Intermittent Motion of a Camphene Disk at the Center of a Cell

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The self-motion of camphene on water was investigated as a simple example of an autonomous motor. When a camphene disk was floated on water in a small Petri dish as an isotropic system, intermittent motion (alternating between rapid motion and rest) was observed at the center of the Petri dish. The floating state of the camphene disk changed periodically in association with the intermittent motion. When a camphene disk connected to a plastic boat as an anisotropic system was floated on water, uniform motion was observed. The nature of this self-motion is discussed in relation to the floating state of the camphene disk depending on convection and the surface tension of the camphene layer as the driving force.

1. Introduction

Studies of autonomous motors under isothermal conditions may help us to not only understand chemomechanical transduction in biological systems but also to create novel artificial motors that mimic living organisms. All motor organs or organelles in living organisms work through the dissipation of chemical energy under almost isothermal and nonequilibrium conditions. Several artificial systems which exhibit self-motion under conditions of chemical nonequilibrium have been studied under almost isothermal conditions.[1−20]

We have been studying the self-motion of a camphor solid or a camphor boat.[16−20] We reported that the nature of the self-motion of a camphor solid changes depending on both internal conditions (e.g., scraping morphology)[16,17] and external conditions (e.g., temperature, surface tension, and the shape of the cell)[18−20] and that the essential features of self-motion can be reproduced by a computer simulation.[16,18−20]

In the present study, the intermittent motion (alternating between bursting motion and rest) of a camphene disk was observed at the center of a cell when the camphene disk was floated on a water surface as an isotropic system. Uniform motion was observed when the camphene boat was floated on a water surface as an anisotropic condition. The floating state of the camphene disk on the water surface changed synchronously with the intermittent motion. The nature of this self-motion is discussed in relation to the distribution of the camphene layer supplied from the solid and the floating state of camphene on the water surface.

2. Experimental Section

Camphene was obtained from Wako Chemicals (Kyoto, Japan). Water was first distilled and then purified with a Millipore Milli-Q filtering system (pH of the obtained water, 6.3; resistance, >20 MΩ). A camphene disk (diameter, 3 mm; thickness, 1 mm) was prepared using a pellet die set for FTIR. A camphene boat was prepared by connecting a camphene disk to a polyester plastic boat (surface area, 9 mm^2; thickness, 0.1 mm).[20] The camphene disk or boat was floated on water (thickness of the water phase, 10 mm) in a glass Petri dish. The temperature of the water cell was adjusted to 293 ± 1 K with a thermoplate (TP-80, AS ONE Co. Ltd., Japan).

The movement of the camphene disk or camphene boat was monitored with a digital video camera (SONY DCR-VX700; minimum time-resolution, 1/30 s) and then analyzed by an image-processing system (Himawari, Library Inc., Japan).

3. Results

Figure 1 shows (a) snapshots of the motion of a camphene disk in a cell with a small surface area, (b) time traces of the velocity of such motion, and (c) time traces of the distance between the camphene disk and the center of the cell, *L*. Initially, the camphene disk moved slowly to the center of the cell and settled there. Several minutes later, the disk rapidly moved away from the center at a maximum velocity of ca. 100 mm s^{-1}, as seen in Figure 1a-1. The disk then slowly returned to the center, as seen in Figure 1a-2. This switching from rest at the center of the cell to bursting motion was repeated at least five times in individual experiments, and the direction of bursting was random. One hour after the camphene disk was placed on the water surface, it almost stopped at the center of the cell.

Figure 2 shows (a) snapshots of the motion of a camphene boat on water with a large surface area and (b) the velocity of this motion. Uniform motion at ca. 30 mm s^{-1} was maintained for at least 30 min, but this sometimes included rapid motion. When the plastic boat was floated in a cell with a small surface area as in Figure 1, uniform motion was maintained for several tens of seconds, and the camphene boat then settled at the center of the cell. When the plastic boat was smaller than in the present experimental condition, rotational motion with a constant velocity was observed and the number of bursts increased.

Figure 3 shows snapshots of the floating state of a camphene disk during bursting motion on water with a small surface area. Figure 4 shows the time variation of the height of camphene from the water surface, *h*, for the phenomena shown in Figure 3. The camphene disk gradually swelled at the water surface and *h* also increased with time, as seen in 1−5. The floating camphene sank and a visible camphene layer developed around the disk simultaneously with the bursting motion, as seen between 5 and 6. After this bursting motion, the camphene gradually floated, as seen in 8−12. Thus, switching between

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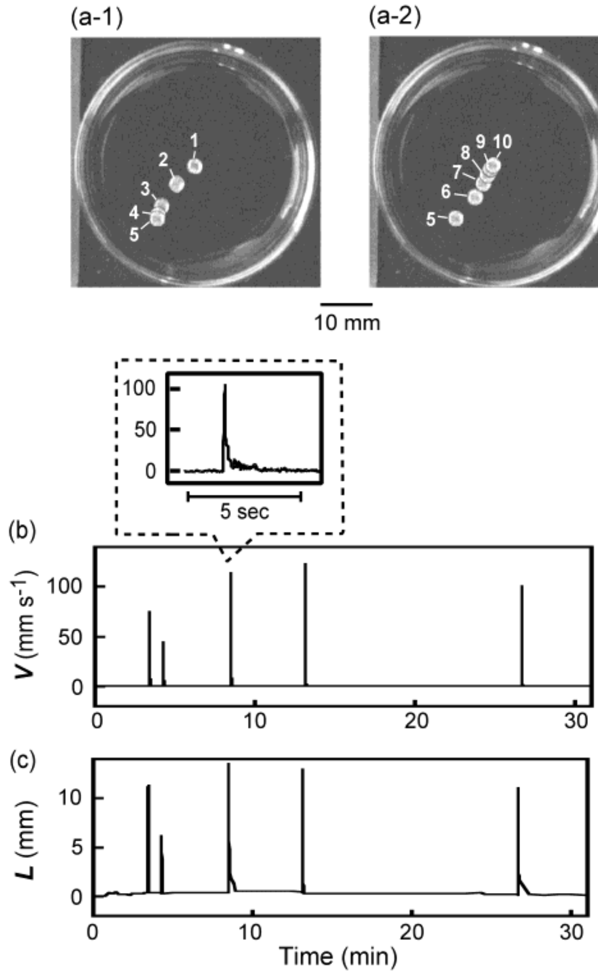

Figure 1. Intermittent motion of a camphene disk starting from the center of a small cell (surface area, 15 cm^2). (a) Snapshots of (1) bursting motion from the center and (2) slow motion to the center (top view). The track of the disk was numbered from 1 to 10 (time interval, (a-1) 0.1 s and (a-2) 1.0 s). (b) Time variation of the velocity of the camphene disk, V (mm s^{-1}). The velocity profile in (a) was expanded in (b) at $t = 8.5$ min. (c) Time variation of the distance from the center of the cell, L (mm).

sinking and floating of camphene was observed in association with bursting motion.

Figure 5 shows the time variation of surface tension during the bursting motion. When a camphene disk was dropped on the water surface, the surface tension rapidly decreased by 7 mN m^{-1} and then gradually decreased with time. The surface tension rapidly decreased by 2 mN m^{-1} with each bursting motion and gradually increased after bursting.

Figure 6 shows the visualization of convective flow with uranin around the camphene disk when the camphene settled at the center of the cell. When the camphene settled, convective flow was clearly observed. On the other hand, the degree of convective flow decreased with an increase in the velocity of the camphene motion (data not shown).

4. Discussion

On the basis of our experimental results and previous papers on the self-motion of camphor,[14-20] we can discuss the mechanism of the intermittent bursting motion of camphene disk at the center of a cell.

For a camphene disk with a small surface area, it is difficult for such a disk to move unidirectionally because a camphene layer develops around the disk isotropically. Therefore, the

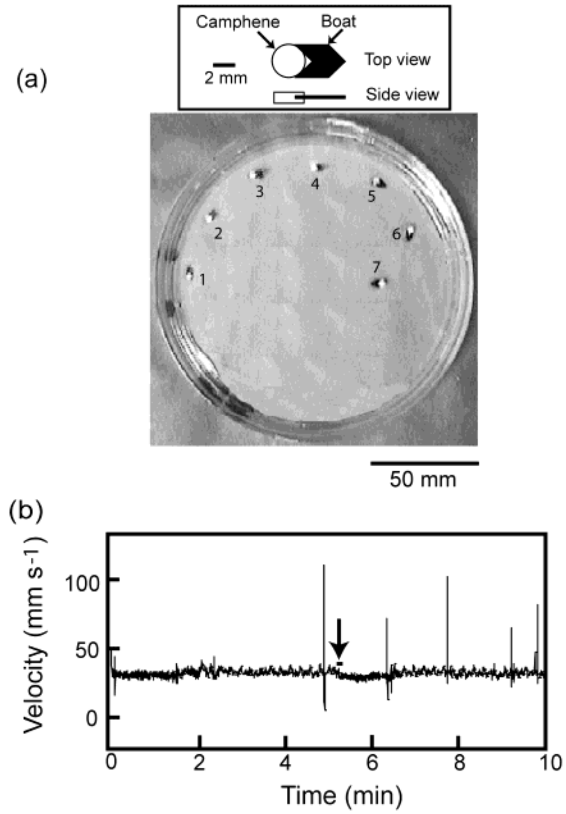

Figure 2. (a) Snapshots of the uniform motion of a camphene boat on water with a large surface area (167 cm^2) at a time interval of 1 s (top view). The track of the disk was numbered from 1 to 7. (b) Time variation of the velocity of the camphene disk. The elapsed time for point 1 in (a) after the boat was dropped on the water surface was 5 min, as marked by a downward arrow in (b).

camphene disk moves to the center of the cell and settles there because an isotropic distribution of the camphene layer is maintained around it as a balanced state. However, convection around the camphene disk is amplified by settling of the camphene disk. Figure 6 suggests that the magnitude of convection, which depends on the concentration gradient of surface active molecules at the air/water interface,[20,24-27] increases with a decrease in the velocity of camphene motion. The floating state becomes unstable with time because of amplified convection. Therefore, the isotropic distribution of the surface concentration of the camphene layer around the disk is disrupted because of the unstable floating state. On the other hand, the surface of a solid camphene disk melts gradually (melting point of camphene, 314 K) and develops as a visibly thick layer at the air−water interface, as seen in 6 of Figure 3. Figure 5 suggests that the rapid decrease in the surface tension is due to the development of the thick camphene layer. The camphene disk sinks because of a miscible contact angle between the thin camphene layer and its solid, as seen in 6 of Figure 3. Thus, the settled camphene disk starts to move, and the motion is accelerated by the further anisotropic sinking state because the area of contact between the camphene and water surfaces increases with sinking.

With a narrow water surface, the camphene disk again moves close to the center to give a minimum concentration gradient for the camphene layer. The sunken camphene floats again because the sublimation of the thick camphene layer changes the miscible interface to the immiscible one with time. The amount of the thick camphene layer for the individual bursting motions is estimated as ca. 1 μmol from the difference in the individual maximum heights of the floating camphene (ca. 20

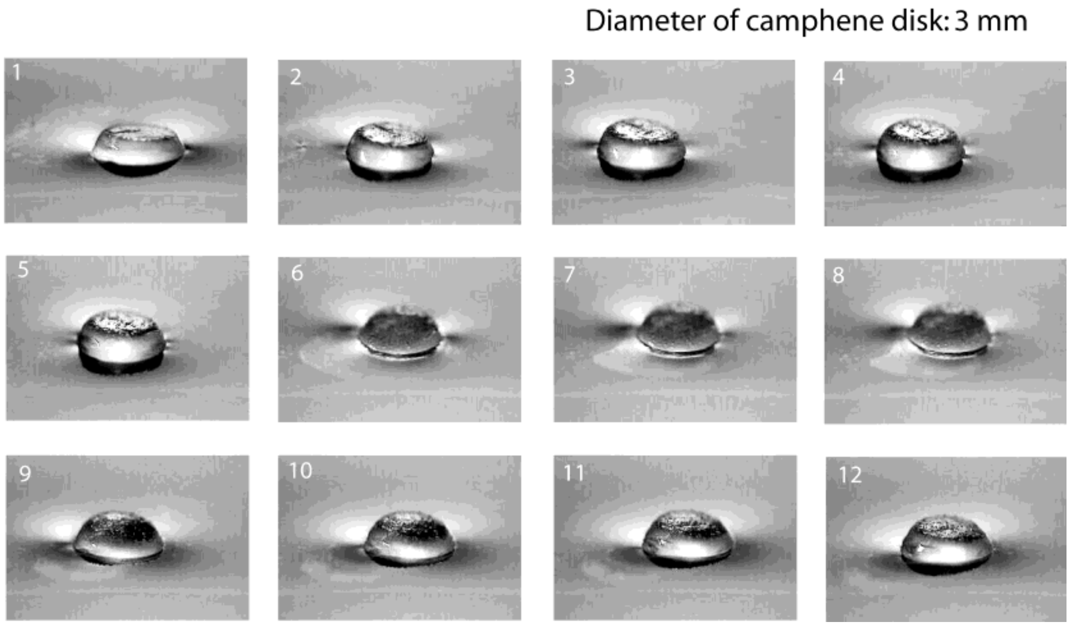

Figure 3. Floating state of a camphene disk during bursting motion in a small cell (surface area, 15 cm^2) (slanting view). The time intervals were (1−5) 60, (5−8) 1/3, and (8−12) 15 s. Bursting motion was observed between points 5 and 6. The elapsed time after the camphene disk was dropped on the water surface was 12.3 min for 1.

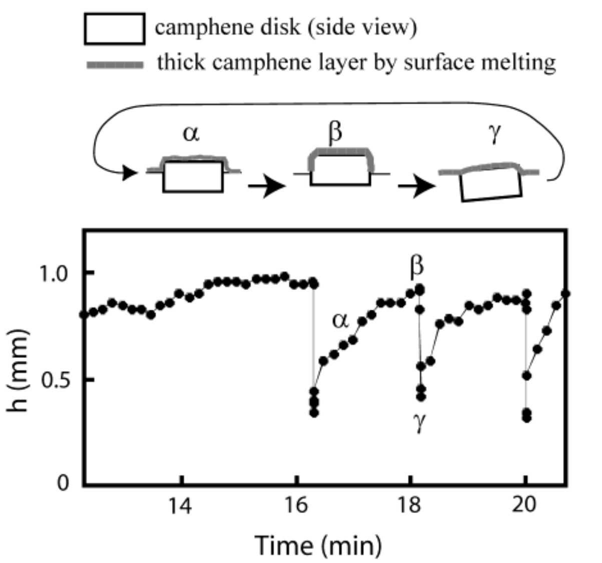

Figure 4. Time variation of the height of the camphene disk from the water surface, *h*. The data partly correspond to Figure 3. The relationship between the floating state of camphene and *h* is schematically illustrated using α, *β*, and *γ* (side view at the air/water interface). The time at which the camphene disk is floated on the water surface is taken as $t = 0$.

μm), as seen in Figure 4. Thus, with a small cell, intermittent motion is repeated from the center of the cell with a small cell.

Regarding the effect of an imbalance between sublimation and the development of a camphene layer, “bursting” self-motion was weakened when the water surface was covered with a glass plate, where the distance between the water surface and the plate was 3 mm. This suggests that the concentration gradient of the camphene layer around the disk, as the driving force of self-motion, is enhanced by sublimation.

Regarding the camphene boat, camphene molecules develop from the solid disk to the water surface as a surface active layer. Because the interfacial tension at the pure water/boat interface without camphene is greater than that at the camphene layer/camphene solid interface, the camphene boat moves to the side

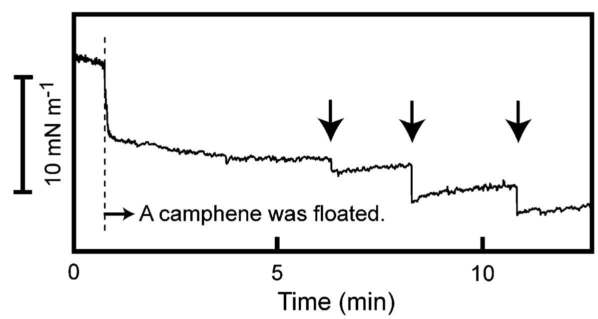

Figure 5. Time variation of surface tension during the bursting motion of a camphene disk on pure water. The camphene disk was dropped on the water surface at the time indicated by the dashed line. Bursting motion was observed at the time indicated by the downward arrow. A platinum wire (diameter, 0.5 mm), which was used to measure the surface tension, was in contact with the water surface at the middle of the edge and center of the cell.

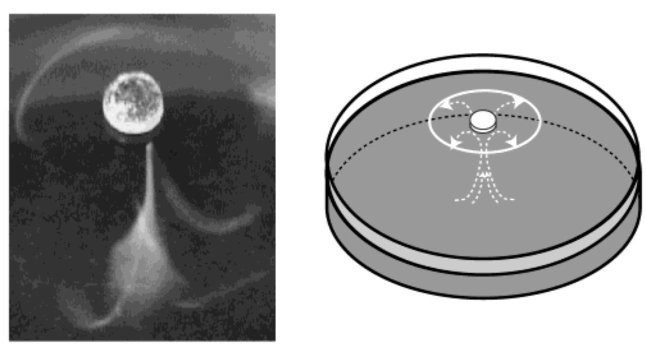

Figure 6. Results regarding convective flow in a slanting view when the camphene disk settled at the center of the cell. (Left panel) Snapshot of convective flow, which was visualized with uranin. An aqueous solution of 0.5 mmol/L uranin (20 μL) was gently added to the bottom of the water phase. (Right panel) Schematic illustration of the direction of convection flow. The experimental conditions were the same as those in Figure 1.

of the plastic boat without being connected to the camphene disk. The concentration gradient of the camphene layer around the camphene boat is almost maintained because of the large surface area and sublimation of the camphene layer. Thus, uniform motion continues for at least 30 min at the water surface purified by sublimation.

5. Conclusion

The mode of self-motion of camphene was discussed in relation to the distribution of the camphene layer around its disk, which depended on surface tension as the driving force. Switching between bursting motion by camphene and laying at rest at the center of the cell is induced by the imbalance between the isotropic distribution of the camphene layer around the disk and floating state of camphene. Disruption of the isotropic distribution is caused by the instability of the floating state because of the convective flow around the settled camphene. This mechanism agrees with the fact that the camphene boat showed uniform motion because an anisotropic distribution of camphene was maintained around the boat. A solutocapillary effect (or solute-Marangoni effect),[24,25] which involves surface convection from low to high surface tension, should be further taken into account to clarify the instability of the floating state of the camphene disk.

According to the Curie–Prigogine theorem, scalar variables cannot couple with vector values under isotropic and linear conditions.[26,27] This implies that a chemomechanical transducer, including a vector and mode, can be created under anisotropic and nonequilibrium conditions. In this experiment, the mode of self-motion changed because of anisotropy of the development of the camphene layer around the disk. Our results suggest that we can create various types of self-motion that depend on the property of the camphor derivative and change their vector and mode by introducing anisotropic conditions to the reaction field.

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References and Notes

(1) Yoshida, R.; Takahashi, T.; Yamaguchi, T.; Ichijo, H. *J. Am. Chem. Soc.* **1996**, *118*, 5134.
(2) Yoshida, R.; Tanaka, M.; Onodera, S.; Yamaguchi, T.; Kokufuta, E. *J. Phys. Chem. A* **2000**, *104*, 7549.
(3) Yamaguchi, T.; Shinbo, T. *Chem. Lett.* **1989**, 935.
(4) Chaudhury, M. K.; Whitesides, G. M. *Science* **1992**, *256*, 1539.
(5) Brochard, F. *Langmuir* **1989**, *5*, 432.
(6) Magome, M.; Yoshikawa, K. *J. Phys. Chem*. **1996**, *100*, 19102.
(7) Scriven, L. E.; Sternling, C. V. *Nature* **1960**, *187*, 186.
(8) Stoilov, Yu. Yu. *Langmuir* **1998**, *14*, 5685.
(9) Stoilov, Yu. Yu. *Phys. Uspekhi* **2000**, *43*, 39.
(10) Bain, C.; Burnett-Hall, G.; Montgomerie, R. *Nature* **1994**, *372*, 414.
(11) Domingues dos Santos, F.; Ondarçuhu, T. *Phys. Rev. Lett.* **1995**, *75*, 2972.
(12) Nakata, S.; Komoto, H.; Hayashi, K.; Menzinger, M. *J. Phys. Chem. B* **2000**, *104*, 3589.
(13) Gennes, P. G. *Phys. A* **1998**, *249*, 196.
(14) Shanahan, M. *Pour Sci.* **1998**, *24* (February), 106.
(15) Rayleigh, L. *Proc. R. Soc. London* **1890**, *47*, 364.
(16) Nakata, S.; Iguchi, Y.; Ose, S.; Kuboyama, M.; Ishii, T.; Yoshikawa, K. *Langmuir* **1997**, *13*, 4454.
(17) Nakata, S.; Hayashima, Y. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3655.
(18) Nakata, S.; Hayashima, Y.; Komoto, H. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2395.
(19) Hayashima, Y.; Nagayama, M.; Nakata, S. *J. Phys. Chem. B* **2001**, *105*, 5353.
(20) Kohira, M. I.; Hayashima, Y.; Nagayama, M.; Nakata, S. *Langmuir* **2001**, *17*, 7124.
(21) Sakurai, T.; Yokoyama, E.; Miike, H. *Phys. Rev. E* **1997**, *56*, 2367.
(22) Kitahata, H.; Aihara, R.; Magome, N.; Yoshikawa, K. *J. Chem. Phys.* **2002**, *116*, 5666.
(23) Boccara, N. *Symmetries and Broken Symmetries in Condensed Matter Physics*; IDSET: Paris, 1981.
(24) Levich, V. G. In *Physicochemical Hydrodynamics*; Spalding, D. B., Ed.; London, 1977; advance publication.
(25) Landau, L. D.; Lifshits, E. M. *Fluid Mechanics*, 2nd ed.; Pergamon Press: London, 1987; Vol.6 (of Course of Theoretical Physics).
(26) Katchalsky, A.; Curie, P. F. *Nonequilibrium Thermodynamics in Biophysics*; Harvard University Press: Cambridge, MA, 1965.
(27) Prigogine, I. *Introduction to the Thermodynamics of Irreversible Process*, 2nd ed.; John Wiley & Sons: New York, 1961.