

Article

Marangoni Convection Velocity in Nonlinear Hanging-Droplet Vibration Phenomena

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Abstract: The Marangoni effect involves a mass transfer along an interface between two phases owing to the gradient of the interfacial tension. The flow caused by this phenomenon is called Marangoni convection, a complex phenomenon that involves mass transfer processes, such as surfactant adsorption/desorption processes, solvent dissolution phenomena, and viscous dissipation processes. Therefore, the strength of the convection depends on the various thermodynamic and physical properties of the fluids. In this study, we experimentally investigated the relationship between the Marangoni convection generated inside a hanging oil droplet and the interfacial tension of the oil droplet in an aqueous phase by the particle image velocimetry method. This convection velocity depended on the initial value of the interfacial tension in the oil–water interfacial tension oscillation phenomenon accompanied by the expansion and contraction of the hanging drop. Additionally, the droplet oscillation frequency decreased as the Marangoni convection velocity increased. Furthermore, continuous convection, which is unlike Marangoni convection, was observed within this spontaneously expanding and contracting hanging-droplet system. This buoyant convection was caused by the mutual dissolution of the hanging-droplet oil phase and the surrounding aqueous phase.

Keywords: Marangoni effect; interfacial tension; oscillation; interfacial instability



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1. Introduction

The interfacial instability of biphasic systems, spontaneous interfacial turbulence, and various rhythmic oscillation phenomena have been studied from the perspective of industrial applications, such as liquid/liquid extraction [1,2], stabilizing foams and emulsions [3,4], performing correct measurements of the dynamic surface tension [5,6], developing chemical motors for microfluidic devices [7,8], and understanding the rhythmic processes in living organisms [9,10]. Sternling and Scriven reported on the Marangoni effect as an interfacial instability and the associated spontaneous interfacial convection that occurs in systems with clear boundaries [11]. Marangoni instability occurs under certain conditions related to the kinematic viscosity of the solvent and the diffusivity of the solute that lead to local stirring at the interface, resulting in mass transfer along the interface called Marangoni convection [12]. The Marangoni phenomenon is known to be caused by differences in the interfacial tension resulting from a chemical or thermal gradient at the interface [13]. The relationship between the Marangoni effect and interfacial tension oscillations has frequently been reported in terms of oscillations of the interfacial potential [14–16]. Numerical simulations based on the behavior of various model systems and experimental confirmation from observations of interfacial tension oscillations have also been reported [17–19]. In these studies, the interfacial tension change is explained by the adsorption and desorption of a surfactant at the oil–water interface via Marangoni convection. However, no experimental studies have been conducted on the Marangoni convection velocity with regard to the nonlinear interfacial tension oscillations. A problem with the previously reported conventional methods is that they were measured using the

Wilhelmy method, which measures the surface tension by a platinum plate attached to the gas–liquid interface and is susceptible to interfacial instability.

In this paper, the Marangoni convection velocity inside a hanging droplet was estimated by particle image velocimetry (PIV), and the interfacial tension was measured by a hanging-droplet method to verify the interaction between the Marangoni convection and the interfacial tension. In this hanging-droplet system, the interfacial tension was ascertained from the image of the droplet using droplet shape analysis. This hanging-droplet method allows for the precise measurement of the dynamic interfacial tension. Studying the relationship between Marangoni convection and oil–water interfacial tension has important industrial significance. For example, in an organic synthesis reaction in an oil–water biphasic system, an organic compound present in the oil phase and an inorganic salt present in the aqueous phase may be reacted as a catalyst or redox agent. The reaction can be accelerated by spontaneously generating micro-agitation at the oil–water interface. Therefore, clarifying the relationship between the spontaneous convection velocity and the oil–water interfacial tension is very meaningful in terms of controlling such chemical reactions.

Regarding the nonlinear droplet oscillation phenomena associated with the Marangoni effect, Ban et al. reported that a hanging droplet containing di-(2-ethylhexyl) phosphoric acid (DEHPA) periodically alternates between expansion and contraction with an oscillating interfacial tension in a buffered aqueous solution [20]. This phenomenon was originally described in previous observations of traveling waves and interfacial tension oscillations at the oil–water interface of a nitrobenzene–water biphasic system containing DEHPA [21,22]. On the basis of these investigations, we found that this expansion occurs simultaneously with Marangoni convection caused by the interfacial tension gradient resulting from the DEHPA adsorption/desorption cycles associated with the formation of reverse micelle aggregates [23]. Our results indicate that the periodic Marangoni convection was induced by the molecular behavior of the surfactant in the oil–water biphasic system. In this study, we again focus on a hanging-droplet system and attempt to elucidate the relationship between the Marangoni convection velocity and the interfacial tension based on the expansion and contraction mechanism revealed in previous studies. We measured the interfacial tension of a hanging oil droplet in aqueous phases with varying polarities, achieved by the addition of an organic solvent, and measured the Marangoni convection velocity within the hanging droplet using PIV. Hanging droplets are quasi-spherical, and the convection that occurs within them is very suitable for convection measurement because the influence of the shape on the flow field can be ignored. In addition, the unique point of this research method is that PIV can be applied under the same conditions as the interfacial tension measurement system.

2. Materials and Methods

2.1. Materials

Nitrobenzene, bromobenzene, di-(2-ethylhexyl)phosphoric acid (DEHPA), sodium carbonate, sodium hydrogen carbonate, methanol, ethanol, and acetone were supplied by Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Aqueous phases with each additive were prepared using Milli-Q water (resistivity of 18.2 M Ω cm at 25 °C). The oil phase was nitrobenzene, and the concentration of the surfactant DEHPA was adjusted to be 100 mM in the oil phase. The pH of the aqueous solution was adjusted to 10.2 by the addition of sodium hydrogen carbonate buffer (Na₂CO₃ and NaHCO₃ aqueous solutions were prepared to be 75 mmol/L each). In this study, an organic solvent, such as methanol, ethanol, or acetone, was added to the aqueous phase to vary the polarity of the aqueous phase. The concentration of methanol, ethanol, or acetone in the aqueous solution was adjusted in the range of 0–4 mol L^{−1}.

2.2. Particle Image Velocimetry (PIV)

In this study, we measured the convection velocity within a hanging droplet by PIV. PIV is a fluid measurement method that can measure instantaneous velocities at multiple points in a flow field without contact. It is a widely used method for measuring fluids because it allows the spatial structure of the flow field to be grasped. PIV visualizes the flow by irradiating a laser sheet onto tracer particles that follow the fluid. The visualized particles are photographed with a camera, the displacement vector (Δx) of the tracer particles during the minute time (Δt) between frames is determined by image processing, and the local velocity vector ($v \cong \Delta x / \Delta t$) of the fluid is calculated. To calculate the displacement vector, a small inspection area is set in the image, and a correlation function of the brightness distribution is determined. The image correlation method is a method that compares the brightness distribution at two points in time and estimates the position where the correlation function has the maximum value as the destination. The hanging oil droplet was formed on the tip of a capillary (15 G) in the prescribed aqueous phase stored in a quartz cell. The Kato Koken PIV system consisted of a PIV laser (G50, power; 50 mW, wavelength; 532 nm, Kato Koken Co., Ltd., Kanagawa, Japan) and a high-speed camera (k-7 USB; Kato Koken Co., Ltd.). Fluorescent particles (FA207; Sinloihi Co., Ltd., Kamakura, Japan) were dispersed in the hanging droplet as the tracer particles and irradiated by the PIV laser. A high-speed camera was used to capture images of the fluorescent particles. The convection velocity was measured with the use of the PIV computation software FLOW EXPERT (2D2C; Ver.1.2.17; Kato Koken Co., Ltd.).

2.3. Interfacial Tension Measurement

In this study, we measured the dynamic interfacial tension at the oil–water interface via the Young–Laplace method. The surface tension was calculated by fitting the Young–Laplace equation using image processing based on the contour shape of the droplet created from the needle tip and the value of the density difference. The precise interfacial tension can be determined by fitting the coordinates of hundreds of points on the contour curve to the Young–Laplace theoretical curve. The dynamic interfacial tension was measured using a contact angle meter (Drop Master DM-501; Kyowa Interface Science Co., Ltd., Saitama, Japan). The hanging oil droplet was formed in the same way as for the convection velocity measurement. The aqueous-phase temperature was set at room temperature.

3. Results and Discussion

3.1. Marangoni Convection Velocity

As previously reported, a periodic spontaneous expansion and contraction of the hanging droplet was observed in all systems tested, and convection within the droplet was observed in synchronization with the expansion process. This convection was considered to be Marangoni convection caused by the interfacial tension gradient of the biphasic suspended-droplet system. The cycles of increasing and decreasing interfacial tension were synchronized with repetitive contraction and expansion cycles, respectively. We measured the convection velocity of the hanging droplet in aqueous solutions containing organic solvent at different concentrations. The Marangoni phenomenon is a mass transport caused by a difference in the linear tension at an interface, causing a flow that involves the surrounding medium. Originally, the flow velocity is the flow rate of this fluid divided by the cross-sectional area of the flow, so the flow velocity can be said to represent the strength of the fluid.

The convection velocity was calculated by the PIV method on the basis of the trajectories of the fluorescent particles. The representative velocity vectors are presented in Figure 1a. From these velocity vectors, we identified three vectors, namely, at the center of the droplet, near the interface of the droplet, and at the central point between these positions. The velocity of the convection flow gradually increased over time and then decreased after the attainment of the maximum value. Figure 1b shows the representative variation in the convection velocity (see also Supporting Information, Video S1). As shown in Figure 1b,

the velocity near the interface was the fastest, which can be explained by the mechanism through which Marangoni convection originates, which is, namely, from an interfacial tension difference that causes mass transport within the hanging droplet. Furthermore, the starting point of convection was also observed near the interface, as shown in Video S1. These trends were observed in all systems in which an organic solvent was added to the aqueous phase. From these results, we define the maximum velocity of the convection flow near the droplet interface as “the velocity of Marangoni convection”. As shown in Figure 2, the velocity of the Marangoni convection decreased with the increasing concentration of organic solvent in the aqueous phase. However, different trends were observed depending on the amount of solvent added. In general, the interfacial tension of an oil–water biphasic system strongly depends on the polarity of the aqueous phase. In the next section, we focus on the oil–water interfacial tension of the hanging droplet.

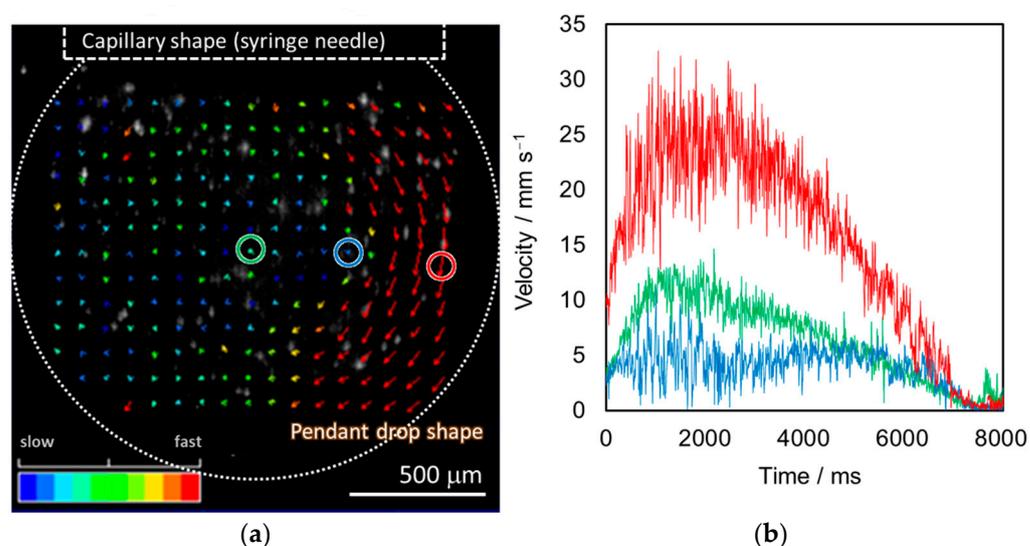


Figure 1. (a) Typical velocity vectors of fluorescent particles in hanging droplets estimated by PIV method. Three velocity vectors were picked from a 13×17 lattice arrangement: at the center of a droplet (green circle), near the interface of a droplet (red circle), and at the central point between these positions (blue circle). (b) Time evolutions of velocities of particles at the center of a droplet (green curve), near the interface of a droplet (red curve), and at the central point between these vectors (blue curve).

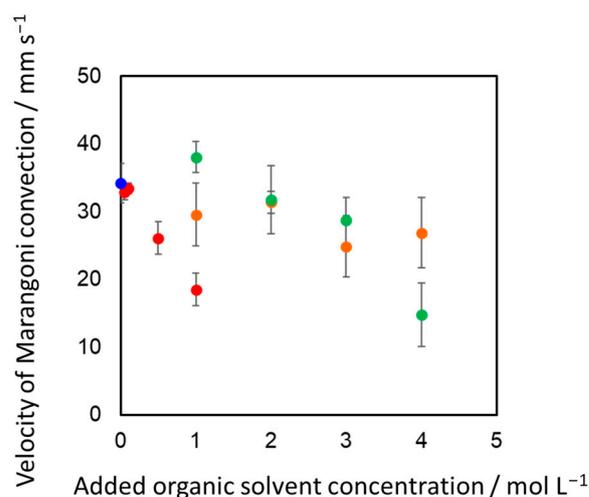


Figure 2. Relationship between the additive concentration in the aqueous phase and the velocity of the Marangoni convection inside the hanging droplet. Each symbol indicates the additive in the aqueous phase: ●: no additive, ●: ethanol, ●: methanol, ●: acetone.

3.2. Initial Interfacial Tension

We propose a mechanism for the spontaneous expansion and contraction phenomenon occurring in a hanging droplet as follows [23]. After the droplet formation, the DEHPA inside the droplet is gradually adsorbed onto the biphasic interface. During this process, the oil–water interfacial tension of the hanging droplet gradually decreases. Then, the DEHPA adsorbed at the oil–water interface is dissociated by the alkaline conditions of the aqueous phase. Subsequently, the dissociated DEHPA desorbs from the interface into the droplet with the simultaneous formation of inverted micelles. Concomitantly, the biphasic interfacial tension increases and becomes close to that of the oil–water interfacial tension without DEHPA. Thus, the oil–water interfacial tension at this time is close to the interfacial tension immediately after the hanging droplet is formed (defined as the initial interfacial tension).

Preliminary results showed that the static interfacial tension without DEHPA was close to the initial interfacial tension. When the biphasic interface was destabilized by the adsorption and desorption of DEHPA, Marangoni convection occurred owing to the interfacial tension difference in the conditions with and without DEHPA. On the basis of this generation mechanism of Marangoni convection, we expected that the biphasic interfacial tension would affect the convection velocity inside the hanging droplet. For the initial interfacial tension, we measured the interfacial tension soon after the hanging droplet was formed. A linear relationship was obtained between this initial interfacial tension and the static interfacial tension without DEHPA, which supported the above suggestions. Figure 3 shows the relationship between the initial interfacial tension of the hanging droplet and the velocity of the Marangoni convection. The velocity of the Marangoni convection increased with the initial interfacial tension of the hanging droplet, regardless of the type of solvent species added to the aqueous phase. The positive correlation indicates that the Marangoni convection in the hanging droplet is dominated by the initial interfacial condition of the biphasic system. This result explains the generation mechanism of Marangoni convection. Marangoni convection that involves the surrounding liquid may be caused by the difference in the linear tension on the oil–water interface before and after the adsorption of the surfactant DEHPA.

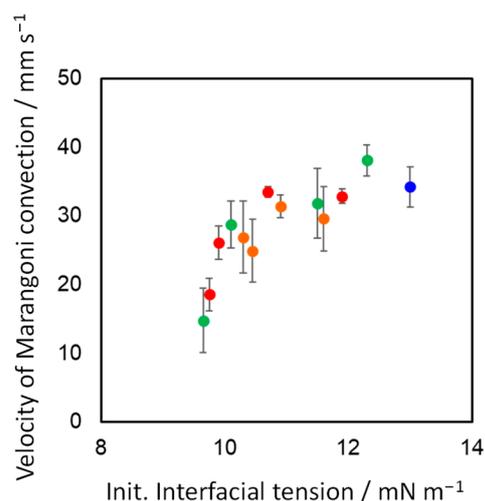


Figure 3. Relationship between the initial oil–water interfacial tension and the velocity of the Marangoni convection inside the hanging droplet. Each symbol indicates the additive in the aqueous phase: ●: no additive, ●: ethanol, ●: methanol, ●: acetone.

3.3. Frequency of Oscillation Phenomena

The oscillation frequency of the spontaneous expansion and contraction phenomenon of the hanging droplet varied with the addition of the organic solvents to the aqueous phase. We previously reported that the oscillation frequency depends on the aqueous-phase

temperature and explained this result in terms of the effect of temperature on the interfacial tension [23]. However, it is unclear why an increase in the biphasic interfacial tension leads to a decrease in the frequency. The convection velocity was difficult to measure under isothermal conditions because the chamber used to control the temperature prevented the quartz cell filled with the aqueous phase from being irradiated by the PIV laser. In a discussion of these results, the effect of the Marangoni convection in the hanging droplet on the oscillation period was assessed, as shown in Figure 4. The oscillation period is the reciprocal of the oscillation frequency and indicates the interval between the expansion and contraction in the hanging droplet. The oscillation period increased with the increasing convection velocity. Previous reports on the Marangoni phenomenon caused by surfactant adsorption and desorption at the gas–liquid interface have indicated that the diffusion and adsorption of surfactants at the gas–liquid interface are promoted by Marangoni convection [24]. On this basis, the amount of the DEHPA surfactant that is diffused and adsorbed onto the hanging-droplet oil–water interface likely depends on the Marangoni convection velocity. When the amount of DEHPA at the oil–water interface increased, the period for DEHPA to dissociate and desorb from the interface became longer. Therefore, a longer time was taken to reach the critical state for the subsequent Marangoni phenomenon. These considerations can explain the results shown in Figure 4 and indicate the possibility that Marangoni convection controls the period of the nonlinear phenomenon that causes this periodic convection.

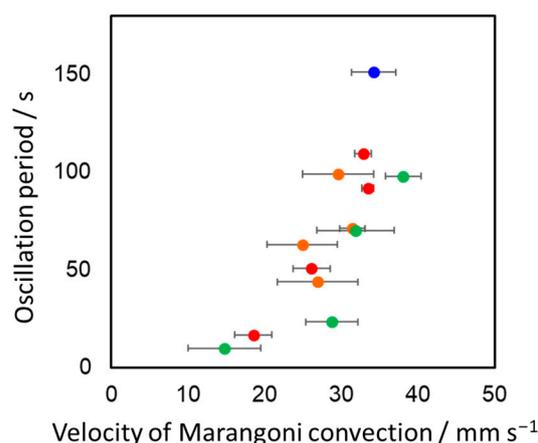


Figure 4. Relationship between the oscillation period of the interfacial tension oscillation and the velocity of the Marangoni convection inside the hanging droplet. Each symbol indicates the additive in the aqueous phase: ●: no additive, ●: ethanol, ●: methanol, ●: acetone.

3.4. Hanging Drop without Marangoni Convection

As described above, the presence of DEHPA is important for the occurrence of Marangoni convection, and the spontaneous expansion and contraction of the hanging droplet is not actually observed in systems without DEHPA. We observed the inside of a hanging-droplet system in a system without DEHPA through the use of the PIV method. Compared with the periodic and fast Marangoni convection, continuous convection at a markedly slower speed was observed (see also Supporting Information, Video S2). Although the direction of the convection varied depending on the system, the convection always showed vertical rotation, and no major changes were observed in the velocity or direction. In a previous study based on observations and numerical calculations [25], we reported that density differences, associated with mass transport in oil–water two-phase systems, were the cause of the buoyant convection observed in the present study. Because the aqueous phase of the biphasic hanging-droplet system presented in Video S2 did not contain additives, such as alcohol, no solutes were transported across the interface. This buoyant convection is thought to be caused by the mutual dissolution of the nitrobenzene oil and water phases. The densities of nitrobenzene and water are 1.2 and 1.0 g/cm³ at

20 °C, respectively. It is thought that buoyant convection was generated from this density difference when the aqueous phase dissolved in the nitrobenzene hanging-droplet phase. This convection was also observed in DEHPA-containing systems during the period between Marangoni convection. These results suggest that this buoyant convection causes interfacial inhomogeneity, creating an interfacial tension gradient that triggers Marangoni convection. The generation of buoyant convection due to mutual dissolution, along with the generation of buoyant convection due to mutual dissolution, were discussed in detail in our previous report [25]. In the next section, we examine the effects of mutual dissolution between the two phases of oil and water.

3.5. Observation of Buoyant Convection

A previous study has suggested that the interfacial instability caused by cross-boundary mass transfer is important for the occurrence of the Marangoni phenomenon [11]. Furthermore, thermodynamic analysis suggests that the mutual-dissolution process is important for the occurrence of nonlinear phenomena [15]. We previously evaluated the amount of elution of the nitrobenzene phase to the aqueous phase to examine the effect of the mutual solubility between the oil and water biphasic systems on the spontaneous expansion and contraction phenomenon of the hanging droplets [23]. As a result, no marked effect was observed. However, because buoyant convection, which could be caused by the mutual dissolution of the oil–water two-phase system, was observed in the hanging droplet, we investigated a system in which each oil–water phase was saturated with the other phase.

A total of four combinations of the saturated and unsaturated systems were studied, as follows: (i) a system in which both the oil and water phases were unsaturated; (ii) an aqueous phase saturated with nitrobenzene and an unsaturated oil phase; (iii) an unsaturated aqueous phase and an oil phase saturated with water; and (iv) a system in which both the oil and water phases were saturated with the other phase. The inside of the hanging droplet in each of these systems can be seen in Videos S2–S5 in the Supporting Information. Figure 5 shows the trajectories of the fluorescent particles in each system obtained from images taken every 1 ms using the PIV method. In the systems without DEHPA, Marangoni convection in the hanging droplet did not occur. Additionally, buoyancy convection within the hanging droplet was observed in all four systems. Figure 5a shows the trajectories of the fluorescent particles for system (i), in which both the oil and water phases were not saturated. Continuous buoyancy convection was observed in this system, as shown in Video S2. In contrast, the inhibition of buoyant convection was observed in the oil–water biphasic systems (ii)–(iv), in which one or both phases were saturated by the other phase, as shown in Figure 5b,c. For systems (ii) and (iv), no buoyant convection was visually observed. For system (iii), weak buoyant convection was visible, but it was markedly slower than the convection observed in system (i). These results confirmed that the cause of the buoyant convection was the mutual dissolution of the oil and water phases. Furthermore, in the saturated systems (ii)–(iv), in which DEHPA was added, Marangoni convection and the associated spontaneous expansion and contraction of the hanging droplets did not occur, indicating that buoyant convection is responsible for the instability of the oil–water interface, as described above. However, it is interesting that it is not only the dissolution of the aqueous phase into the oil hanging droplet that has an effect but also the elution from the oil phase to the aqueous phase. To confirm this, bromobenzene, which has lower solubility in water (<0.1 g/100 mL at 20 °C) than nitrobenzene (0.2 g/100 mL at 20 °C), was used as the oil phase. We selected bromobenzene as the hanging-droplet phase because its density (1.5 g/cm³ at 20 °C) is close to that of nitrobenzene and is larger than that of water, making it easier to compare the systems. The effects on the buoyancy convection and spontaneous expansion and contraction phenomena within a hanging droplet were investigated.

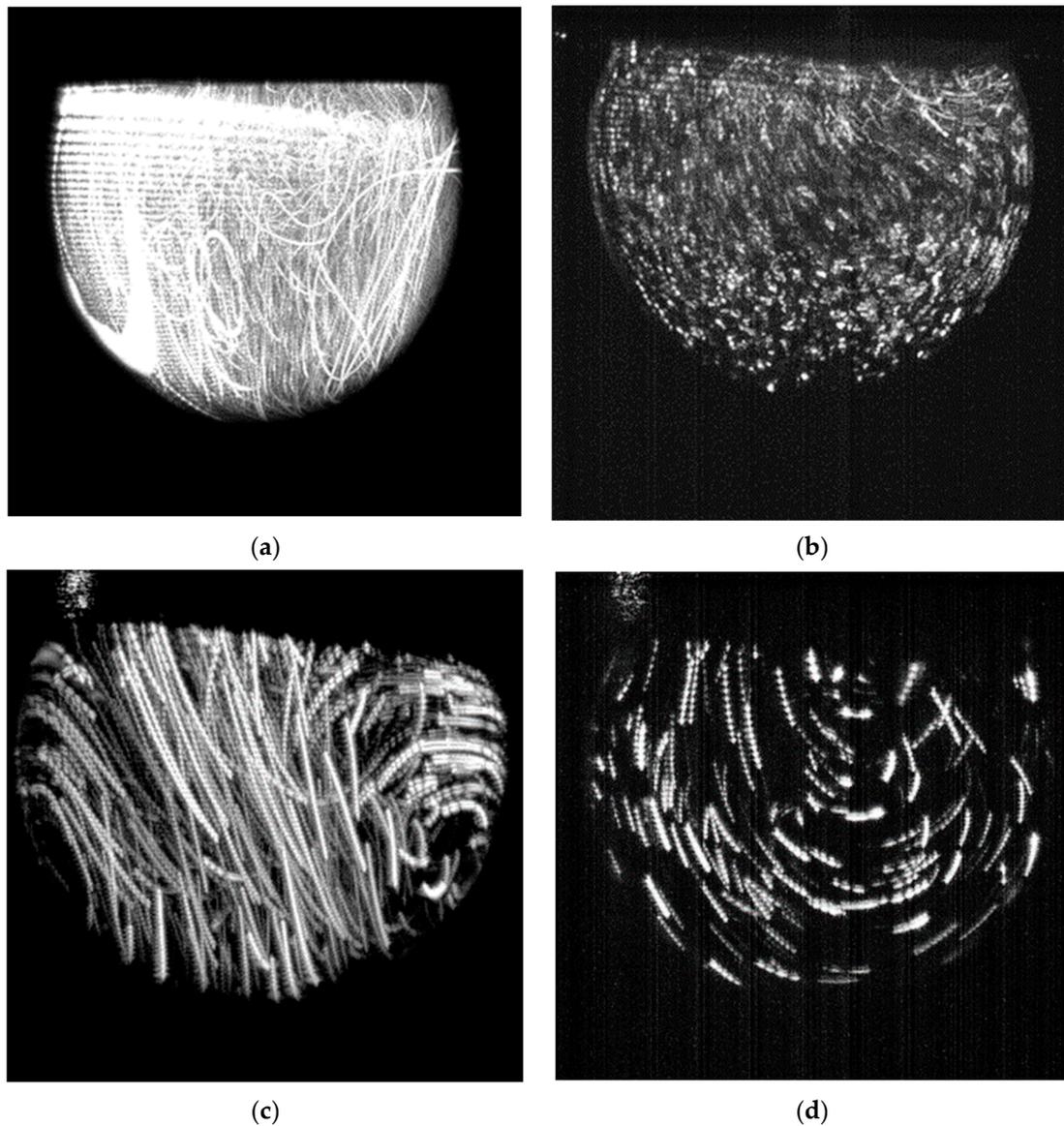


Figure 5. Trajectories of fluorescent particles in a hanging-droplet system with varying saturation and unsaturation conditions for each phase to consider the influence of the mutual dissolution of the two phases of oil and water. Aqueous phase/oil phase: (a) unsaturated/unsaturated; (b) saturated/unsaturated; (c) unsaturated/saturated; (d) saturated/saturated.

3.6. Bromobenzene Hanging Droplet

Figure 6 shows the trajectories of the fluorescent particles when bromobenzene was used as the solvent for the hanging oil droplet. As shown in Figure 6a, no buoyant convection was observed. This result supports the proposal in the previous section that buoyant convection is caused by the mutual dissolution of the oil and water phases. As we have previously reported, adding an organic solvent to the aqueous phase reduces its polarity, promoting the elution of the hanging-droplet oil phase to the aqueous phase [23]. Therefore, we observed the hanging droplet in a system in which bromobenzene oil was placed in an aqueous phase containing 4 mol/L of ethanol. As shown in Figure 6b, notable buoyancy convection was observed within this hanging droplet. This result indicates that the dissolution of the hanging-droplet oil phase into the aqueous phase greatly contributes to the generation of buoyant convection within the hanging drop. Taken together, these results are consistent with our proposed mechanism.

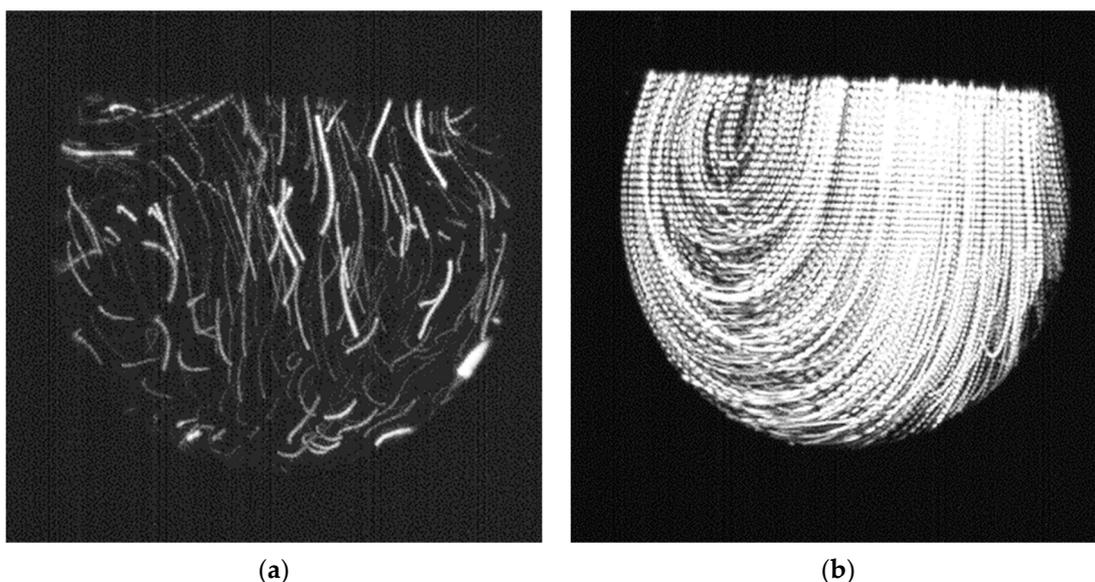


Figure 6. (a) Trajectories of fluorescent particles in the bromobenzene hanging-droplet phase. (b) System with 4 mol/L ethanol added to the aqueous phase.

4. Conclusions

To experimentally support the mechanism of the Marangoni phenomenon, we focused on the spontaneous expansion and contraction phenomenon of an oil–water biphasic system. This nonlinear phenomenon was observed in some aqueous phases in which the oil–water interfacial tension was varied as the polarity of the aqueous phase was changed by the addition of different types and concentrations of organic solvents. The velocity of the Marangoni convection within a hanging oil droplet depends on the oil–water interfacial tension of this two-phase system. Our findings suggest that this convective velocity may control the phenomenon itself. These are the first experimental results to demonstrate the mechanism by which the Marangoni phenomenon occurs, and they will provide useful knowledge to guide industrial applications. Additionally, buoyant convection within a hanging droplet was observed as a phenomenon that causes interfacial instability that triggers the occurrence of Marangoni convection. Buoyant convection is caused by the mutual dissolution of the hanging-droplet oil and aqueous phases, and the convection velocity increases with the magnitude of the dissolution. Many previous studies have reported that mass transport across the interface leads to interfacial instability and nonlinear periodic oscillation phenomena accompanied by spontaneous interfacial convection. In this study, we report an experimental system that enables visual and quantitative observations of these results.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr12030609/s1>, Video S1: Visualization of Marangoni convection in a hanging drop using fluorescent particles, Video S2: Buoyant convection in biphasic system without DEHPA, Video S3: Observation inside a hanging drop of system ii, $\times 16$ speed, Video S4: Observation inside a hanging drop of system iii, $\times 16$ speed, Video S5: Observation inside a hanging drop of system iv, $\times 16$ speed.

Author Contributions: K.O. and B.N. worked on the experiments and analyses and wrote the whole paper. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

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