

A novel turbine driven by chemical potential gradient

Kenichi YOSHIKAWA and Nobuyuki MAGOME

Graduate School of Human Informatics, Nagoya University, Nagoya 464-01, Japan

A new kind of cool chemical engine is reported. It is shown that spatially directed mechanical movement is generated with a simple experimental system composed with oil, water and an aluminum rotor. The spontaneous movement is driven by rhythmic oscillation of interfacial tension accompanied with the repetitive change of the contact angle. The rhythmic change of the interfacial tension is induced through the high nonlinearity of the transportation process of the surfactant molecules through the interface in a far-from-equilibrium condition on the concentration of the surfactant.

1. INTRODUCTION

A conventional chemical engine, such as gasoline engine, works with the conversion of chemical energy through the generation of thermal energy into mechanical force. There exists, thus, severe limitation of the conversion efficiency due to the second law of thermodynamics for the thermal engine working at room or environmental temperature. In modern science, it is still one of the most important problems how to realize the direct transduction from chemical energy to mechanical work. In this paper, we report a novel turbine driven by the gradient of concentration of chemical species, which works in an isothermal condition with essentially no dissipation of heat.

It is well known that instability of the interfacial tension due to the tempera-

ture gradient or the chemical concentration-gradient causes spontaneous agitation of the interface between liquids. For example, when water containing surfactant is placed in contact with oil, interfacial agitation of the order of cm is generated spontaneously. Such a phenomenon is known as the "Marangoni effect"[1, 2]. In this phenomenon chemical energy stored in the non-equilibrium of the solute concentrations is directly converted to macroscopic kinetic energy[3-8]. Concerning the Marangoni effect, it is also noted that rhythmic change of the interfacial tension and electrical potential have been reported for oil/water systems in the presence of various kinds of surfactant[9-14]. In the present article, we have special interest in the self-movement of an oil/water system induced by the periodic change of the interfacial tension.

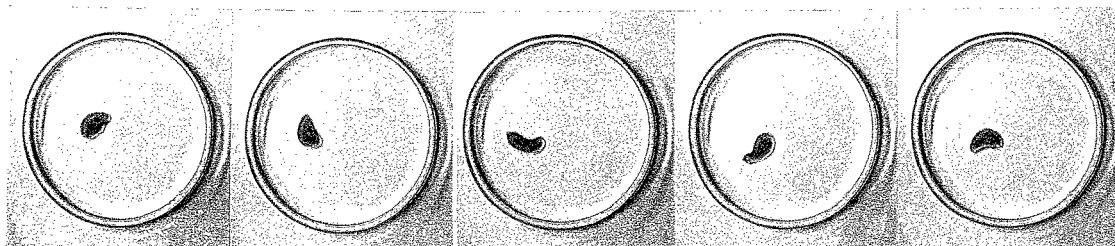


Figure 1. An oil droplet moving spontaneously in an aqueous phase in a petri dish.

2. EXPERIMENTAL

Throughout the experiments, aqueous and oil phases were 1 mM trimethyloctadecylammonium chloride and 2 mM iodine solution of nitrobenzene saturated with potassium iodide, respectively. The surfactant was purified through recrystallization from acetone. All experiments were carried out at room temperature. The movements of the oil/water system were recorded in a video tape and then analyzed with the aid of a microcomputer.

3. RESULTS AND DISCUSSION

Figure 1 exemplifies the self-movement in an oil-water system in a petri dish, indicating random motion of the oil droplet. It is noted that the oil droplet deforms spontaneously and that the portion with the negative curvature in the oil droplet seems to push the droplet. Figure 2a shows the video images of the self-movement of an oil droplet under an aqueous phase in an annular container, where outer and inner diameter are 50 mm and 35 mm, respectively. We analyzed time-dependence of the angular velocity of the center of mass of the oil droplet. It has been con-

firmed that the periodic change of the contact angle of oil-water interface onto the glass solid-surface is neatly connected with the acceleration process of the oil droplet. The analysis of the movement also indicated that the oil droplet tends to keep one-directional rotation for a while, then it switches to the other direction, and so on, suggesting that the self-movement preserves weak memory for short period. The comparison between the results in Figs. 1 and 2 clarifies that the liquid motion is strongly affected by the boundary condition, i.e., the shape of the container.

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 between the wings. With this simple apparatus, the aluminum rotor exhibits cyclic movement for only one-direction in a deterministic manner depending on the chiral asymmetry of the shape of rotor(Fig. 3b, d). Figures 3a and 3c show video image of the deterministic rotational movement of the system. As the self-movement is maintained accompanied with the dissipation of the chemical energy, the magnitude of the angular velocity gradually decays.

The mechanism of such a curious

motion is interpreted as follows[15]: i)At first, the contact angle is grater than 90° and Young's equation[16], $\gamma_{os} + \gamma_{ow} \cos\theta = \gamma_{ws}$, almost holds. ii)Surfactant molecules in the aqueous phase tend to migrate to-

ward the interface and form monolayer, which results in the decrease of the interfacial tension. iii)When the surface tension reaches a lower critical value, the monolayer collapses and the cationic surfactants

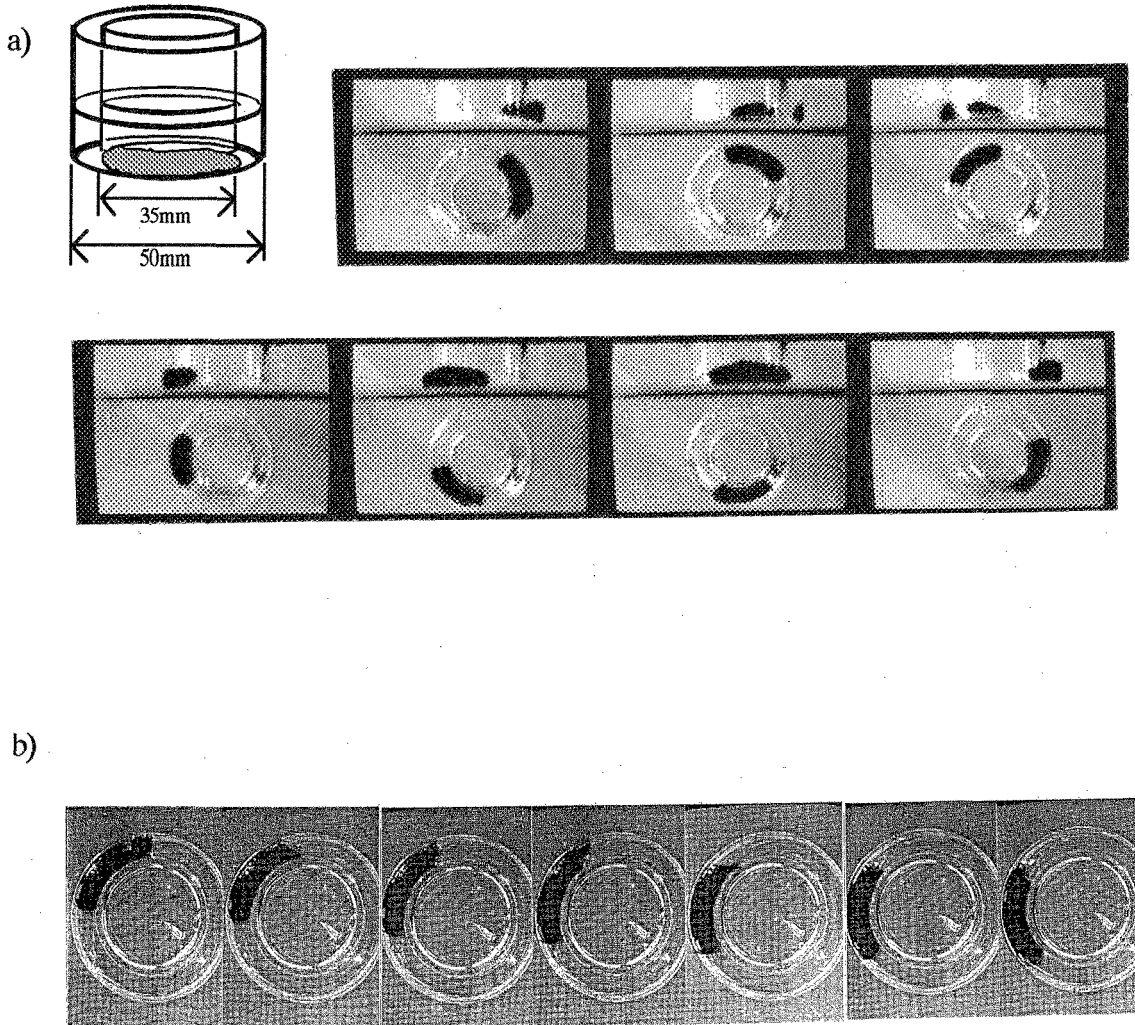
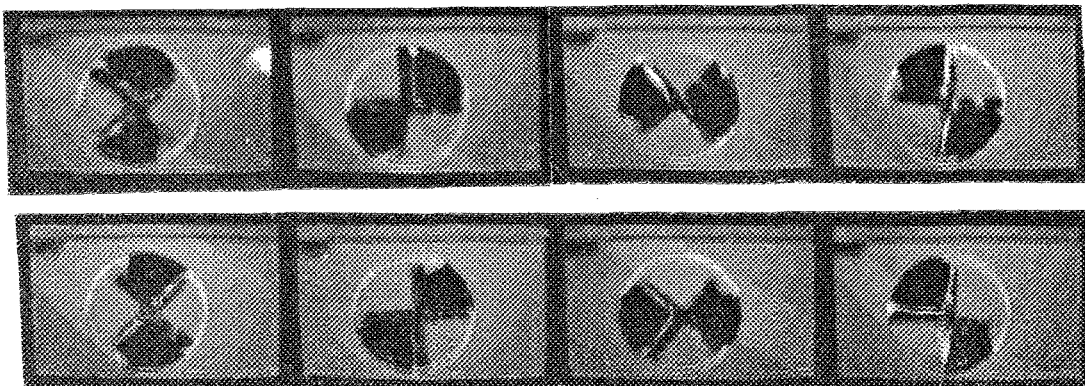
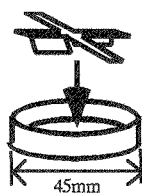


Figure 2. a)Spontaneous movement of an oil droplet under aqueous phase in an annular container, with the time interval of 0.5 sec. The amount of the oil and aqueous solutions were about 15 ml and 2 ml, respectively. b)Scrutinized view of the time variation of the shape of the droplet in the same apparatus, with the time interval of 0.3 sec.

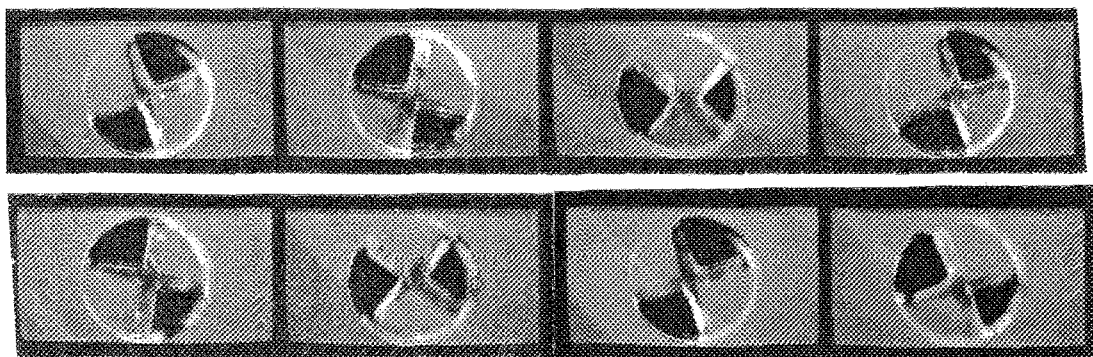
a)



b)



c)



d)



Fig. 3 a) Clockwise rotation of the chemical turbine with the experimental system of b). c) Anticlockwise rotation with the system of d). The amount of the oil and aqueous solutions were 3.5 ml each.

migrate into the bulk oil-phase in a cooperative manner, forming reversed micelles and/or microemulsions together with the hydrophobic I_3^- anions. In this process, the interfacial tension abruptly increases. Actually, the contact angle inverts through 90° . As the result, the oil droplet is pushed from the side of the interface with inverted contact angle accompanied with the breakdown of the Young's equation. iv) Accompanied by the gradual decrease of the interfacial tension, the balance of the forces as in the Young's equation recovers owing to the increase of the contact angle above 90° . Then the next cycle begins from the step i).

As the oil and water solutions have the effect of inertia in the movement, the spontaneous movement shows the tendency to keep the direction for a while as in the experiment shown in Fig. 2. However, the direction of the movement is still stochastic in this experiment. In Fig. 3, we have shown that deterministic one-directional movement is generated with the introduction of asymmetry onto the oil/water system.

According to the Currie-Prigogine theorem[17-19], vector processes can not couple with scalar variables, such as chemical reactions, in a "linear" system with an isotropic environment. Thus, mechano-chemical coupling becomes possible with either violation of linear or isotropic condition. However, it is expected that effective mechano-chemical coupling is realized with the double neglect of linear and isotropic conditions. In this report, we have demonstrated that macroscopic "deterministic" movement is generated in a chirally asymmetric environment for a nonlinear dynamical system driven by the chemical potential gradient.

REFERENCES

1. L. E. Scriven and C. V. Sternling, *Nature*, 187(1960)186.
2. H. Linde, P. Schwartz, and H. Wilke, "Dynamics and Instability of Fluid Interface", ed. by T. S. Sørensen, Springer-Verlag, Berlin(1979), pp. 75-119.
3. M. Dupeyrat and E. Nakache, *Bioelectrochem. Bioenerg.*, 5(1978)134.
4. S. Kai, E. Ooishi, and M. Imasaki, *J. Phys. Soc. Japan*, 54(1985)1274.
5. T. Yamaguchi and T. Shinbo, *Chem. Lett.*, 1989(1989)935.
6. K. D. Barton and R. S. Subramanian, *J. Colloid and Interface Sci.*, 133, (1989)211.
7. M. K. Chaudhury and G. M. Whitesides, *Science*, 256(1992)1539.
8. E. Sackmann, "Chemomechanical Interfacial Instabilities and Waves: Their Possible Role for the Cell Locomotion on Substrates" in "Temporal Order" ed. by L. Rensing and N. I. Jaeger, Springer-Verlag(1985), pp. 153-162.
9. S. Nakata, K. Yoshikawa, and T. Ishii, *Nippon Kagaku Kaishi*, 1987, 495.
10. K. Yoshikawa and Y. Matsubara, *J. Am. Chem. Soc.*, 105(1983)5967.
11. K. Yoshikawa and Y. Matsubara, *Biophys. Chem.*, 17(1983)183.
12. K. Yoshikawa and Y. Matsubara, *J. Am. Chem. Soc.*, 106, (1984)4423.
13. K. Yoshikawa, S. Maeda, and H. Kawakami, *Ferroelectrics*, 86(1988)281.
14. K. Yoshikawa and M. Makino, *Chem. Phys. Lett.*, 160(1989)623.
15. K. Yoshikawa and N. Magome, *Bull. Chem. Soc. Japan*, in press

16. N. K. Adam, "The Physics and Chemistry of Surface" 2nd ed., chap. 5, Oxford Univ. Press, Great Britain, 1938.
17. A. Katchlsky and P. F. Curie, "Equilibrium Thermodynamics in Biophysics", Harvard Univ. Press, Cambridge, 1965.
18. I. Prigogine, "Introduction to the Thermodynamics of Irreversible Process", 2nd ed., John Wiley & Sons, New York, 1961.
19. N. Boccara (ed.), "Symmetries and broken symmetries in condensed matter physics", IDSET, Paris, 1981.