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Chemomechanical Transduction in an Oil–Water System. Regulation of the Macroscopic Mechanical Motion[#]

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Self-movement of an oil–water system induced by chemically-driven Marangoni instability was studied. Depending on the shape of the vessel and the amount of oil and water solutions, various modes of movement were generated, such as random, rotational, and ameba-like. The most significant finding is the realization of a spatially directed mechanical movement. The mechanism of such chemomechanical transduction is discussed in relation to an imbalance of the interfacial tension due to a nonlinear oscillation at the interface.

Instability of the interfacial tension due to temperature gradient or chemical concentration-gradient causes a spontaneous agitation of the interface between liquids. For example, when water containing a surfactant is placed in contact with an oil, interfacial agitation of the order of a cm is generated spontaneously. Such a phenomenon is known as the "Marangoni effect."[1,2] In the 1970's Dupeyrat and Nakache found a quasi-periodic variation of the electrical potential and interfacial tension in an oil–water system, where a cationic surfactant was dissolved in the water phase.[3] They also reported on a macroscopic self-agitation of the oil and water interface. It is noted that in this phenomenon the chemical energy stored in the non-equilibricity of the solute concentrations between the oil and water phases is directly converted to macroscopic kinetic energy. Such a chemomechanical transduction is quite interesting compaired with the mechanism of energy transduction in muscle, which is based on a dissipation of the chemical energy in ATP. In relation to this, several kinds of motion in oil–water systems have been described.[1—9] However, there has been no report concerning the macroscopic vectorial motion induced to a desired direction, along with the direct conversion of chemical energy.

We are currently studying rhythmic phenomena in oil–water systems. We have found the followings.[9—14] 1) A periodic oscillation in the electrical potential and surface tension is generated with high reproducibility; 2) Oscillations have been observed in the presence of various kinds of surfactant molecules, such as hexadecyltrimethylammonium bromide, sodium dodecyl sulfate, sodium oleate, and phosphatide; 3) The driving force of the oscillation is the difference in the chemical potential of the surface-active compounds between the oil and water phases; 4) The oscillation and self-movement of the interface are attributed to a periodic formation and destruction of the surfactant monolayer at the interface. In the other words, high nonlinearity in the process of transportation of surfactant molecules through the interface is deeply concerned with the oscillation.

As an extension of these studies we report here on the spontaneous vectorial movement in an oil–water system. We discuss the mechanism of such a macroscopic motion in relation to the interfacial instability due to the periodic change of the interfacial tension.

Experimental

Analytical-grade reagents were commercially available. The compositions of the aqueous and oil solutions were as follows: The aqueous phase was 1 mM trimethyloctadecylammonium chloride ($1\text{M}=1\ \text{mol}\,\text{dm}^{-3}$), and the organic phase was a 2 mM iodine solution of nitrobenzene saturated with potassium iodide. Trimethyoctadecylammonium chloride was prepared through recrystallization from acetone. All at the measurements were carried out at room temperature (18±2 °C). The movement of the oil–water system was successively monitored with a VHS video camera (Panasonic NV-S9) and recorded on video tape. Each frame on the video image was fed to a personal computer with a desired time interval using a digitizer, and was numerically analyzed so as to obtain the desired physico-chemical parameters, such as the position of the interface and the contact angle. The minimum time resolution was 1/30 s.

Results

Figure 1 exemplifies the self-movement in an oil–water system in a petri dish having a diameter of 45 mm, and shows the random motion of the oil–water boundary. Figure 2a shows the self-movement of an oil droplet under an aqueous phase in an annular container, where the outer and inner diameters are 50 and 35 mm, respectively. In order to evaluate the oil motion quantitatively, the time dependence of the angular velocity of the center of mass was analyzed (Fig. 2b). This indicates that the oil droplet tends to maintain one-directional rotation for a while, but then switches to the other direction, and so on; in other words, the self-movement maintains a weak memory for a short period. A comparison of the results given in Figs. 1 and 2 shows that the liquid motion is strongly affected by such boundary conditions as the shape of the container and the amounts of aqueous and oil solutions.

As the next step, we introduced an aluminum rotor with a chiral asymmetric shape onto a petri dish, and then poured oil and water solutions successively between the wings. With this simple apparatus, the

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[#] Dedicated to the late Professor Hiroshi Kato.

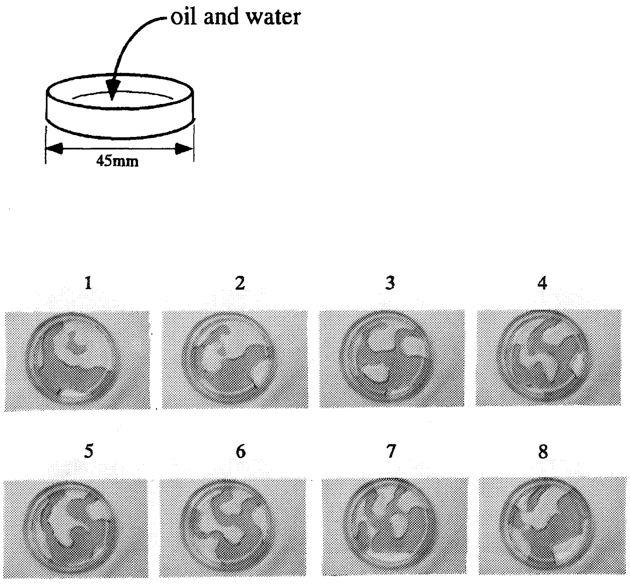

Fig. 1. Random motion of an oil–water system in a petri dish with a time interval of 0.3 s. The volume of aqueous and oil phases was 2 ml each. Such a spontaneous agitation continued for about 10 min.

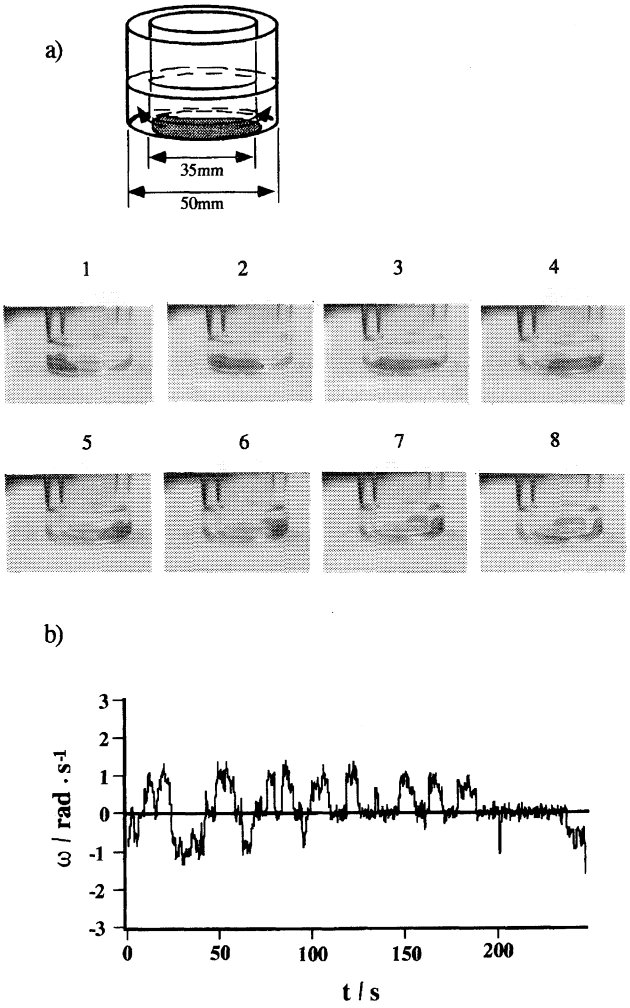

Fig. 2. a) Spontaneous motion of an oil droplet (2 ml) under an aqueous phase (10 ml) in an annular container. b) Time trace of the angular velocity of the center of mass for the oil droplet. The movement was digitized with a time interval of 1/10 s. The angular velocity was obtained as the first derivative thought the procedure of a 9 point least-squares fitting.[19]

aluminum rotor exhibits a cyclic-type movement in only one-direction in a deterministic manner, depending on the chiral asymmetry of the shape of the rotor (Fig. 3a and c). As the self-movement is maintained, accompanied by dissipation of the chemical energy, the magnitude of the angular velocity gradually decays (Fig. 3b and d).

We have thus succeeded in realizing regulated macroscopic motion driven by chemical nonequilibrium. In order to shed light on the mechanism by which the asymmetric boundary condition induces directional motion, we carried out an experiment with a smaller number of interfaces between the oil and water, as in Fig. 4a. In this experiment, there was only one "free" interface, whereas the other interface was fixed almost perpendicularly to the bottom wall due to the effect of contact with the "wing" of the aluminum rotor. Here again, we also succeeded in generating a directed rotational motion of the oil–water solutions. From the video record of the motion, the temporal change in the contact angle of the "free interface" at the bottom surface of the petri dish was measured together with the time dependency of the angular velocity. It has been confirmed that the contact angle of the "fixed interface" to the aluminum wing remained at almost 90° during the rotational motion (see Fig. 5).

Figure 6 shows the relationship between a) the angular velocity and b) the angular acceleration of the aluminum rotor with the contact angle of the "free interface". The contact angle was read directly from the video image without any correction. This implies that the experimental error is relatively large in the left- and right-hand portions of the figure. The angular acceleration was calculated based on a simple fine-differentiation of the angular velocity. It is clear that the temporal changes were almost synchronized between the contact angle and the angular acceleration. Only when the contact angle became below 90°, did the system exhibit a positive acceleration. We analyzed the movement for five experiments under the same experimental condition as given in Figs. 4 and 5, and confirmed the general tendency of the temporal change of this system, as is schematically represented in Fig. 7. It is noted that the oscillatory profile of the interfacial tension (γ) has already been confirmed in our previous studies.[9,14] In the next section we try to clarify the mechanism of the directed chemomechanical transduction based on the general trend given in Fig. 7.

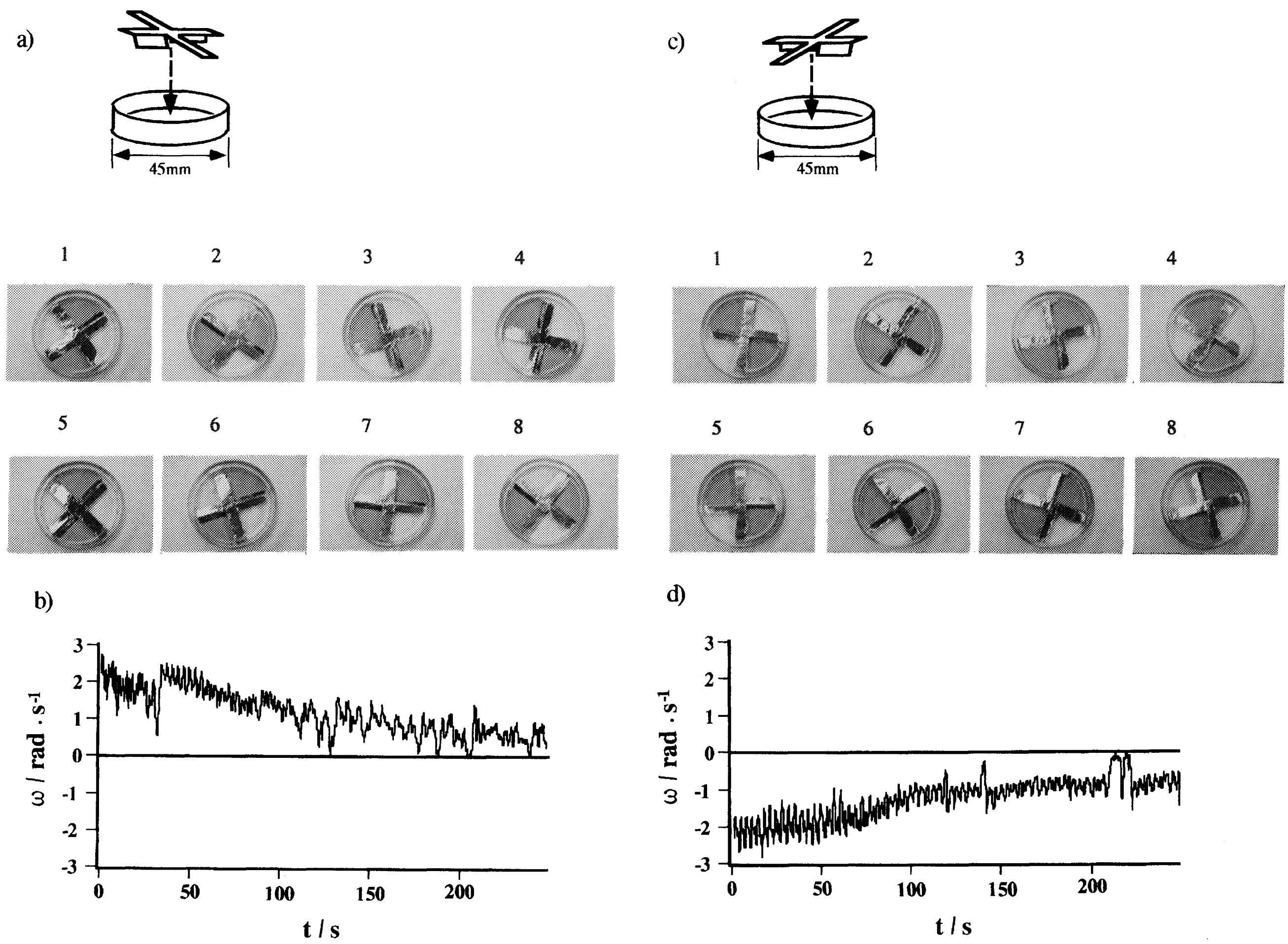

Fig. 3. a) Clockwise rotation and c) anticlockwise rotation of the chiral aluminum rotor in a petri dish. The aqueous and oil solutions, 3.5 ml each, were poured between the wings, individually. The photographs in b) and d) are the time-dependency of the angular velocity in experiments a) and c), respectively.

Discussion

More than a couple of decades ago, Dupeyrat and Nakache found that spontaneous self-movement is generated in a quasi-periodic manner in an oil–water system,[3] in which a cationic surfactant is dissolved in the water, and potassium iodide, together with iodine, is dissolved in nitrobenzene. We found that a rhythmic oscillation of the electrical potential and pH is spontaneously generated in a similar system.[9—11] In the present article, we have already demonstrated that a uni-directional rotational movement is generated upon the introduction of an "achiral" rotor. We now briefly describe the mechanism of the temporal oscillation of the interfacial tension and the electrical potential, based on knowledge obtained from our extensive studies concerning the oscillation at the oil/water interface.[9—14]

During the initial stage of our experiment, surfactant molecules were present only in the aqueous phase; potassium iodide and iodine were in the oil phase. The surfactant molecules diffused onto the surface and gradually formed a monolayer at the interface. In the mean time, I^- anions interacted with I_2 molecules to form hydrophobic anions, I_3^-. These I_3^- anions also diffused onto the interface and were located near to the interface as the counter anions of the cationic head groups of the surfactant molecules. The concentration of the surfactant molecules at the interface thus gradually increased. In other words, the surface pressure increased with time. When the surface pressure reached an upper critical value, the monolayer collapsed and the cationic surfactants migrated into the bulk oil-phase in a cooperative manner, forming reversed micelles together with the hydrophobic I_3^- anions. As a result, the surface concentration of the cationic surfactant at the interface or the surface pressure abruptly decreased and, then, a gradual formation of the monolayer began again. Since the change in the surface pressure due to the surfactant molecules is directly related to that of the interfacial tension, the above-mentioned process causes a "macroscopic" fluctuation of the interfacial tension due to a "nonlinear" transportation, or diffusion, of the surfactant molecules through the interface. It is therefore, plausible that a macroscopic movement of oil droplets in an aqueous solution (Fig. 1) is induced when the temporal fluctuation of the surface tension is not syn-

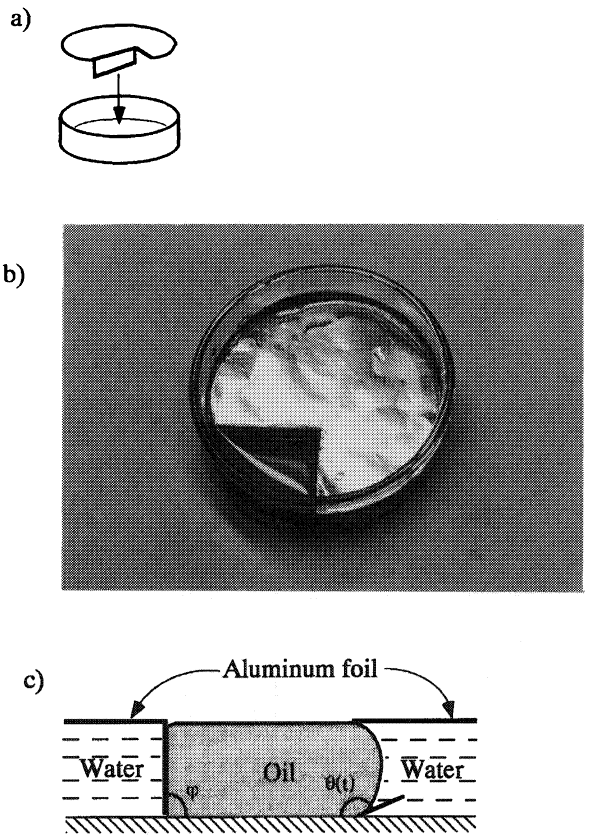

Fig. 4. a) Experimental apparatus with an aluminum rotor. b) Photograph of a). c) Schematic representation of the shape of the interface. The contact angle (φ) with an aluminum wing was fixed at around 90° due to the effect of contact with an aluminum wing. The contact angle (θ) at the "free interface" shows a marked rhythmic change. In this case, the oil droplet moves from right to left accompanied by the motion of the aluminum rotor. The volumes of the organic and aqueous phases were 2 and 5 ml, respectively.

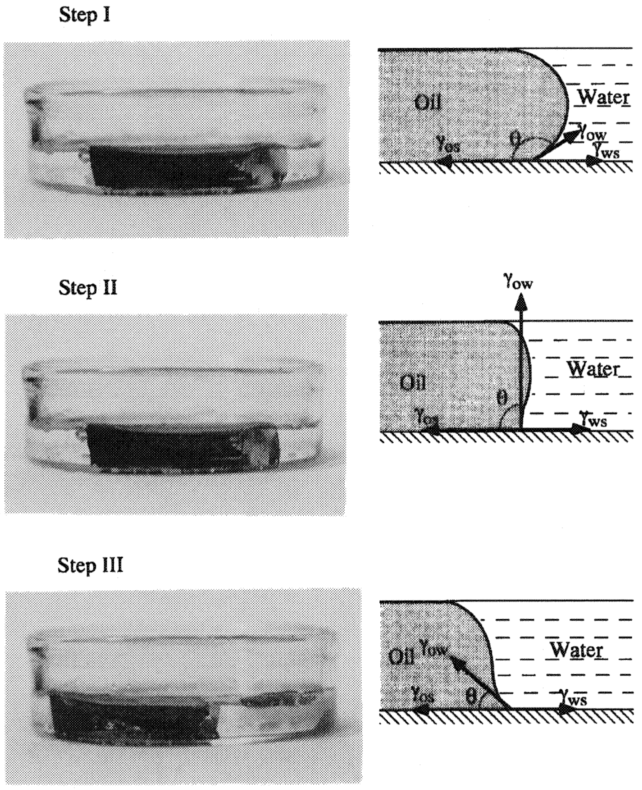

Fig. 5. Photographs (left side) and their schematic representation (right side) indicating the oscillatory change of the contact angle at the back-side portion of the oil droplet, and the entire rotational motion in a petri dish.

Step I: Young's relationship almost holds; $\gamma_{ws} = \gamma_{os} + \gamma_{ow} \cos\theta$. There is essentially no driving force due to the imbalance of the interfacial tension.

Step II: Accompanied by an abrupt increase of γ_{ws}, θ decreases rapidly.

Step III: Due to an abrupt increase of γ_{ow} in Step II, the contact angle (θ) temporally decreases below 90°. A relatively large driving force exists because of the imbalance, $\gamma_{ws} \ll \gamma_{os} + \gamma_{ow} \cos\theta$. Thus, the oil droplet is accelerated in the left direction.

chronize over the entire interface.

As already mentioned in the Results section with respect to Fig. 6, a sudden decrease in the contact angle (θ) or the phase inversion through 90°, is clearly associated with the acceleration process. This suggests a mechanism according to the following cycle of steps: I→II→III (Fig. 5). In step I, θ is greater than 90° and Young's equation,[15] $\gamma_{os} + \gamma_{ow} \cos\theta = \gamma_{ws}$, almost holds. Here, γ is the interfacial tension and suffixes o, w, and s represent the oil, water, and solid substrate, respectively. There exists essentially no driving force in this step. In step II, accompanied by a sudden increase in the interfacial tension, θ decreases toward 90°. The abrupt decrease in θ may induce a motion of the liquid around the free interface. Due to the inertial effect of the liquid motion, the contact angle (θ) overshoots below 90°, as in step III. As a result, an inversion of the contact angle generates a large imbalance of the interfacial tension. Since it is expected that the temporal changes of γ_{os} and γ_{ws} are rather slow, the change in the sign of $\cos\theta$ produces a large acceleration force. The contact angle changes from step III to step I spontaneously, since step III is unstable due to an instability of the surface tension. Thus, similar cycles of steps continue.

We now evaluate the effect of the instability of the interfacial tension on the macroscopic motion in a semi-quantitative manner.

We start the discussion with the Navier–Stokes equation for an incompressive fluid. We consider only the mass of the fluid, since the weight of the aluminum rotor (0.05 g) is negligibly small:

$$\frac{\partial \boldsymbol{u}}{\partial t} + \boldsymbol{u}\, grad\, \boldsymbol{u} = \boldsymbol{K} - \frac{1}{\rho}\, grad\, p + \nu \nabla^2 \boldsymbol{u}, \qquad (1)$$

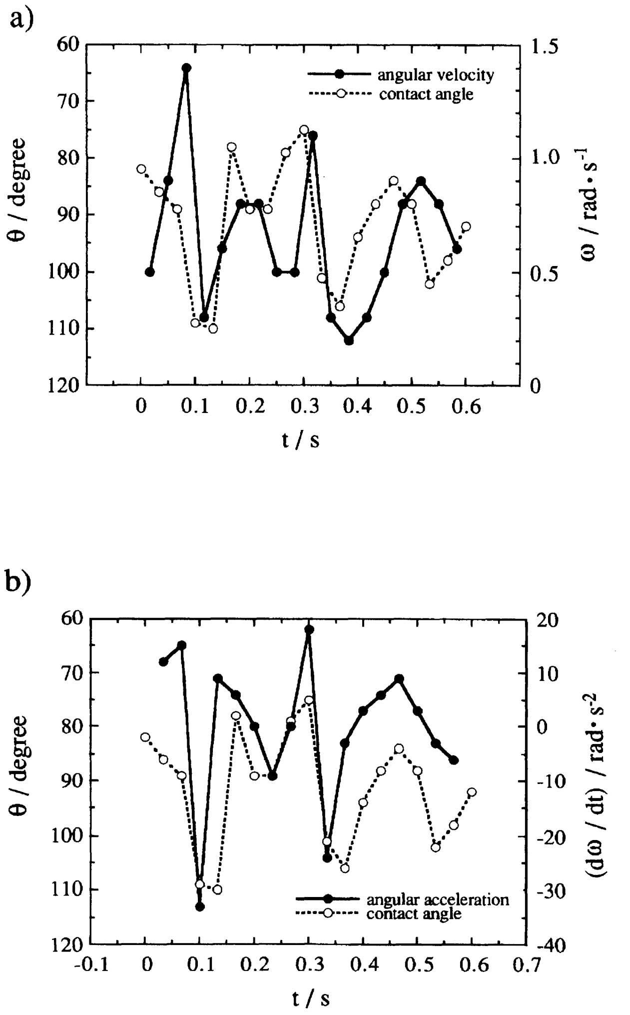

Fig. 6. Relationship of a) the angular velocity and b) the angular acceleration of the aluminum rotor with the contact angle θ in the experimental system of Fig. 4.

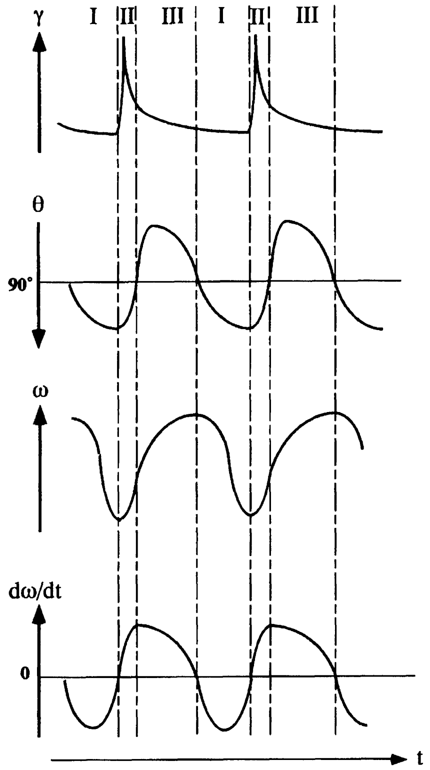

Fig. 7. Schematic diagram of the temporal changes of the interfacial tension (γ), contact angle (θ), angular velocity (ω), and angular acceleration ($\mathrm{d}\omega/\mathrm{d}t$).

where $\boldsymbol{u}$ is the velocity of the fluid, ρ the density, $\boldsymbol{K}$ the external force (including the effect of the interfacial instability), p the pressure and $\nu=\mu/\rho$ the kinematic viscosity, where μ is the coefficient of viscosity. Taking *rot* for both sides of the equation, we obtain

$$\frac{\partial}{\partial t}(rot\ \boldsymbol{u}) = rot\ \boldsymbol{K} + rot(\boldsymbol{u} \times rot\ \boldsymbol{u}) + \nu\nabla^2(rot\ \boldsymbol{u}). \quad (2)$$

The term (*rot* $\boldsymbol{u}$) is usually referred to as the vorticity in fluid mechanics, and is correlated with the angular velocity ($\boldsymbol{\omega}$) of a certain small part of the fluid, as follows:

$$\omega = \frac{1}{2} rot\ \boldsymbol{u}. \quad (3)$$

Figure 4 shows that the motion of the oil/water system has a nearly uniform angular velocity, on the whole. Thus, it may be possible to describe the motion of a system with only the vertical z component of $\boldsymbol{\omega}$, i. e., $\boldsymbol{\omega}=(0,0,\omega)$, where $\omega=\omega(z)$. From this assumption, the viscous term becomes as in Eq. 4, where $\boldsymbol{k}$ is the unit vector along the z-axis perpendicular to the bottom plane.

$$\nu\nabla^2(rot\ \boldsymbol{u}) = 2\nu\frac{\partial\omega^2}{\partial z^2}\boldsymbol{k} \quad (4)$$

For the rotational motion in our system, the second term on the right-hand side of Eq. 2 does not contribute much to the change of ω, because $\partial\omega/\partial z$ is rather small. From these considerations, the motion of the system becomes similar to the rotation of a "rigid body", except for the term due to the viscosity. Thus, by substituting the *rot* $\boldsymbol{K}$ term in Eq. 2 into $2N/I$, the temporal change in the angular velocity (ω) becomes

$$\frac{\mathrm{d}\omega}{\mathrm{d}t} = \frac{N}{I} + \nu\frac{\partial^2\omega}{\partial z^2}, \quad (5)$$

where I is the moment of inertia and N is the momentum of the force originating from the interfacial instability. In our experimental system, as in Fig. 4, I and N are given as

$$I = \int_0^R \rho h r^2(2\pi r)\mathrm{d}r = \frac{\pi\rho h}{2}R^4 \quad (6)$$

and

$$\begin{aligned} N &= f(t)\int_0^R r\mathrm{d}r + hRf(t) \\ &= \frac{1}{2}R^2 f(t) + hRf(t), \end{aligned} \quad (7)$$

where ρ is the density of the liquid, h the height of the solution, and R the radius of the petri-dish. Function $f(t)$ is the net force per unit length which works along the line of the "free" interface on the bottom of the solid surface, which originates from an imbalance of the interfacial tension. It is assumed that $f(t)$ is an independent function with respect to r. The first and second terms in Eq. 7 correspond to the effect due to the interfacial tension on the bottom wall and on the side wall, respectively. For simplificity, the difference of the ρ's between oil and water and the mass of the aluminum rotor are ignored.

It seems to be difficult to evaluate the viscous term precisely, due to the rather complicated boundary condition of the system. From a careful observation of the motion, the effect of friction with the solid surface seems to contribute more significantly to the viscous term, rather than the bulk viscosity in the liquid phases. Here, we discuss only the magnitude of the positive acceleration of ω driven by the interfacial instability. We would like to try to obtain the essential feature for accelerating ω immediately after an inversion of the contact angle from step I to step III (see Fig. 7).

Using Eqs. 6 and 7, the acceleration of ω can be evaluated as

$$\frac{\mathrm{d}\omega}{\mathrm{d}t} = \frac{f(t)(1+2h/R)}{\pi\rho h R^2}. \tag{8}$$

From previous studies[9,14] concerning measurements of the temporal change of the interfacial tension, it is assumed that $f(t) \sim \Delta(\gamma \cos\theta) \approx 10$ dyn cm^{-1}. Using the parameters $h \approx 0.6$ cm, $R \approx 2.5$ cm, and $\rho \approx 1$ g cm^{-3}, $\mathrm{d}\omega/\mathrm{d}t$ is cstimated as

$$\frac{\mathrm{d}\omega}{\mathrm{d}t} \sim 1 \text{ rad/s}^2.$$

The sign "$\sim$" denotes the order of the quantity. As indicated in Fig. 5, in step III the difference between γ_{os} and γ_{ow} is expected to contribute to the driving force in addition to the above effect. Thus, the angular acceleration will become the order of several rad/s^2. In Fig. 6, the acceleration of the angular velocity just after the inversion of $\cos\theta$ is several rad/s^2. We therefore believe that the essential feature of the chemomechanical motion in our system has been clarified. For a detailed consideration, an additional term of acceleration should be taken into account due to the mass flow induced by the sudden change of θ from step I to step III. Viscous damping of the motion is also very important in order to explain the characteristics in a quantitative manner. Further studies are awaited which include these effects on the macroscopic motion. Though the present study is only preliminary, we believe that we have found the most essential part of the mechanism of chemomechanical transduction in an oil–water system.

According to the Curie–Prigogine theorem,[16—18] the vector processes connot couple with the scalar variables, such as chemical reactions, in a "linear" system with an isotropic environment. Thus, chemomechanical coupling becomes possible along with either a violation of the linear or isotropic condition. However, it is expected that effective chemomechanical coupling is realized with a double neglect of the linear and isotropic conditions. In this report we have demonstrated that the generation of a macroscopic "deterministic" vectorial-movement is generated in a chirally asymmetric environment for a nonlinear dynamical system driven by a chemical potential gradient.

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