μm. The digital camera images show that the total length of the interface on the nitrobenzene droplet was obviously larger than 1.3 μm.

As the rotor was rotated, the attached magnet on the rotor also rotated around the coil. The electric current in the coil was plotted in Figure 2. The baseline showed the negative value.

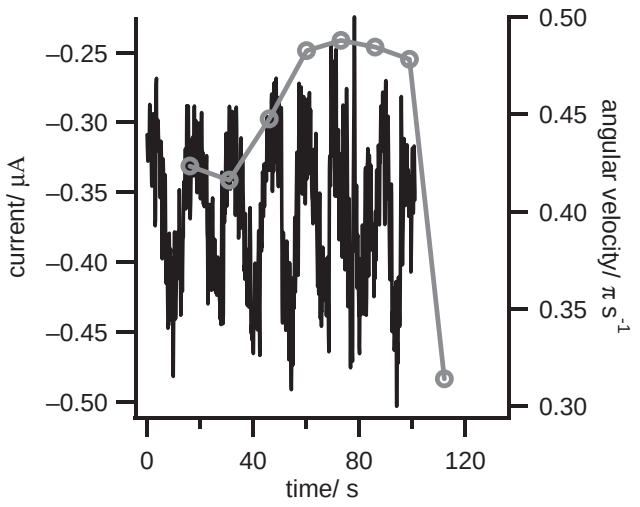

Figure 2. Time-dependent induced current (solid line) and angular velocity (full square).

This was because of the fluctuation of the ambient electromagnetic wave. Despite the existence of noise, the current was increased and decreased repeatedly. The angular velocity of the nitrobenzene droplet, ω, was also measured at each cycle (Figure 2). ω was measured slightly longer than the induced current. This is because the maximum memory of our picoammeter was 1500 times per measurement, and the oil rotation continued longer, i.e., longer than 0.07 [s/time] $\times$ 1500 [times] = 105 [s]. The longevity of the rotation is discussed below. ω was in the range of 0.3π–0.5π/s. Let us discuss ω and the current. For the first 30 s, ω was ca. 0.41π/s, the amplitude of the current was ca. 0.12 μA, and the period of the current was $\approx$10 s. ω was gradually increased and reached 0.5π/s. As ω was increased, the current also increased till 0.15 μA, and the period of the current became shorter. Obviously, the phase of the current was in agreement with the phase of ω. The authors conclude that the current was the induced electric current by the spontaneous rotation of the magnet.

The red color of the droplet, which was due to I_3^- anions, became diluted during the rotation because the anions were consumed in a chemical reaction with the surfactant. The final products should be $H_{46}C_{21}{}^-N^+$–I_3^- and KCl. Simultaneously, the droplet became cloudy. The aggregation of $H_{46}C_{21}{}^-N^+$–I_3^- was the components of the cloudiness. Gradually, the velocity of the droplet became slow and the shape of the droplet became flattened. This change of the shape means the tension at nitrobenzene/water interface became weak during this spontaneous movement. Finally, the movement of the droplet was stopped at the bottom of the Petri dish, and the induced current was removed. The longevity of the spontaneous movement was not uniform (1–15 min). The longevity seems to be related with many experimental parameters, such as the geomagnetic force, temperature, humidity, etc. The spontaneous motion could be restarted by the addition of I_2, as has already been reported.[12] This result suggests that the longevity of the electric current generation can be controlled by the amount of I_2.

It has been pointed out that the role of the solid wall is crucial for this spontaneous rotation experimentally[13] and theoretically.[14] However, we observed the oil droplet was rotated without any contact with the glass wall. The buoyant force due to our rotor acted on the droplet, resulting in such noncontact-droplet movement. Clockwise and anticlockwise rotations were observed. That means the oil/water interface was moved to both phases: from oil to water and from water to oil. The anticlockwise rotations had higher angular velocities than the clockwise rotations had. Concretely, the mean angular velocities of the anticlockwise and clockwise rotations were 1.1π/s–1.2π/s and 0.8π/s–0.9π/s, respectively. The authors are speculating that the Marangoni convection caused the difference of the angular velocities. The oil droplet that rotated anticlockwise moved into the surfactant-rich water phase and may have the larger fluctuation of the o/w interface.

Previous researchers have pointed out that the cationic-surfactant transfer from the water phase to the oil phase is an important factor of this spontaneous oscillation.[8,13,14] In these studies, the surfactant adsorption on the glass wall was reported as the dominant factor for the spontaneous movement. Meanwhile, the potassium ion had not been considered. Now we consider that K^+ concentration near the o/w interface is also an important factor for the oscillation, resulting in such noncontact-droplet movement.

We reported an induced-current-generated system using a spontaneous surface-tension change at the nitrobenzene/water interface. The longevity of the electric current generation could be controlled by the amount of I_2. We also observed that the spontaneous rotation was occurred without any contact with the solid substrate. We hope these results will help growing and understanding of this spontaneous oscillation phenomenon.

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15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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