

Self-Motion of a Camphanic Acid Disk on Water with Different Types of Surfactants

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Control of the self-motion of a camphanic acid disk on water was investigated upon the addition of different kinds of surfactants (Triton X-100 and Brij58 as neutral surfactants, cetyltrimethylammonium bromide (CTAB) as a cationic surfactant, and sodium dodecyl sulfate (SDS) as an anionic surfactant) to the water phase. With an increase in the concentration of surfactant, continuous motion changed to no motion via intermittent motion (repetition between motion and rest), and the concentration regions of these motions were different among these surfactants. Although the concentration regions of these motions were determined by the surface tension for neutral surfactants, they were different than those for CTAB and SDS. These characteristics of self-motion are discussed in relation to the surface tension, depending on the concentration of individual surfactants, and the hydrophilic effect of the surfactants.

Introduction

Studies of autonomous systems, which mimic moving living objects, may help us not only to understand the mechanism of their self-motion but also to design artificial motors which adapt to the environment.^{1–4} All motor organs or organelles in living organisms work through the dissipation of chemical energy under almost isothermal conditions, such as the hydrolysis of ATP.^{5,6} For isothermal and artificial systems, 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 chemical gradient around the droplet or fragment.^{7–12} Thus, the anisotropic distribution of surface active molecules around the droplet or the fragment on the surface induces a difference in the surface tension around it, and therefore becomes the driving force of self-motion.^{13–19}

Several autonomous motors have been designed by applying various surface modifications.^{3,4,20,21} We have investigated experimental systems with camphor that show several features of self-motion, e.g., unidirectional motion,²² mode-switching depending on the shape of the water chamber or the initial condition,^{23–25} and synchronized motion.^{26,27} It has also been reported that camphor derivatives exhibit characteristic self-motion.^{28–30} The essential features of this self-motion can be reproduced by a computer simulation.^{22–24,25–28}

In this article, we investigated the nature of the self-motion of a camphanic acid disk on water upon the addition of different surfactants, i.e., Triton X-100 ($C_{14}H_{21}(C_2H_4O)_{10}OH$) and Brij58 ($C_{16}H_{33}(C_2H_4O)_{20}OH$) as nonionic surfactants, sodium dodecyl sulfate (SDS) as an anionic surfactant, and cetyltrimethylammonium bromide (CTAB) as a cationic surfactant. With an increase in the concentration of surfactant, continuous motion changed to no motion via intermittent motion, except for SDS. The values of surface tension at the boundary regions for Triton X-100 were similar to those for Brij58, i.e., mode-switching

among these motions was determined on the basis of the relationship between surface tension vs concentration for the nonionic surfactants. In contrast, CTAB inhibited self-motion even at a low concentration, and only continuous motion was observed for SDS even at a high concentration; i.e., the hydrophilic group of the surfactant influenced the self-motion. We believe that self-motion can be variously created depending on the chemical structure of the surfactant 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) since 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, 20 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., 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. The atomic force microscopy (AFM) system used in this study was a commercial microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA). A crystal silicon cantilever (length, 125 μ m; resonant frequency, 324–382 kHz) with tapping mode was scanned over the sample in pure air at room temperature.

Results

Figure 1a shows snapshots of (a-1) continuous motion of a camphanic acid disk on pure water and (a-2) intermittent motion on a Triton X-100 aqueous solution. On pure water, continuous

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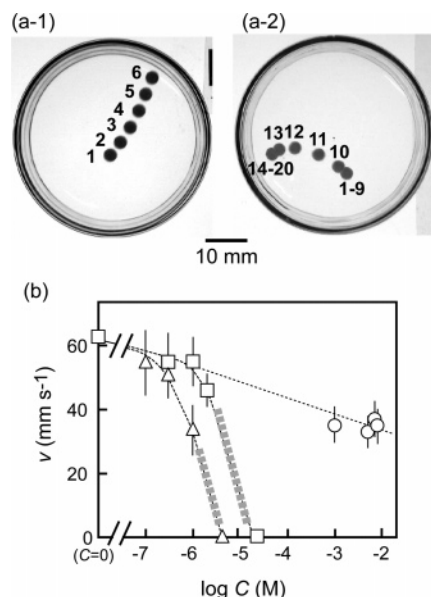


Figure 1. (a) Snapshots of the self-motion of a camphanic acid disk on water (a-1) without and (a-2) with Triton X-100 at a concentration of $4.0 \mu\text{M}$ (top view). Time intervals between snapshots were (a-1) $1/15$ and (a-2) 0.1 s. (b) Concentration (C) dependence of the velocity of the motion, v (mm s^{-1}), for different surfactants (Triton X-100 (empty squares), CTAB (empty triangles), and SDS (empty circles)). Gray dotted lines for Triton X-100 and CTAB correspond to their concentration regions for intermittent motion, respectively. Values greater than C at $v = 0$ for Triton X-100 and CTAB correspond to their concentration regions of no motion, respectively.

motion at ca. 60 mm s^{-1} was maintained for ca. 5 min, as shown in Figure 1a-1. With the addition of $4.0 \mu\text{M}$ Triton-X100, intermittent motion, i.e., repetition among rapid acceleration \rightarrow slow deceleration \rightarrow rest, was observed for ca. 4 min with an interval of ca. 1 s, as shown in Figure 1a-2. Figure 1b shows the concentration (C) dependence of the velocity (v) of self-motion for different surfactants (Triton X-100, CTAB, and SDS). Here, v was obtained as the average value for 1 min after the disk was dropped on the aqueous phase, and the minimum concentration at $v = 0$ corresponds to the boundary region between intermittent and no motion. A change from continuous motion to no motion via intermittent motion depending on the concentration was observed for CTAB and Triton X-100, but only continuous motion was observed for SDS below 10 mM. The degree of the decrease in v depending on C and the concentration region of intermittent motion were different among these surfactants.

Figure 2 shows (a) a phase diagram of the mode of camphanic acid motion and (b) the surface tension (γ) depending on the concentration of neutral surfactant (Triton X-100 and Brij 58). The thicknesses of the gray lines correspond to the regions of ambiguity at the two boundaries (continuous and intermittent motion, and intermittent and no motion). The concentration dependence of γ for Brij 58 was greater than that for Triton X-100, and the concentrations at both of the boundary regions for Brij 58 were higher than those for Triton X-100. The γ at these concentrations for Triton X-100 were similar to those for Brij 58, i.e., γ at the boundary concentration between continuous and intermittent motion was ca. 60 mN m^{-1} , and that between intermittent and no motion was ca. 50 mN m^{-1} .

Figure 3 shows (a) a phase diagram of the mode of camphanic acid motion and (b) the surface tension depending on the concentration of Triton X-100, CTAB, and SDS (1) without and (2) with 10 mM camphanic acid. The degree of the C

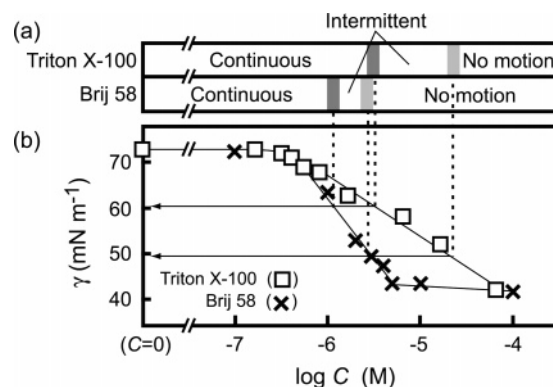


Figure 2. (a) Phase diagram of the mode of camphanic acid motion and (b) surface tension (γ) depending on the concentrations (C) of Triton X-100 (empty squares) and Brij 58 (x marks). The thickness of the gray line corresponds to the region of ambiguity between the individual motions.

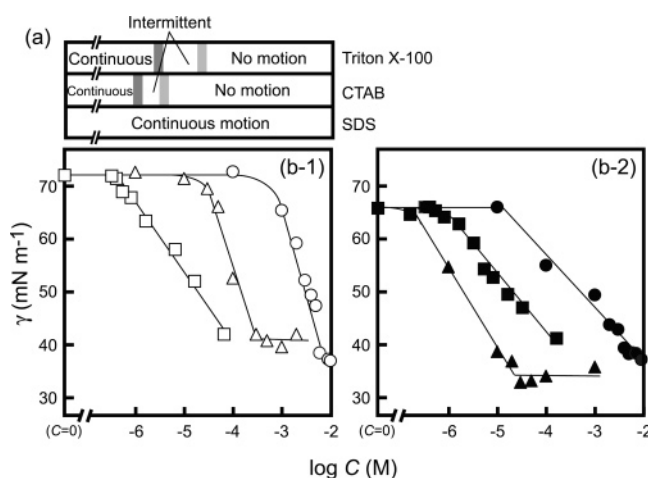


Figure 3. (a) Phase diagram of the mode of camphanic acid motion and (b) surface tension (γ) depending on the concentration (C) of Triton X-100 (squares), CTAB (triangles), and SDS (circles) (1) without and (2) with 10 mM camphanic acid. The thickness of the gray line corresponds to the region of ambiguity between the individual motions.

dependency of γ was on the order of Triton X-100 > CTAB > SDS, as shown in Figure 3b-1. In contrast, the concentrations at both of the boundary regions for CTAB were lower than those for Triton X-100, and only continuous motion, i.e., no boundary, was observed for SDS in this experimental condition, as shown in Figure 3a. To clarify the interaction between surfactant and camphanic acid, the dependence of γ on C for Triton X-100, CTAB, and SDS with 10 mM camphanic acid was measured, as shown in Figure 3b-2. The degree of the C dependency of γ was on the order of CTAB > Triton X-100 > SDS in the presence of camphanic acid.

To observe the existence of a complex formed by camphanic acid and CTAB, adsorbates on a mica surface were observed by AFM, as shown in Figure 4. Here, the preparation of the sample for AFM observation was as follows. The mica surface was in contact with the surface of an aqueous solution using a horizontal-lifting method for several seconds and was dried in a pure air. Different features of adsorbates on the order of a few hundred nanometers were observed for camphanic acid and CTAB, as shown in Figure 4a,b. In contrast, adsorbates of ca. $1 \mu\text{m}^2$ were observed for the mixture of camphanic acid and CTAB, as shown in Figure 4c. We confirmed that the density of such large adsorbates changed depending on the concentrations of camphanic acid and CTAB.

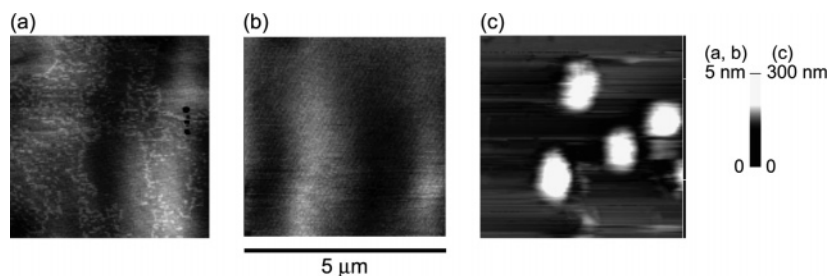


Figure 4. AFM images of mica surfaces that were in contact with the surfaces of different aqueous solutions ((a) 10 mM camphanic acid, (b) 0.1 mM CTAB, and (c) 10 mM camphanic acid plus 0.1 mM CTAB) using a horizontal-lifting method.

Discussion

On the basis of our experimental results and previous papers on the self-motion of camphor,^{28–30} we can discuss the mechanism of the intermittent motion of a camphanic acid disk on a water surface depending on the kind of surfactant.

Figure 2 suggests that a hydrophobic surfactant reduces self-motion. Since Brij 58 is more hydrophobic than Triton X-100, a molecular layer of Brij 58 more easily adsorbed on water than Triton X-100. Therefore, Brij 58 reduces self-motion in comparison with Triton X-100. In addition, the mode of self-motion with the addition of neutral surfactant is determined by the surface tension, since the surface tension values at the two boundary concentrations for Triton X-100 are similar to those for Brij 58, i.e., the surface tension at the boundary region between continuous and intermittent motion was ca. 50 mN m⁻¹, and that between intermittent and no motion was ca. 60 mN m⁻¹.

Figures 1 and 3 suggest that the hydrophilic group of the surfactant affects the self-motion.³¹ Thus, a cationic surfactant, such as CTAB, reduces self-motion since no motion is observed even at a high surface tension, e.g., 71 mN m⁻¹ for $C = 10^{-5}$ M (see Figure 3b-1). In contrast, an anionic surfactant, such as SDS, maintains the self-motion since continuous motion is observed even at a low surface tension, e.g., 37 mN m⁻¹ for $C = 10^{-2}$ M (see Figure 3b-1), and the average velocity was 35 mm s⁻¹ (Figure 1b). The decrease in the surface tension for the mixture of CTAB and camphanic acid (Figure 3b-2) and large adsorbates (Figure 4) suggests the formation of a complex composed of cationic CTAB and anionic camphanic acid. In a related paper,³² an aqueous solution composed of dodecyltrimethylammonium bromide (DTAB) and SDS was reported to form a complex and to show a marked decrease in the surface tension. Thus, the reduction in the self-motion of the camphanic acid disk with the addition of CTAB may occur via a decrease in surface tension due to complex formation. In contrast, the weak reduction of the motion with the addition of SDS even at a surface tension lower than the critical value, i.e., 50 mN m⁻¹, may be due to the greater solubility of SDS in comparison with other surfactants and the repulsive force between the sulfate ion of SDS and the carboxylate ion of camphanic acid.³¹ That is, due to the greater solubility of SDS, the camphanic acid layer easily develops to the water surface and the repulsive force may further help to dissolve SDS into the aqueous phase rather than the existence as the surface molecular layer on water.

When the camphanic acid disk is dropped on water without surfactant, nonionic camphanic acid molecules are dissolved as camphanic acid ions into the water phase from the disk, and the pH decreases rapidly.³⁰ When the pH around the disk is lower than the pK_a ($=4.87$), camphanic acid molecules rapidly develop as a surface active molecular layer around the disk. Thus, the camphanic acid disk exhibits continuous motion due

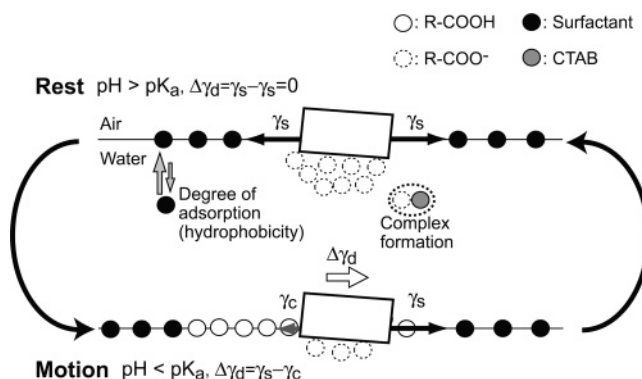


Figure 5. Schematic illustration of the mechanism of intermittent motion of a camphanic acid disk depending on the kind of surfactant. R-COOH denotes a camphanic acid molecule. Intermittent motion occurs through the repetition of Rest and Motion. Hydrophobic surfactant (e.g., Brij 58) and a complex composed of CTAB and camphanic acid, which tends to adsorb on water rather than the water phase, reduces motion and reduces the concentration region for the mode of self-motion.

to the continuous development of a surface active camphanic acid molecular layer.

Due to 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). When unidirectional motion starts, the anisotropic distribution of the camphanic acid layer persists depending on the velocity.²⁵ In addition, dissolution of the camphanic acid layer into the water phase helps to maintain continuous motion because of the decrease in the surface concentration of the surface active camphanic acid.

The surface tension around the disk (γ_d) plays an important role in the mode of self-motion with the addition of surfactant. Figure 5 shows a schematic representation to explain intermittent motion of a camphanic acid disk depending on the kind of surfactant. In the resting state, the camphanic acid disk cannot acquire driving force since the disk is surrounded by a surfactant molecular layer due to $\gamma_c > \gamma_s$ (γ_c , the surface tension of the camphanic acid layer; γ_s , the surface tension of the surfactant), and γ_d is balanced at γ_s . When pH decreases below pK_a , the camphanic acid layer can develop from the disk due to $\gamma_c < \gamma_s$, and the disk can then rapidly start to move due to the driving force ($\propto \Delta\gamma_d \approx \gamma_s - \gamma_c$). When the disk moves to another surface, γ_c again becomes higher than γ_s because of the decrease in the concentration of camphanic acid around the disk; i.e., the resting state is restored. Thus, intermittent motion is repeated. The hydrophobic surfactant reduces disk motion and reduces the concentration region of the mode of self-motion because of adsorption on water. As the surface tension for the complex of

CTAB and camphanic acid is lower than that around the camphanic acid disk, the camphanic acid disk cannot obtain the driving force. Due to the influence of the hydrophilic group of the surfactant, CTAB characteristically reduces motion by forming a more hydrophobic complex with camphanic acid.

Conclusion

The nature of the self-motion of a camphanic acid disk was discussed in relation to the dissolution and development of a camphanic acid layer around the disk, which depended on not only the surface tension as the driving force but also the chemical structure of the surfactant included in the water phase. Although the details of the surfactant on the nature of self-motion are not yet clear, e.g., conservation of motion with the addition of SDS, the surfactants in the water phase characteristically change the nature of motion depending on their chemical structures, i.e., hydrophobicity and hydrophilic groups.

Our results suggest that we can design self-motion with various characteristics that depend not only on the surface tension as the driving force but also on the chemical structure of the surfactant.³³ A solutocapillary effect or solute–Marangoni effect, which involves surface convection from a 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 self-motion coupled with convection.^{12,24} In addition, the direction of motion can be controlled by introducing anisotropic conditions to the reaction field with a specific morphology.

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References and Notes

- (1) Sakai, T.; Yoshida, R. *Langmuir* **2004**, *20*, 1036.

- (2) Sumino, Y.; Magome, N.; Hamada, T.; Yoshikawa, K. *Phys. Rev. Lett.* **2005**, *94*, 068301.
- (3) Fournier-Bidoz, S.; Arsenault, A. C.; Manners, I.; Ozin, G. A. *Chem. Commun. (Cambridge)* **2005**, 441.
- (4) Ichimura, K.; Oh, S.-K.; Nakagawa, M. *Science* **2000**, *288*, 1624.
- (5) Carter, S. B. *Nature* **1967**, *213*, 256.
- (6) Darnell, J.; Lodish, H.; Baltimore, D. *Molecular Cell Biology*; Scientific American Books: New York, 1990.
- (7) Linde, H.; Schwartz, P.; Wilke, H. In *Dynamics and Instability of Fluid Interfaces*; Sørensen, T. S., Ed.; Springer-Verlag: Berlin, 1979.
- (8) Levich, V. G. In *Physicochemical Hydrodynamics*; Spalding, D. B., Ed.; Advance Publications: London, 1977.
- (9) Brochard, F. *Langmuir* **1989**, *5*, 432.
- (10) Kovalchuk, V. I.; Kamusewitz, Vollhardt, H. D.; Kovalchuk, N. M. *Phys. Rev. E* **1999**, *60*, 2029.
- (11) Kitahata, H.; Aihara, R.; Magome, N.; Yoshikawa, K. *J. Chem. Phys.* **2002**, *116*, 5666.
- (12) Kitahata, H.; Hiromatsu, S.; Doi, Y.; Nakata, S.; Islam, M. R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2409.
- (13) Rayleigh, L. *Proc. R. Soc. London* **1890**, *47*, 364.
- (14) de Gennes, P. G. *Physica A* **1998**, *249*, 196.
- (15) Stoilov, Y. Yu. *Langmuir* **1998**, *14*, 5685.
- (16) Magome, N.; Yoshikawa, K. *J. Phys. Chem.* **1996**, *100*, 19102.
- (17) Chaudhury, M. K.; Whitesides, G. M. *Science* **1992**, *256*, 1539.
- (18) dos Santos, F. D.; Ondarçuhu, T. *Phys. Rev. Lett.* **1995**, *75*, 2972.
- (19) Bain, C.; Burnett-Hall, G.; Montgomerie, R. *Nature* **1994**, *372*, 414.
- (20) Ismagilov, R. F.; Schwartz, A.; Bowden, N.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 652.
- (21) Lorenceau, É.; Quéré, D. *J. Fluid Mech.* **2004**, *510*, 29.
- (22) Nakata, S.; Iguchi, Y.; Ose, S.; Kuboyama, M.; Ishii, T.; Yoshikawa, K. *Langmuir* **1997**, *13*, 4454.
- (23) Hayashima, Y.; Nagayama, M.; Nakata, S. *J. Phys. Chem. B* **2001**, *105*, 5353.
- (24) Nakata, S.; Doi, Y.; Kitahata, H. *J. Colloid Interface Sci.* **2004**, *279*, 503.
- (25) Nagayama, M.; Nakata, S.; Doi, Y.; Hayashima, Y. *Phys. D* **2004**, *194*, 151.
- (26) Kohira, M. I.; Hayashima, Y.; Nagayama, M.; Nakata, S. *Langmuir* **2001**, *17*, 7124.
- (27) Nakata, S.; Doi, Y.; Kitahata, H. *J. Phys. Chem. B* **2005**, *109*, 1798.
- (28) Hayashima, Y.; Nagayama, M.; Doi, Y.; Nakata, S.; Kimura, M.; Iida, M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1386.
- (29) Nakata, S.; Hiromatsu, S.; Kitahata, H. *J. Phys. Chem. B* **2003**, *107*, 10557.
- (30) Nakata, S.; Kirisaka, J. *J. Phys. Chem. B* **2006**, *110*, 1856.
- (31) Yamaguchi, T.; Shibo, T. *Chem. Lett.* **1989**, 935.
- (32) Frese, Ch.; Ruppert, S.; Sugár, M.; Schmidt-Lewerküne, H.; Wittern, K. P.; Fainerman, V. B.; Eggers, R.; Miller, R. *J. Colloid Interface Sci.* **2003**, *267*, 457.
- (33) Joo, P. In *Dynamic Surface Phenomena*; Fainerman, V. B., Loglio, G., Eds.; VSP: Zeist, The Netherlands, 1999 (ISBN: 9067643009).