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Editor's Choice

Spontaneous Motion of *o*-Toluidine Droplets: Repetitive Motion of Running and Squashing

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We observed a unique spontaneous motion for an *o*-toluidine droplet containing iodine in an aqueous solution of cation surfactant. The droplet repeated a running motion and a squashing motion on the glass surface. The contact angle determines the motion of droplets on the glass surface. We analyzed this motion quantitatively using video capture. As the initial trigger of the running motion, the receding contact angle increased before the advancing contact angle increased. The predominant squashing span increased with time, although little change was found in the running span.

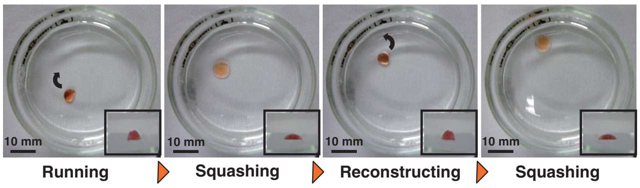

Figure 1. Time-lapse photographs of the repetitive cycle between running motion and squashing motion of a droplet. The interval between frames is less than 1 s. The small inset at the lower right shows the sideways observation. Each scale bar shows 10 mm.

Spontaneous motion phenomena are expected to be useful for applications related to energy transduction, from chemical energy to kinetic energy. Droplet motions on a substrate with an interfacial tension gradient derived from thermal,[1,2] chemical,[3,4] electrochemical,[5,6] and photochemical[7,8] treatments have been discussed. In addition, spontaneous droplet motions of some types produced by chemical reactions inside or around droplets have been observed. The first is self-propulsion of a liquid droplet or solid piece on a water surface.[9,10] The gradual dissolution and reaction of a floating object produce a surface tension gradient. The second is swimming droplet motion in a bulk aqueous solution.[11,12] A droplet generates propulsive force by taking up forward surfactant and ejecting lipophilic product backward. The third is running droplet motion on a glass substrate in aqueous solution.[13,14] The interfacial concentration gradient of a surfactant on a glass surface is generated by creation of an ion pair between the ionic surfactant and the counter ion. These running motions were induced by contact angle change, as is true for spontaneous motions on the substrate with thermal or electrochemical gradation. Nevertheless, these droplets show no marked change of shape when they move on the substrate with chemical gradation.

In this study, we identified a unique running motion with significant shape change of an *o*-toluidine droplet in the trial to generate spontaneous droplet motions using solvents of various kinds for a droplet. We analyzed this motion based on images obtained using video capture. Results showed that the change of the receding contact angle as the trigger of running motion produced the unique shape-shift.

Aqueous solutions of trimethylstearylammonium chloride (TSAC) were prepared at 1 mM using Milli-Q pure water. The critical micelle concentration of TSAC is about 0.3 mM at room temperature.[15] The droplet solution of *o*-toluidine with 10–50 mM Iodine (I_2) was saturated with potassium iodide (KI). As an aqueous phase, 10 mL of aqueous TSAC solution was placed in a glass petri dish (ϕ 45 mm). Then, 20 µL of *o*-toluidine solution was dropped on the petri dish immersed the aqueous solution. The droplet motion was observed until the motion stopped, which is defined as the moment with no motion for over 30 s. The droplet motion, which was recorded using a web camera (CMS-V27SET; Sanwa Supply Inc.), was analyzed using Windows Live Movie Maker software (Microsoft Corp.). In this operation, the video footage of droplet motion was checked using a frame-by-frame advance every 0.03 s.

Immediately after dropping the *o*-toluidine solution into the aqueous TSAC solution, it started to run briskly. However, the round running droplet suddenly stopped and was squashed flat. Subsequently, it reverted to a round shape and ran again. These motions occurred in a rapidly repeated cycle, as presented in Figure 1. The running span was quite short, and the droplet ran in a random direction without losing its round shape during the span. During the squashing span, the droplet was squashed and remained still. These motions resembled ameba motion and appear to be quite characteristic, as distinct from other droplet motions reported previously.

Moreover, the initial shape change in the shift from the squashing motion to the running motion started at the rear of droplet (see Supporting Information video[20]). A side view revealed that the receding contact angle increased before the advancing contact angle. In the previous case of a nitrobenzene droplet, the advancing contact angle decreased first as if to step forward with a front paw.[13] In the shift from the running motion to the squashing motion, the receding contact angle decreased first.

Video analysis data led us to classify the motion into a running span and a squashing span. A temporal change of droplet motion is presented in Figure 2. A striated dark section and blank section respectively show the running span and the squashing span. The running span showed high frequency in the early stage of motion. Then the frequency decreased with time. Each figure (a, b, and c) respectively shows the case of different I_2 concentration systems, 10, 30, and 50 mM. The running motion occurred more continually in the case of higher I_2 concentration. Furthermore, not only the lifetime but also the

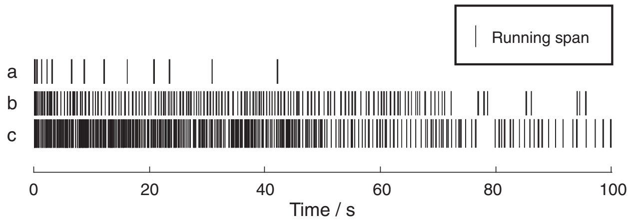

Figure 2. Droplet motion in different I_2 concentration systems: (a) 10, (b) 30, and (c) 50 mM. The running span is shown as striated marks. The other blank part shows the squashing span.

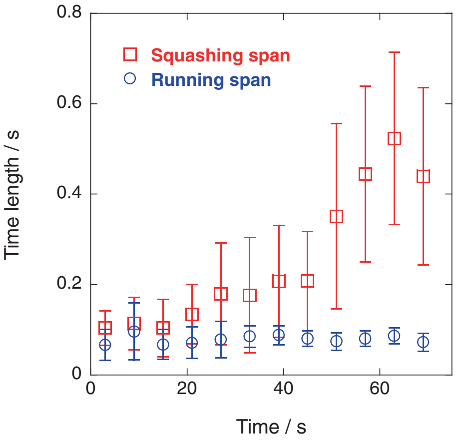

Figure 3. Temporal changes of squashing and running span in one cycle. I_2 concentration is 50 mM. Each value represents the average of 10–30 cycles. The error bar shows the standard deviation.

frequency of consecutive motion increased concomitantly with increasing I_2 concentration.

Figure 3 portrays the temporal change of squashing and running span ($[I_2] = 50$ mM); the time duration of intervals when the droplet is squashing and running. These plots present the average value of each span length during every 6 s. The squashing span increased with time, although the running span varied little from the beginning to the stopping of the motion. Moreover, the error bar of the squashing span was greater than that of running span. These results demonstrate that the frequency and irregularity of the droplet motion were determined by the squashing span. Furthermore, at other I_2 concentrations (10 and 30 mM), the same tendency of span length was obtained, although the squashing span in 10 mM I_2 was much longer than those of the other concentrations. In addition, the running spans remained at 0.07–0.10 s in all cases.

The results presented above suggest a mechanism for the repetitive motion of running and squashing as described below. As the initial state, TSA^+ surfactant ions in the aqueous solution adsorb and form a bilayer on the glass–aqueous interface, directing their hydrophilic head groups both for the interface and the aqueous solution.[16] (1) Immediately after dropping the *o*-toluidine solution, the droplet started to run because of a subtle difference between receding and advancing contact angles. During the running motion, TSA^+ surfactant ions are dissolved in the droplet and form a monolayer on the glass–droplet interface and the aqueous–droplet interface, which engenders wetting of the droplet on the glass interface; the droplet appears to be squashed. (2) The head group of TSA^+ on the glass–droplet interface is associated with I_3^- or I^-;[17] then the ionic associate diffuses into the droplet of organic phase. The TSA^+ concentration on the glass–droplet interface decreases. Consequently, the receding contact angle increases and the contact angle hysteresis generate the droplet motion. At the same time, the change of interfacial tension induces the Marangoni flow, which causes the droplet to run: this state represents the running span. Although being based on previous studies,[18,19] this mechanism differs greatly from that of the previous droplet motion produced by the decrease of advancing contact angle: a difference in the glass–droplet interfacial tension between front and rear of the droplet was proposed as the trigger of the motion.[13] (3) During the running span, TSA^+ adsorbs again on the glass–droplet interface, and the decrease of interfacial tension squashes the droplet. In this state, the droplet is restored to state (1). These behaviors of TSA^+ represent a repetitive cycle of squashing and running of the droplet.

The results presented in Figure 2 demonstrate that I_2 molecules play a key role in the droplet motion. The decrease of the I_2 concentration might affect the supplying quantity of I_3^- to the droplet interface via a reaction: $I_2 + I^- \rightarrow I_3^-$; then TSA^+ only slightly associated with I_3^- or I^- and remained on the glass interface. Consequently, the TSA^+ concentration on the glass–droplet interface increases and the interfacial energy decreases. Therefore, the squashing span increased concomitantly with the decreasing I_2 concentration.

The increase of the squashing span with time shown in Figure 3 might reflect that the I_3^- or I^- was consumed gradually by the ion association with TSA^+ and that they decreased over time. In addition, the higher I_2 concentration, the longer the droplet motion continued, as presented in Figure 2. These results show agreement with the squashing motion mechanism proposed above. Nevertheless, it is difficult to ascertain the meanings of the constant running spans without additional information. Now we continue to investigate this droplet motion. The quantitative determination of surfactant and iodine in the droplet and the measurement of interfacial tension have to be conducted because the mechanism described above still lacks sufficient evidence. In addition, the predominant factor of different droplet motion between nitrobenzene and *o*-toluidine remains unclear. We cannot define the values underlying the physicochemical properties and their relation to self-motion although considering the effect of specific permittivity (polarity) and viscosity (solute diffusivity) of solvents.

In conclusion, we observed unique spontaneous motion of *o*-toluidine droplet that was markedly different from that of a nitrobenzene droplet. The droplet repeated the quick running motion and the predominant squashing motion. The preceding movement of the rear side of droplet in the initial state might be related to this characteristic motion. We supposed that the change of glass–droplet interfacial tension dependent on the TSA^+ concentration controls the droplet squashing motion.

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20 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.