Characteristic Motion of a Camphanic Acid Disk on Water Depending on the Concentration of Triton X-100

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As a simple autonomous motor, the self-motion of a camphanic acid disk on the aqueous phase with a neutral surfactant (Triton X-100) was investigated. Whereas only continuous motion was observed on water, intermittent motion (alternating between motion and rest) was observed upon addition of Triton X-100. Under the experimental conditions that gave intermittent motion, the surface tension of the aqueous phase changed periodically, synchronous with the contact angle around the camphanic acid disk. These characteristics of self-motion are discussed in relation to the surface tension depending on the concentration of camphanic acid with or without Triton X-100 as the driving force of the motion.

Introduction

The self-motion of a liquid droplet on a solid surface, a solid fragment on a liquid surface, or a solid fragment on a liquid surface occurs as a result of Marangoni flow, which is induced by the effect of a chemical or thermal gradient on the droplet or fragment.[1−7] For an isothermal system, the anisotropic distribution of the surface-active molecular layer around the droplet or fragment induces a difference in the surface tension around it and, therefore, becomes the driving force of self-motion.[8−14]

Several autonomous motors have been designed by various surface modifications.[15−19] We have investigated systems with camphor that show several types of self-motion, e.g., unidirectional motion,[20] mode-switching depending on the shape of the water chamber or the initial condition,[21−24] and synchronized motion.[25,26] It has also been reported that camphor derivatives exhibit characteristic self-motion.[27−29] The essential features of this self-motion can be reproduced by a computer simulation.[20−22,24−27]

In this article, we investigated the characteristics of the self-motion of a camphanic acid disk on water depending on the concentration of a neutral surfactant, Triton X-100. With an increase in the concentration of Triton X-100 in the water phase, continuous motion changed to the intermittent motion, and the camphanic acid disk stopped at the center of the cell with a further increase in concentration. The surface tension around the camphanic acid disk changed periodically in association with intermittent motion. The mechanism of mode-switching among these motions is discussed with respect to the relationship between the surface tension and the concentrations of camphanic acid as the driving force and Triton X-100 as the resistive force. We believe that the self-motion can be variously created according to the characteristics of the surface tension and the concentration of the surface-active substance at the molecular-layer level.

Experiments

All chemicals were purchased from Sigma-Aldrich (St. Louis, MO). Water was deionized with ion-exchange resin, distilled, and then purified with a Millipore Milli-Q filtering system. Camphanic acid including 12.5 wt % KBr was packed into a pellet die set (3-mm diameter, 1-mm thickness) because it was difficult to make an indestructible disk without additives, and therefore, KBr was used as a surface-inactive binder. The camphanic acid disk was floated on water in a Petri dish (inner diameter, 45 mm; volume of water, 15 mL). All of the experiments were performed at 293 ± 1 K. Movement of the camphanic acid disk 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., Tokyo, Japan). The surface tension of water was measured with a surface tensiometer (Kyowa Interface Science Co., Ltd., CBVP-A3, Saitama, Japan), and a platinum plate (length, 23.85 mm; thickness, 0.15 mm) was used as the Wilhelmy plate. In the measurement of surface tension, we confirmed the absence of any change in the force due to the collision between the Wilhelmy plate and the camphanic acid disk.

Results

Figure 1 shows (a) snapshots of the self-motion of a camphanic acid disk and (b) the time variation of velocity on (1) pure water and (2) a Triton X-100 aqueous solution. On pure water, continuous motion with an average velocity of 49 ± 17 mm s^{-1} was maintained for ca. 3 min, although the velocity often changed suddenly because the camphanic acid disk collided with the wall of the Petri dish, as shown in Figure 1-1. With the addition of 4.5×10^{-4} vol % Triton X-100, intermittent motion, i.e., repeated rapid acceleration → slow deceleration → rest, was observed, as shown in Figure 1-2. Figure 2 shows a phase diagram of the mode of camphanic acid motion depending on the concentration of Triton X-100. With an increase in the concentration of Triton X-100, the velocity of the continuous motion decreased, and intermittent motion was noted at around 3.0×10^{-4} vol %. Intermittent motion was observed between 3.0×10^{-4} and 7.0×10^{-4} vol % and maintained for ca. 4 min. The period of the intermittent motion increased with an increase in the concentration of Triton X-100, e.g., 1.1 ± 0.4 s at 4.0×10^{-4} vol % and 2.8 ± 1.5 s at 4.5×10^{-4} vol %. No motion was observed above 8.0×10^{-4} vol %.

Figure 3 shows (a) snapshots and (b) the time variation of the surface tension around the camphanic acid disk on water

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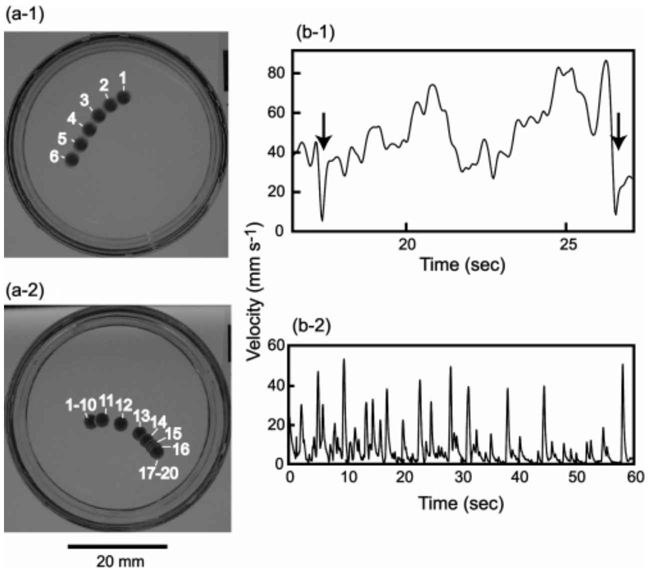

Figure 1. (a) Snapshots of the self-motion of a camphanic acid disk on water (top view) and (b) the time variation of velocity (1) without and (2) with Triton X-100 at a concentration of 4.5×10^{-4} vol %. Time intervals between snapshots were (1) 1/30 and (2) 1/10 s. The downward arrows indicate the time when the camphanic acid disk collided to the wall.

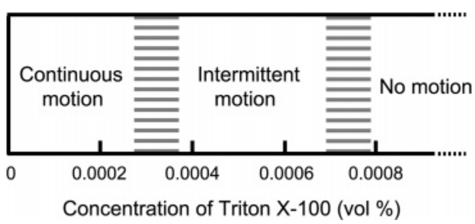

Figure 2. Phase diagram of the mode of camphanic acid motion depending on the concentration of Triton X-100. The thickness of the dotted line corresponds to the ambiguous boundary region between the individual motions.

with or without Triton X-100. In this experiment, one end of a platinum wire (diameter, 0.5 mm; length, 30 mm) was impaled into the center of the top face of the camphanic acid disk, and the rear face of the disk was placed into contact with the water surface. Without Triton X-100, the surface tension monotonically decreased with time. In contrast, the surface tension periodically oscillated (period, ca. 3 s; amplitude, 8 mN m^{-1}) with Triton X-100. The slow increase and rapid decrease in the surface tension showed an oscillatory nature, and this behavior was maintained for ca. 2 min. When the contact angle between the camphanic acid disk and the water surface, θ, was lower than $\pi/2$, the surface tension was high, as shown in snapshot I. On the other hand, when θ was nearly $\pi/2$, the surface tension was low, as seen in snapshot II.

It was difficult to measure the surface tension and the concentration of camphanic acid around the disk when it was moving. Therefore, we separately measured the surface tension depending on the concentration of camphanic acid. The surface tension (γ) monotonically decreased and converged to a minimum value of ca. 45 mN m^{-1} with an increase in the concentration of camphanic acid in water (c_w), as shown in Figure 4. The surface tension of a Triton X-100 (γ_{TX}) solution, the concentration of which corresponds to the region of continuous motion (see Figure 2), was higher than that of camphanic acid solution (γ) for most values of c_w. In contrast, γ_{TX} at the region of no motion was lower than γ for most

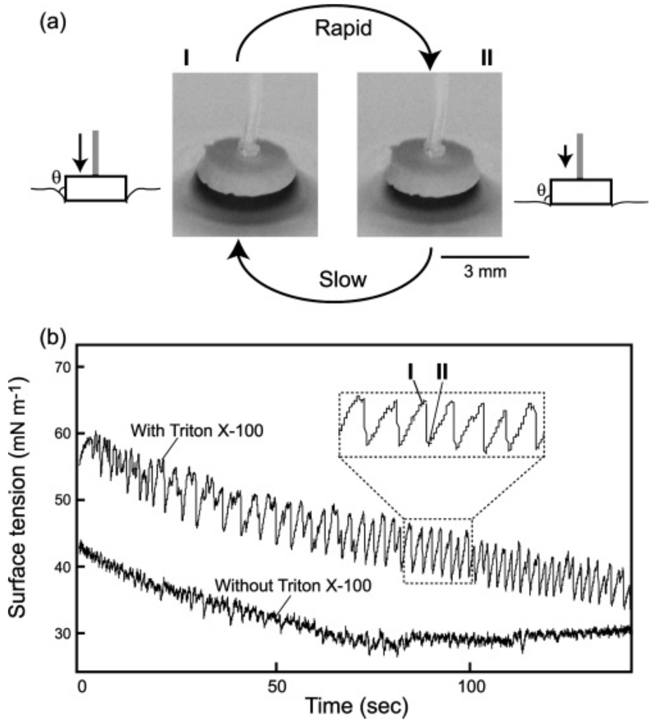

Figure 3. (a) Snapshots of a camphanic acid disk on water with Triton X-100 (slanting view) and (b) time variation of the surface tension around the camphor disk on water with or without Triton X-100. The concentration of Triton X-100 was 4.5×10^{-4} vol %. The relationships between the surface tension and the meniscus at the high and low surface tensions are illustrated schematically. The downward arrows indicate the vertical force around the disk, and its length corresponds to the magnitude of the force.

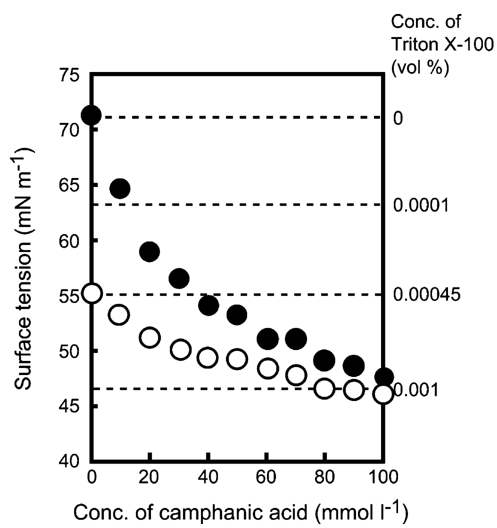

Figure 4. Surface tension (γ) depending on the concentration of camphanic acid (c_w) with (○) and without (●) 4.5×10^{-4} vol % Triton X-100. Dotted lines denote the surface tension (γ_{TX}) for Triton X-100 aqueous solutions, the concentrations of which are indicated on the right side of the individual lines.

values of c_w. As for the intermittent region, e.g., γ_{TX} at 4.5×10^{-4} vol % was less than γ below 40 mM c_w, whereas an opposite relation was observed above 40 mM c_w. In comparison with the measurement of surface tension for the individual substances (Triton X-100 and camphanic acid), the surface tension for the aqueous solution including both Triton X-100 and camphanic acid is also shown in Figure 4. The surface tension was less than γ_{TX} at 4.5×10^{-4} vol % for most values of c_w and monotonically decreased with increasing c_w.

Discussion

On the basis of our experimental results and previous papers on the self-motion of camphor,[27,29,30] we can discuss the mechanism of the intermittent motion of a camphanic acid disk on a water surface with Triton X-100.

Figure 3 suggests that the nature of dissolution and the development of camphanic acid molecules from the solid disk to the water phase without Triton X-100 are different from those with Triton X-100. Without Triton X-100, the monotonic decrease in the surface tension suggests that the camphanic acid molecules are successively dissolved into and developed to the water phase. With Triton X-100, the periodic change in the surface tension suggests that the camphanic acid molecular layer periodically develops from the solid to the water surface. At a higher surface tension, the surface concentration of camphanic acid is low and θ is less than $\pi/2$, and therefore, the water/solid interface is hydrophobic, as indicated in snapshot I. At a lower surface tension, the surface concentration of camphanic acid is high and θ is nearly $\pi/2$, and therefore, the water/solid interface in snapshot II is more lipophilic than that in snapshot I. In addition, the slow increase and rapid decrease in the surface tension might correspond to the slow decrease and rapid increase in the surface concentration of surface-active camphanic acid.

Figure 4 suggests that these characteristic motions are related to the γ vs c_w curve and to γ_{TX}. In the Triton X-100 concentration region that is associated with continuous motion, γ_{TX} is equal to or greater than γ for most concentrations of camphanic acid. Thus, γ_{TX} scarcely affects the self-motion, and the monotonic decrease in γ depending on c_w can produce a continuous difference in the surface tension, i.e., the driving force of the motion is provided continuously. Thus, continuous motion is produced by the monotonic concentration dependence of the surface tension free from the influence of Triton X-100. Two states will exist in the intermittent motion. For example, in the presence of 4.5×10^{-4} vol % Triton X-100, whereas γ_{TX} is lower than γ when c_w is lower than 40 mmol L^{-1}, γ_{TX} is higher than γ when c_w is higher than 40 mmol L^{-1}. When c_w is lower than 50 $mmol^{-1}$, the camphanic acid disk cannot provide the driving force of motion because $\gamma_{TX} < \gamma$. On the other hand, the camphanic acid disk can continuously provide the driving force depending on the γ vs c_w curve when c_w is higher than 50 $mmol^{-1}$. As for no motion, γ_{TX} is equal to or lower than γ for most values of c_w, i.e., the camphanic acid disk cannot provide the driving force. The surface tension for the aqueous solution including both Triton X-100 and camphanic acid suggests that the mixture of these substances is not very effective for intermittent motion (open circles in Figure 4). In other words, the intermittent motion might be induced under inhomogeneous mixtures of these substances.

Figure 5 shows a schematic representation to explain the continuous and intermittent motion of a camphanic acid disk. When the camphanic acid disk is dropped on water without Triton X-100, camphanic acid ions dissolve into the water phase around the disk, and then the surface-active camphanic acid molecules rapidly accumulate around the disk because of the rapid decrease in pH. When the camphanic acid was dropped on water, the pH near the water surface decreased with time and was lower than the pK_a of camphanic acid (pK_a = 4.87) after a lapse of 30 s. Thus, nonionic camphanic acid, which is dissolved into the water phase, is partly adsorbed on the water surface as a surface-active substance. Therefore, the camphanic acid disk can start to move because of the continuous development of a surface-active camphanic acid molecular layer.

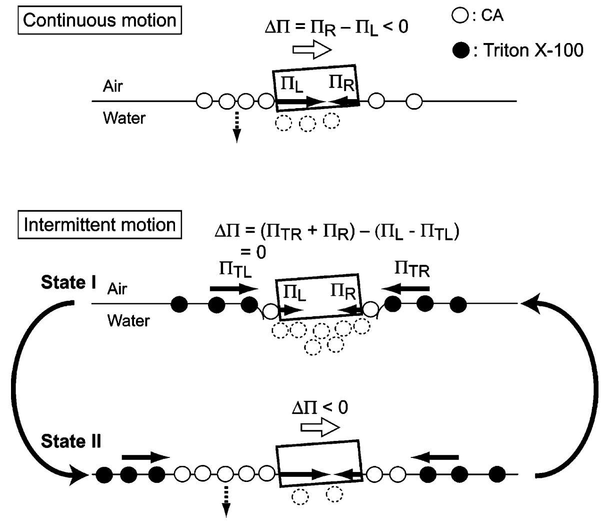

Figure 5. Schematic illustration of the mechanism of continuous and intermittent motion of the camphanic acid disk. Intermittent motion occurs by repeating states I and II.

If the shape and initial floating state of the camphanic acid disk on water are completely symmetrical, a camphanic acid layer distributes isotropically on the water around the disk, and the disk is unable to move because the gradient of surface tension around the disk is isotropic and does not provide a driving force. If there is a slight asymmetry in the shape or the initial floating state of the disk, the development of the camphanic acid layer becomes anisotropic, and the isotropic surface tension gradient around the disk is broken. The camphanic acid disk then moves toward the region with a lower concentration of camphanic acid at the surface (or higher surface tension) to reduce the spatial gradient of the surface tension. When unidirectional motion starts, the anisotropic distribution of the camphanic acid layer persists depending on the velocity.[24] In addition, dissolution of the camphanic acid layer into the water bulk phase helps to maintain continuous motion because of the decrease in the surface concentration of the surface-active camphanic acid.

When the camphanic acid disk is dropped on water with Triton X-100, the camphanic acid disk cannot move in the initial state (state I) because $\Pi_{TX} > \Pi$ at lower c_w, where Π_{TX} ($= \gamma_w - \gamma_{TX}$) is the surface pressure of the Triton X-100 aqueous surface, Π ($= \gamma_w - \gamma$) is the surface pressure of the camphanic acid aqueous surface around the disk, and γ_w is the surface tension of pure water. c_w around the disk increases with time because of dissolution from the disk. When Π becomes greater than Π_{TX}, camphanic acid molecules that have accumulated below the disk move to the water surface as a surface-active molecular layer, and therefore, the surface tension around the disk decreases (state II). Thus, the slow dissolution of camphanic acid and the rapid development of a camphanic acid layer are reflected in the slow increase and rapid decrease in surface tension, as indicated in Figure 3. Thus, the camphanic acid disk can move. Here, the direction of motion depends on the slight asymmetry of the disk floating on water or the anisotropic dissolution of camphanic acid from the disk. When the disk moves to another surface, the value of c_w around the disk decreases, state I is reproduced, and intermittent motion occurs by repeating states I and II. These mechanisms also agree with the experimental results in Figure 4.

Conclusion

The nature of self-motion of a camphanic acid disk was discussed in relation to the accumulation, dissolution, and development of a camphanic acid layer around the disk, which depend on the surface tension as the driving force. Switching between motion and rest is induced by the alternation between c_w-dependent and -independent surface tension. A soluto-capillary effect or solute-Marangoni effect, which involves surface convection from low to high surface tension, should be further considered to clarify the instability of the state of the camphanic acid disk. We have previously reported the effect of convection on self-motion.[7]

Our results suggest that one can design self-motion with various natures that depend on the surface tension and surface concentration of the surface-active substance.[31] In addition, the direction of motion can be controlled by introducing anisotropic conditions to the reaction field.

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References and Notes

(1) Linde, H.; Schwartz, P.; Wilke, H. In *Dynamics and Instability of Fluid Interfaces*; Sørensen, T. S., Ed.; Springer-Verlag: Berlin, 1979.
(2) Levich, V. G. In *Physicochemical Hydrodynamics*; Spalding, D. B., Ed.; Advance Publications Limited: London, 1977.
(3) Brochard, F. *Langmuir* **1989**, *5*, 432.
(4) Sakurai, T.; Yokoyama, E.; Miike, H. *Phys. Rev. E* **1997**, *56*, 2367.
(5) Kovalchuk, V. I.; Kamusewitz, Vollhardt, H. D.; Kovalchuk, N. M. *Phys. Rev. E* **1999**, *60*, 2029.
(6) Kitahata, H.; Aihara, R.; Magome, N.; Yoshikawa, K. *J. Chem. Phys.* **2002**, *116*, 5666.
(7) Kitahata, H.; Hiromatsu, S.; Doi, Y.; Nakata, S.; Islam, M. R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2409.
(8) Rayleigh, L. *Proc. R. Soc. London* **1890**, *47*, 364.
(9) de Gennes, P. G. *Physica A* **1998**, *249*, 196.
(10) Stoilov, Yu. Yu. *Langmuir* **1998**, 14, 5685.
(11) Magome, N.; Yoshikawa, K. *J. Phys. Chem*. **1996**, *100*, 19102.
(12) Chaudhury, M. K.; Whitesides, G. M. *Science* **1992**, *256*, 1539.
(13) dos Santos, F. D.; Ondarçuhu, T. *Phys. Rev. Lett.* **1995**, *75*, 2972.
(14) Bain, C.; Burnett-Hall, G.; Montgomerie, R. *Nature* **1994**, *372*, 414.
(15) Ismagilov, R. F.; Schwartz, A.; Bowden, N.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 652.
(16) Ichimura, K.; Oh, S.-K.; Nakagawa, M. *Science* **2000**, *288*, 1624.
(17) Lorenceau, É.; Quéré, D. *J. Fluid Mech.* **2004**, *510*, 29.
(18) Sakai, T.; Yoshida, R. *Langmuir* **2004**, *20*, 1036.
(19) Nakata, S.; Komoto, H.; Hayashi, K.; Menzinger, M. *J. Phys. Chem. B* **2000**, *104*, 3589.
(20) Nakata, S.; Iguchi, Y., Ose, S.; Kuboyama, M.; Ishii, T.; Yoshikawa, K. *Langmuir* **1997**, *13*, 4454.
(21) Hayashima, Y.; Nagayama, M.; Nakata, S. *J. Phys. Chem. B* **2001**, *105*, 5353.
(22) Nakata, S.; Doi, Y.; Kitahara, H. *J. Colloid Interface Sci*. **2004**, *279*, 503.
(23) Nakata, S.; Hiromatsu, S. *Colloids Surf. A* **2003**, *224*, 157.
(24) Nagayama, M.; Nakata, S.; Doi, Y.; Hayashima, Y. *Phys. D* **2004**, *194*, 151.
(25) Kohira, M. I.; Hayashima, Y.; Nagayama, M.; Nakata, S. *Langmuir* **2001**, *17*, 7124.
(26) Nakata, S.; Doi, Y.; Kitahata, H. *J. Phys. Chem. B* **2005**, *109*, 1798.
(27) Hayashima, Y.; Nagayama, M.; Doi, Y.; Nakata, S.; Kimura, M.; Iida, M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1386.
(28) Nakata, S., Doi, Y.; Hayashima, Y. *J. Phys. Chem. B* **2002**, *106*, 11681.
(29) Nakata, S.; Hiromatsu, S.; Kitahata, H. *J. Phys. Chem. B* **2003**, *107*, 10557.
(30) Nakata, S.; Matsuo, K. *Langmuir* **2005**, *21*, 982.
(31) Joo, P. In *Dynamic Surface Phenomena*; Fainerman, V. B., Loglio, G., Eds.; VSP: Leiden, The Netherlands, 1999.