Nonlinear Properties of Water/Oil Interface Containing Surfactants

under Nonequilibrium

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Abstract: Spontaneous interfacial flow at water/oil interface containing ionic surfactants were investigated, and the oscillation of the interfacial tension for the system was discussed. For the present system, both of hydrodynamic instability at the interface and thermodynamic instability of adsorbed surfactants play important roles [reference 1-12]. The hydrodynamic aspect of the water/oil system is mainly focused, and successive interfacial flow was visualized by moving tracer particles at the interface. It was found that the flow is randomly generated. We estimated a probability for generation of the flow per unit time and unit area and it was dependent on oil species. Dynamic interfacial tension was measured for the water/oil system, and the mean amplitude of the tension oscillation was obtained against the size of vial containing the sample. Mean amplitude depended on the vial size. This characteristics was discussed in relation to the interfacial flow.

Key words: surfactant, water/oil interface, nonequilibrium, oscillation, interfacial properties

1. Introduction

Surfactant monolayer at water/oil interface is one of the simplest systems for the investigation of self-assembly of amphiphiles. Thus, a large number of experimental and theoretical investigations have been performed for the structural studies under thermodynamic equilibrium. Recently, interfacial properties of water/oil system under nonequilibrium attract great interest because of the novel time-dependent properties. Some water/oil interfaces through which surfactants move from a bulk phase to another exhibit nonlinear oscillation of interfacial tension and interfacial potential[1-6]. The oscillation is random and sometimes looks periodic. These time dependent properties have potential usage for new kinds of technology such as a sensor and a chemomechanical energy conversion[7-9]. In such a nonlinear system, the hydrodynamic instability at the interface and thermodynamic instability of adsorbed surfactants cooperatively generate the time dependent interfacial tension[11,12]. This nature is different from the well-known Benard-Marangoni convection at liquid surface or interface, where fluid motion can be described by

hydrodynamic instability alone. Experimental investigations for the spatial hydrodynamic effect relating the time dependent properties for the water/oil system have not been carried out. In this work, we examined macroscopic nature of the interfacial flow under the nonequilibrium interface and discussed the relationship between the hydrodynamic phenomenon and the oscillation of interfacial tension.

2. Experimental

Di-2-ethylhexyl phosphoric acid DEHPA was purchased from Tokyo Kasei and used as supplied. Reagent grades of n-heptane, n-decane and calcium chloride were provided by Kanto chemical and used without further purification. Water used was fully deionized. A method for measuring the interfacial tension is the same as reported earlier[6]. Wilhelmy plate was placed at aqueous solution surface of 5M-CaCl$_2$ and organic phase containing 5mM-DEHPA was poured onto the aqueous phase. The dynamic interfacial tension was measured by an electric scale (Sartorius BP221S), and the data were stored in a personal computer. Data acquisition was done by 2 Hz. Three kinds of platinum plate with width 2 cm, 1

cm, 0.7 cm were used. When using the plate with 1cm and 0.7cm, the effect of plate-edge was not negligible for calculating the interfacial tension. Then, we measured the surface tension of pure water and interfacial tension of n-heptane/water without surfactant to compare the literature values. Calibration constants were obtained by the comparison and all of the interfacial tension measured by the small plates was multiplied by the constant value. Spontaneous interfacial flow was visualized by tracer silica powder spread over the interface. We checked no effect of silica powders on time dependency of the interfacial tension. As another experiment, an alumina particle was put on the interface and its movement was observed. Motion of the silica powders or an alumina particle were recorded by digital video camera and analyzed by a PC.

3. Motion of Tracer Particles

Figure 1 shows a snap shot of silica powders on water/oil interface. Just after the oil phase containing silica powders was poured, they were homogeneously spread over the interface. However, surfactant transfer at the interface induced spontaneous interfacial flow which moves silica powders. The interfacial flow was initiated at a certain point and was propagated radially. The flow-inducing point (FIP) appeared randomly, and a flow has a limited lifetime. Then, silica powders were gathered at the periphery to form domain structure shown in Figure 1. When another flow meets the periphery, original quasi-circular shape begins to deform. The structure was changed randomly time by time. Figure 2 shows the square root of the mean square displacement $R(t)=\sqrt{<r^2(t)>}$ of an alumina particle as a function of time t. $<r^2(t)>$ is the ensemble average of squared-distance between particle positions with time zero and time t. $R(t)$ is approximately proportional to the square root of time, which indicates the motion of alumina particle is a random process like Brownian motion. Therefore, the interfacial flow moving particles was generated quite randomly.

Due to the radial propagation of the flow, periphery of a domain formed by silica powders

was approximately circular until the collision with the neighboring flow. We measured the maximum size d beyond which the circular geometry was deformed and the results are shown in Figure 3. The pattern is not perfectly circular and we took the average of two lengths along the directions orthogonal to each other.
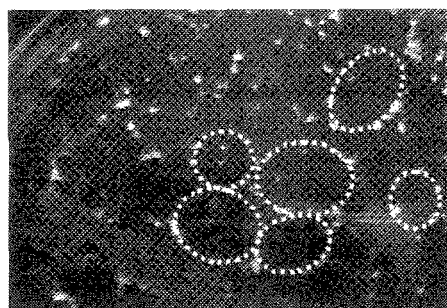

Fig.1 Pattern formed by silica powders, 5mM-DEHPA/n-heptane/5M-CaCl$_2$ at 25°C. Ten seconds after contact of water/oil phases. White dots are silica powders and their blocks. Edges of some domains are traced by dashed curves.
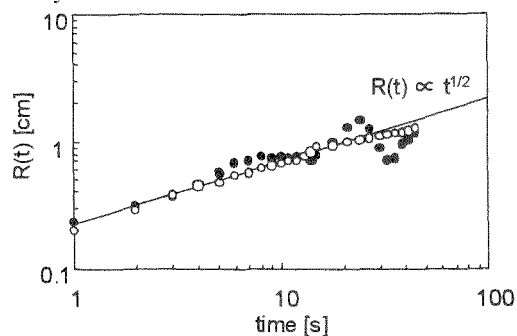

Fig.2 Mean distance of alumina particle moved by interfacial flow as a function of time. Oil is n-heptane and temperature is 25°C. ○ vial diameter 6cm, ● vial diameter 8.6cm.
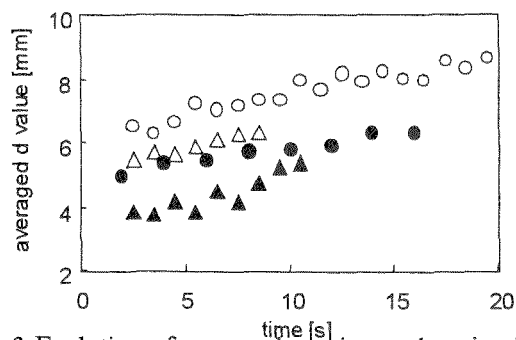

Fig.3 Evolution of averaged maximum domain size. Domain sizes at a certain time are within the averaged value ±1 mm. Oil is n-heptane and temperature is 25°C. ○ vial diameter 8.6cm, △ vial diameter 6cm, ● vial diameter 3.1cm, ▲ vial diameter 1.2cm.

At least, more than several domains were measured at a certain time and the average value was calculated. The maximum diameter d increases with time, which means the probability of generating FIP decreases with time. The d values at 10 s after the contact of the two phases are shown in Figure 4. The domain size decreases with decreasing temperature, and the dependency on oil species is not seen. We define a probability of generating FIP, ρ(t), per unit area and unit time as

$$\rho(t) = 1/(\pi d^2 \, \tau /4), \quad \tau = (d/2)/v \quad (1).$$

Here, v denotes the speed of propagation which can be estimated by the video image. When evaluating the value of v, we used the data for the largest vial, because for smaller vials smaller d value made it difficult to measure the time required for the propagation. ρ(t) calculated is shown in Figure 5. ρ(t) is almost independent of temperature. (Temperature-dependency of d and v are cancelled.) Thus, the temperature-dependency of the maximum domain size is caused by temperature changing the propagation speed. This probably results from the increase in viscosity at low temperature. ρ(t) is dependent on oil species and the vial size. Structural study for molecular assembly composed of DEHPA indicated that attractive interaction between the surfactants is stronger in n-decane than in n-heptane[13]. This may be responsible for lower ρ(t) values in n-decane: Brian pointed out that densely packed surfactant molecules at a surface or a water/oil interface reduce the hydrodynamic instability due to the Marangoni effect[14]. This agrees with the present result that ρ(t) value is smaller for decane than for heptane. Effects of vial diameter on domain sizes and ρ(t) probably arise from boundary conditions for the interfacial hydrodynamics.

4. Oscillation of Interfacial Tension

Figure 6 shows dynamic interfacial tension at water/oil interface. The characteristics of the tension oscillation have been discussed in detail[6]. Some parts of the oscillation look periodic, but the Fourier transformation indicates that the oscillation is a nearly random process. We picked up the time range in which the oscillation was
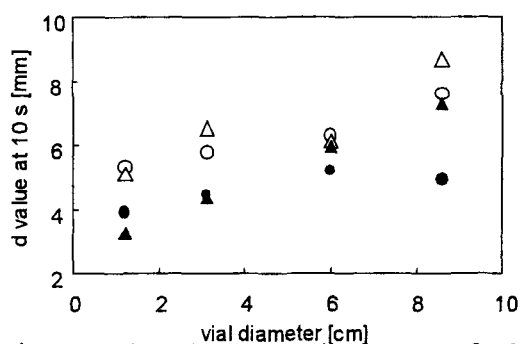

Fig.4 Averaged maximum domain size at 10s for four kinds of vials. Domain sizes are within the averaged value ±1 mm. ○ heptane 25°C, ● heptane 5°C, △ decane 25°C, ▲ decane 5°C
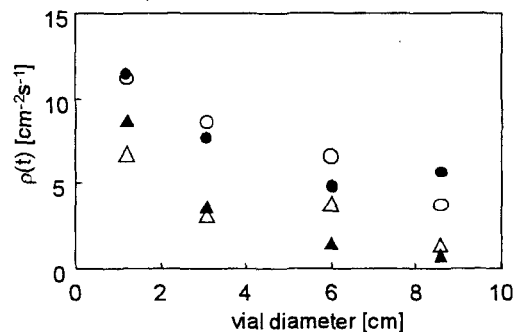

Fig.5 ρ(t) shown for different vial sizes. Oil is n-heptane. Keys are the same as shown in Figure 4.
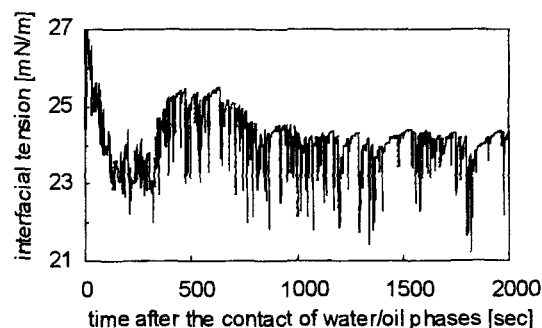

Fig.6 Oscillation of interfacial tension for 5mM-DEHPA/decane and 5M-CaCl₂ system at 25°C. Vial diameter is 3.1cm.
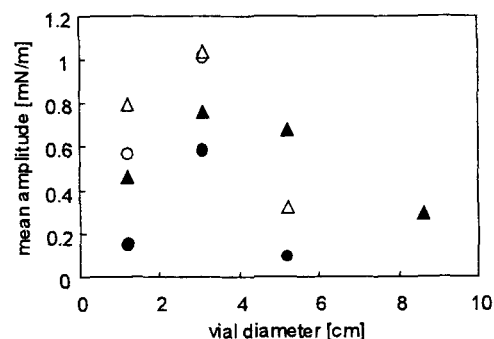

Fig.7 Mean amplitude of tension oscillation for different vial sizes. Oil is n-heptane.
△, 5°C; ○,15°C; ▲, 25°C; ●, 45°C

outstanding and calculated the mean amplitude as a function of vial sizes for four temperatures, and the results are shown in Figure 7. The mean amplitude is the largest near diameter being 3 cm. This suggests that there should be an important relationship between the mean amplitude and interfacial hydrodynamics. We may discuss the tension oscillation in terms of the interfacial flow described in the preceding section. It was observed that the dynamic interfacial tension suddenly decreases when an interfacial flow caused by the Marangoni instability reaches the Wilhelmy plate. After that, the interfacial tension gradually recovers by surfactants desorption. However, when another interfacial flow reaches the Wilhelmy plate during the recovery, the interfacial tension suddenly decreases again. In this case, the mean amplitude should be smaller. Oppositely, unless the second flow comes, the mean amplitude is expected to be larger. When the length of the Wilhelmy plate is close to the vial diameter, the interfacial area surrounding the plate is small. This leads to the low probability that the second flow comes to the plate. Therefore, smaller vial size results in larger amplitude, which is established for the vial diameter larger than 3 cm. However, if the side wall is too close to the Wilhelmy plate, then the Marangoni flow may be reflected by the side wall to affect the measured interfacial tension. Since the local interface influenced by the reflected flow is reduced to the state with a low interfacial tension, the dynamic interfacial tension cannot be fully recovered. Then, the mean amplitude gets smaller. Thus, it becomes small for too small vials. We can understand the results shown in Figure 7 in this way.

5.Conclusion

Characteristics of spontaneous flow at water/oil interface were investigated, and they were associated to oscillation of dynamic interfacial tension. Di-2-ethylhexyl phosphoric acid and calcium chloride were used as a surfactant and an electrolyte, respectively. The spontaneous interfacial flow propagated radially, and the probability for generating the flow per unit area and per unit time was deduced. It was independent

of temperature and affected by oil species. This could be understood based on the linear stability theory for the Marangoni instability. The pattern formed by tracer particles indicated that the flow randomly forms a domain structure at the interface, the size of which depends on the vial sizes for samples. The interfacial hydrodynamics decisively influences the mean amplitude of the tension oscillation.

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